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3*H*-Benzophosphepine Complexes: Versatile Phosphinidene Precursors

Mark L. G. Borst,[†] Rosa E. Bulo,[†,‡] Danièle J. Gibney,[†] Yonathan Alem,[†] Frans J. J. de Kanter,[†] Andreas W. Ehlers,[†] Marius Schakel,[†] Martin Lutz,[§] Anthony L. Spek,[§] and Koop Lammertsma*[,†]

Contribution from the Department of Chemistry, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV, Amsterdam, The Netherlands, and the Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH, Utrecht, The Netherlands

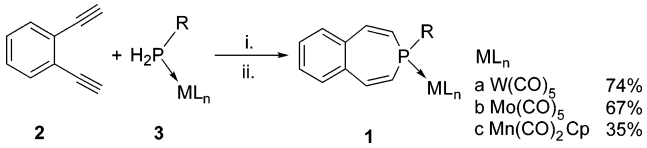
Received July 21, 2005; E-mail: k.lammertsma@few.vu.nl

Abstract: The synthesis of a variety of benzophosphepine complexes [R = Ph, *t*-Bu, Me; $ML_n = W(CO)_5$, $Mo(CO)_5$, $Cr(CO)_5$, $Mn(CO)_2Cp$] by two successive hydrophosphinations of 1,2-diethynylbenzene is discussed in detail. The first hydrophosphination step proceeds at ambient temperature without additional promoters, and subsequent addition of base allows full conversion to benzophosphepines. Novel benzeno-1,4-diphosphinanes were isolated as side products. The benzophosphepine complexes themselves serve as convenient phosphinidene precursors at elevated, substituent-dependent temperatures (>55 °C). Kinetic and computational analyses support the proposal that the phosphepine−phosphanorcaradiene isomerization is the rate-determining step. In the absence of substrate, addition of the transient phosphinidene to another benzophosphepine molecule is observed, and addition to 1,2-diethynylbenzene furnishes a delicate bidentate diphosphirene complex.

Introduction

Phosphines are valuable organometallic ligands and are important in catalysts for stereoselective organic reactions. In a continuous demand for atom-efficient, fast, and versatile routes to functionalized phosphines, their reaction with unsaturated bonds (hydrophosphination), especially under catalytic conditions,[1,2] is gaining attention. While radical-initiated[3] and base-promoted[4,5] hydrophosphinations are already known for decades, mechanistic knowledge is required to take better advantage of the more readily occurring reactions when the phosphine is complexed to BH_3[6] or transition metals,[7−9] which both activate the P−H bond.[10] This understanding can aid in the design of selective hydrophosphination catalysts.

Scheme 1. Synthesis of Benzophosphepine Complexes 1[a]



2 3 1

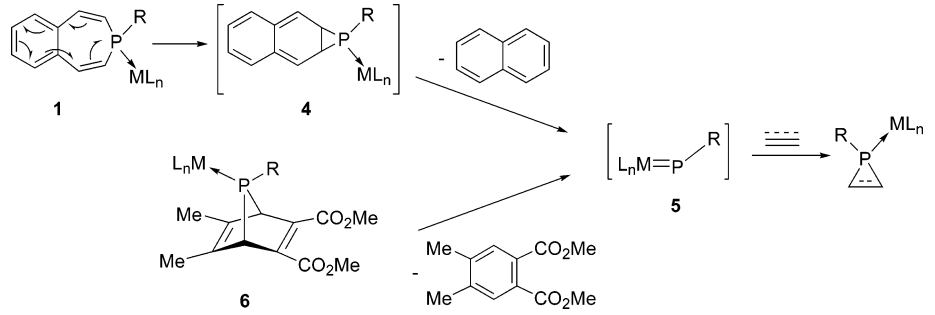
[a] (i) THF, rt, 12h. (ii) KOH, rt.

Because of our recent interest in benzophosphepine complexes **1** (Scheme 1),[11] we were attracted to a report by Märkl and co-workers[12] on the base-catalyzed hydrophosphination of diethynylbenzene **2** with primary phosphines **3**. We found that base (KOH) is required only for full conversion when complexed phosphines are used and that reaction proceeds exclusively in a trans fashion at *ambient* temperatures. The present study gives mechanistic details and also insight into the use of the product.

[†] Vrije Universiteit.
[‡] Present address: ETH Zurich, Switzerland.
[§] Utrecht University.

(1) For reviews: (a) Wight, D. K.; Glueck D. S. In *Catalytic Heterofunctionalization*; Togni, A. Grützmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; Chapter 5, p 143. (b) Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25. (c) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.
(2) (a) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2368. (b) Sadow, A. D.; Haller, I.; Fadini, L.; Togni, A. *J. Am. Chem. Soc.* **2004**, *126*, 14704.
(3) (a) Mitchell, T. N.; Heesche, K. *J. Organomet. Chem.* **1991**, *409*, 163. (b) Heesche-Wagner, K.; Mitchell, T. N. *J. Organomet. Chem.* **1994**, *468*, 99. (c) Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79. (d) Schoufs, M.; Meijer, J.; Vermeer, P.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1974**, *93*, 241.
(4) (a) Bunlaksananusorn, T.; Knochel, P. *J. Org. Chem.* **2004**, *69*, 4595. (b) Märkl, G.; Baier, H.; Liebl, R. *Synthesis* **1977**, 842. (c) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177.
(5) (a) Malysheva, S. F.; Sukhov, B. G.; Larina, L. I.; Belogorova, N. A.; Gusarova, N. K.; Trofimov, B. A. *Russ. J. Gen. Chem.* **2001**, *71*, 1907. (b) Khachatryan, R. A.; Grigoryan, N. Y.; Indzhikyan, M. G. *Russ. J. Gen. Chem.* **1994**, *64*, 1134.
(6) (a) Mimeau, D.; Gaumont, A.-C. *J. Org. Chem.* **2003**, *68*, 7016. (b) Mimeau, D.; Delacroix, O.; Gaumont, A.-C. *Chem. Commun.* **2003**, 2928. (c) Soulier, E.; Yaouanc, J.-J.; Laurent, P.; des Abbayes, H.; Clément, J.-C. *Eur. J. Org. Chem.* **2000**, 3497.
(7) With base: (a) Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95. (b) Adams, H.; Bailey, N. A.; Blenkiron, P.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **2000**, 3074. Mo−CCH: (c) Adams, H.; Atkinson, M. T.; Morris, M. J. *J. Organomet. Chem.* **2001**, *633*, 125.
(8) With radical initiation: Lang, H.; Lay, U. *J. Organomet. Chem.* **1992**, *441*, 389.
(9) Without additives: Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1993**, *12*, 4503.
(10) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921.
(11) Borst, M. L. G.; Bulo, R. E.; Winkel, C. W.; Gibney, D.; Schakel, M.; Ehlers, A. W.; Lammertsma, K. *J. Am. Chem. Soc.* **2005**, *127*, 5800.
(12) Märkl, G.; Burger, W. *Tetrahedron Lett.* **1983**, 2545.

Scheme 2. Isomerization of Benzophosphepines **1** and Generation of Phosphinidenes

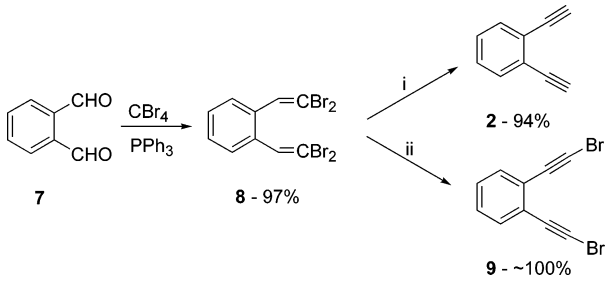


Benzophosphepines have synthetic potential, because they rearrange to the phosphanorcaradienes **4**, cf. the cycloheptatriene−norcaradiene valence isomerization.[13] Phosphanorcaradienes themselves are unstable and dissociate into naphthalene and phosphinidene complexes [R−P═ML_n] (**5**), which are the phosphorus analogues of carbenes (Scheme 2).[14] Apart from a separate class of isolable positively charged complexes,[15] electrophilic phosphinidene complexes are transient reagents that display a rich and versatile chemistry,[16] but their access has been restricted to only a few synthetic routes,[17] of which the cheletropic elimination from 7-phosphanorbornadiene complexes **6** is the most used one.[18] Even this reaction is limited to group 6 (Cr, Mo, W) transition-metal−carbonyl complexes and by the reaction temperature of 110 °C. Using CuCl as catalyst lowers the reaction temperature, but it likely also changes the nature of the reagent.[19] Benzophosphepine **1** offers advantages because of its short, convergent synthesis with the phosphorus group being introduced in the last step; access to a broader range of transition-metal complexes; a more modest decomposition temperature of 75−80 °C; and a simpler workup procedure.[11] The applicability of this new complexed phosphinidene precursor will be further detailed with additional mechanistic insights.

Results and Discussion

Synthesis of Benzophosphepine Complexes. Of the two reported syntheses[12,20] leading to 3*H*-benzophosphepines, the base-catalyzed hydrophosphination of 1,2-diethynylbenzene is the most attractive one, but it requires better access to the dialkyne. An improved synthesis starts with the Corey−Fuchs one-carbon homologation[21] of commercially available *o*-phthaldialdehyde (**7**) to give tetrabromide **8**, followed by debromination using LDA to furnish diethynylbenzene **2** in 91% overall yield (Scheme 3). Bases such as *n*-BuLi are less selective. Surprisingly, treatment of **8** with KO-*t*-Bu at −78 °C gave quantitatively the known[22] 1,2-bis(bromoethynyl)benzene **9**, whereas other aromatic bromoalkynes are reported to undergo smooth conversion to terminal alkynes under similar conditions.[23]

Scheme 3. Synthesis of 1,2-Diethynylbenzene[a]



[a] (i) (1) LDA, −78 °C; (2) $(NH_4)_2SO_4$ aq, −78 °C. (ii) (1) KO*t*Bu, −78 °C; (2) H_2O, −78 °C.

We pursued the procedure reported by Märkl et al.[12] for the uncomplexed benzophosphepines, but the addition of the various complexed phosphines **3** to diethynylbenzene **2** showed unsatisfactory reproducibility on using KOH with 18-crown-6 in toluene, likely because of its heterogeneous character. This problem was solved by using THF/KOH instead, thereby eliminating the use of the crown ether (Table 1, method A). Unfortunately, similar to the original prodedure, yields never exceeded 50%, despite full consumption of **8** in ca. 10 min. Moreover, this method proved inadequate for the synthesis of 3-amino derivative **1g** because of the instability of the Et_2NPH_2−$W(CO)_5$ complex (**3g**) in THF. This limitation could be overcome by eliminating the use of base entirely for the first hydrophosphination reaction. Thus, monitoring by ^{31}P NMR spectroscopy of the careful addition of an ethereal solution of **3g** to a THF solution of diethynylbenzene showed the appearance of a major resonance at 21 ppm (d, $^1J_{PH}$ = 381 Hz), which we assign to the intermediate *cis*-vinylphosphine complex **11g** (Scheme 4, Table 1), and a smaller one at 56 ppm. On addition of KOH, full conversion resulted in the evolution of the signal at 21 ppm into the one at 56 ppm. Workup of the reaction

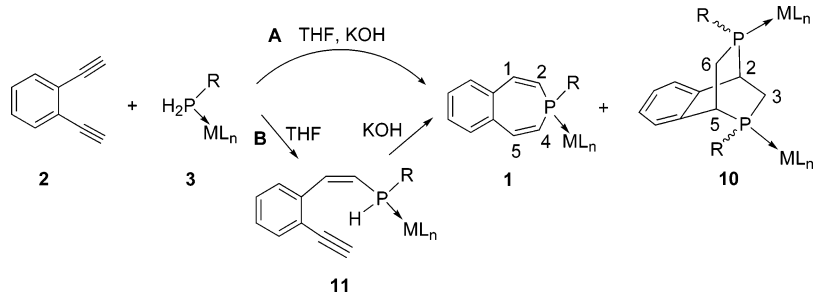
(13) Jarzêcki, A. A.; Gajewski, J.; Davidson, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 6928 and references therein.
(14) Dillon, K. D.; Mathey, F.; Nixon, J. F. In *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998.
(15) (a) Graham, T. W.; Cariou, R. P.-Y.; Sánchez-Nieves, J.; Allen, A. E.; Udachin, K. A.; Regragui, R.; Carty, A. J.; *Organometallics* **2005**, *24*, 2023. (b) Sánchez-Nieves, J.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 2404. (c) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2003**, *22*, 3927. (d) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 2657. (e) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 4463. (f) Sterenberg, B. T.; Carty, A. J. *J. Organomet. Chem.* **2001**, *617*−*618*, 696.
(16) For recent reviews: (a) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95. (b) Lammertsma, K.; Vlaar, M. J. M.; *Eur. J. Org. Chem.* **2002**, 1127. (c) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938.
(17) (a) Wit, J. B. M.; van Eijkel, G. T.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2596. (b) Wit, J. B. M.; van Eijkel, G. T.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Tetrahedron* **2000**, *56*, 137. (c) Borst, M. L. G.; van der Riet, N.; Lemmens, R. H.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Mills, A. M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2005**, *11*, 3631. (d) Streubel, R.; Wilkens, H.; Ostrowski, A.; Neumann, C.; Ruthe, F.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1492. (e) Wilkens, H.; Ruthe, F.; Jones, P. G.; Streubel, R. *Chem. Commun.* **1998**, 1529. (f) Mercier, F.; Deschamps, B.; Mathey, F. *J. Am. Chem. Soc.* **1989**, *111*, 9098.
(18) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.
(19) Lammertsma, K.; Ehlers, A. W.; McKee, M. L. *J. Am. Chem. Soc.* **2003**, *125*, 14750.
(20) Yasuike, S.; Kiharada, T.; Tsuchiya, T.; Kurita, J. *Chem. Pharm. Bull.* **2003**, *51*, 1283.
(21) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.
(22) Bowles, D. M.; Anthony, J. E. *Org. Lett.* **2000**, *2*, 85.
(23) Michel, P.; Gennet, D.; Rassat, A. *Tetrahedron Lett.* **1999**, 8575.

Table 1. Yields and ^{31}P NMR Chemical Shifts of 3*H*-Benzophosphepine Complexes **1** (Scheme 4)

	R	ML_n	A[a] (%)	B[b] (%)	^{31}P[c] (ppm) **1**	**11**	**3**	$^1J_{PH}$[d] (Hz)	byproduct[e]
a	Ph	$W(CO)_5$	47	74	−14.8	−43	−89	365	−
b	Ph	$Mo(CO)_5$	40	67	5.8	−23	−69	345	A: 10
c	Ph	$MnCp(CO)_2$	35	−	64.0	−	+2[f]	−	−
d	Ph	$Cr(CO)_5$	37	39	23.1	+2	−38	352	A: polymer?
e	Me	$W(CO)_5$	47	19	−34.2	−69	−122	348	A: 10
f	*t*-Bu	$W(CO)_5$	41	−	10.5	−	−48	−	−
g	NEt_2	$W(CO)_5$	−	40	+56.8	+21	−14	381	−

[a] Method A, using KOH from the start. [b] Method B, using KOH only for completing the conversion of **11** to **1**. [c] ^{31}P NMR chemical shift recorded in $CDCl_3$ for **1** and THF for **11** and **3**. [d] ^{31}P NMR coupling constants for **11**. [e] Only when identified. [f] We assign the +2 ppm signal to $(PhPH_2)MnCp(CO)_2$ instead of the reported $(PhPH_2)_2MnCp(CO)$ (ref 24).

Scheme 4. Synthesis of Benzophosphepines **1**, with (A) and without (B) Initial Base, and Side Product



mixture gave the desired 3-aminobenzophosphepine $W(CO)_5$ complex **3g** in 40% yield as yellow crystals. The same one-pot sequential process, using base to complete the conversion of **11** to **1**, also worked well for the syntheses of several of the other 3*H*-benzophosphepine complexes listed in Table 1 (method B) and for some (**1a**,**b**) with better yields.

Tolerance of this method to variation of both transition-metal complexes [$M(CO)_5$ (M = Cr, Mo, W) and $MnCp(CO)_2$] and substituents (Ph, Me, *t*-Bu, and NEt_2) at the phosphorus center is evident (Table 1). Noteworthy is molybdenum complex **1b** (yellow crystals), because the corresponding phosphanorbornadiene **6b** is difficult to synthesize (29%), as traces of $Mo(CO)_6$ catalyze the polymerization of acetylenedicarboxylate. Therefore and because of the stability of the final products, most phosphinidene chemistry has revolved around the $W(CO)_5$ complexes. The ^{1}H NMR characteristics for **1d** with H(2) and H(4) resonances at 6.18 ppm, a sizable $^2J_{HP}$ coupling constant of 24.1 Hz, and a $^3J_{HH}$ of 12.4 Hz for the *cis*-olefin are also representative for the other benzophosphepine complexes. Using method A enables the synthesis of the sterically demanding *tert*-butyl derivative (**1f**, orange crystals), whereas amino derivative **1g** is accessible via method B, as discussed. The large difference in ^{31}P NMR chemical shifts between the methyl and *tert*-butyl derivatives (**1e**, −34.5 ppm; **1f**, 10.5 ppm) is due to the substituent effect, which is even more pronounced in the phosphine complexes **3**. The low-field ^{31}P NMR chemical shift of **1g** (56.8 ppm) indicates significant shielding due to electron donation of the nitrogen.

Side-Product Formation and Mechanism. The synthesis of 3-methyl-3*H*-benzophosphepine complex **1f** gives **10e** as byproduct in about 10%, which we believe to be the first complexed 2,5-diphosphabicyclo[2.2.2]octane[25] (or benzeno-1,4-diphosphinane). The meso and one of the rac-isomers that were formed could be isolated by chromatography. The ^{31}P NMR resonances at −15.0 and −16.6 ppm (J_{PP} = 17.4 Hz) for the meso-isomer consist of double doublets, indicating nonequivalent phosphorus atoms. The rac-isomer shows a single ^{31}P NMR resonance at −15.7 ppm, but the complexity of its W-satellites is consistent with the presence of two phosphorus atoms. Also the ^{1}H NMR spectrum of the symmetric **10e** (rac) isomer is less complex compared to the asymmetric meso-isomer. The bridgehead protons give a single resonance at δ 3.64 ppm with a large $^2J_{HP}$ of 22.7 Hz and smaller $^3J_{HH}$ coupling constants of 5.3 and 2.1 Hz. Two resonances are observed at 2.67 and 2.54 ppm for the *endo*- and *exo*-protons at C3 and C6. All other NMR data of these stable compounds that have melting points >170 °C are consistent with the bicyclo[2.2.2]octane structure **10e**.

In the X-ray crystal structure of *rac*-**10e**, the molecule has an approximate, noncrystallographic C_2 symmetry. Deviations from the exact symmetry are due to a different arrangement of the $W(CO)_5$ groups, which are both located over the ring system (Figure 1). The P−CH_3 bond distances are relatively short [1.826(3) and 1.822(3) Å] compared to the P−C bonds in the 1,4-diphosphinane part [1.854(3)−1.865(3) Å]. The arrangement around the bridge-head carbon C11 is nearly tetrahedral (Σ 329.4°) and the C−C bonds of the benzene-ring [all 1.386(4)−1.395(4) Å] are indicative of electron delocalization.

$Mo(CO)_5$-complexed diphosphinanes (*rac*- and *meso*-**10b**) were likewise obtained as byproducts (12%) in the synthesis of **1b** (also method A) and isolated by fractional crystallization. The rac-isomer has a ^{31}P NMR resonance at δ 19.7 ppm and the asymmetric meso-isomer has two at 27.2 and 25.1 ppm with a $^3J_{PP}$ coupling of 11.7 Hz. The molecular structure in the crystal of *meso*-**10b** (mp >116 °C), shown in Figure 2, is similar to that of *rac*-**10e**, but the pseudosymmetric bonds and angles differ slightly due to the asymmetry of the molecule, which has slightly longer bonds around the P2 than the P1 atom.

(24) Rehder, D.; Keçeci, A. *Inorg. Chim. Acta* **1985**, *103*, 173.
(25) 2,5-Diphosphabicyclo[2.2.2]octane as a structural motive can be recognized in several polycyclic compounds. See: (a) Märkl, G.; Beckh, H. J.; Mayer, K. K.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 236. (b) Kojima, T.; Ishioka, Y.; Matsuda, Y. *Chem. Commun.* **2004**, 366.

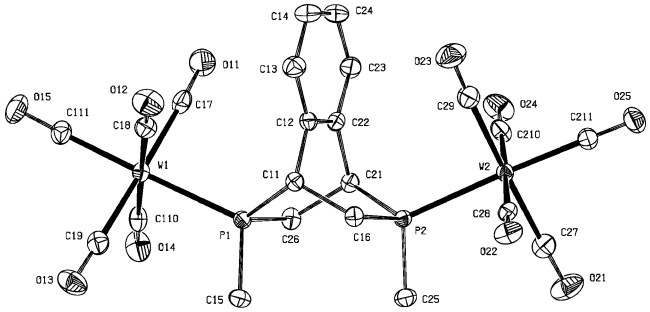


Figure 1. Displacement ellipsoid plot (50% probability level) of *rac*-**10e**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): P1−W1, 2.5058(7); P2−W2, 2.5048(7); P1−C11, 1.860(3); P2−C21, 1.854(3) P1−C26, 1.861(3); P2−C16, 1.865(3); P1−C15, 1.826(3); P2−C25, 1.822(3); C11−C12, 1.513(3); C12−C22, 1.395(4); C12−C13, 1.393(4); P1−C11−C12, 105.66(17); P2−C21−C22, 105.32(17); P1−C11−C16, 113.85(17); P2−C21−C26, 113.71(17); C11−C12−C13, 123.2(2); C19−W1−P1−C15, 12.35(13); C27−W2−P2−C25, 11.57(13); C16−C11−C12−C13, −118.3(3); C15−P1−C11−C16, 45.8(2); P1−C11−C12−C13, 118.5(3).

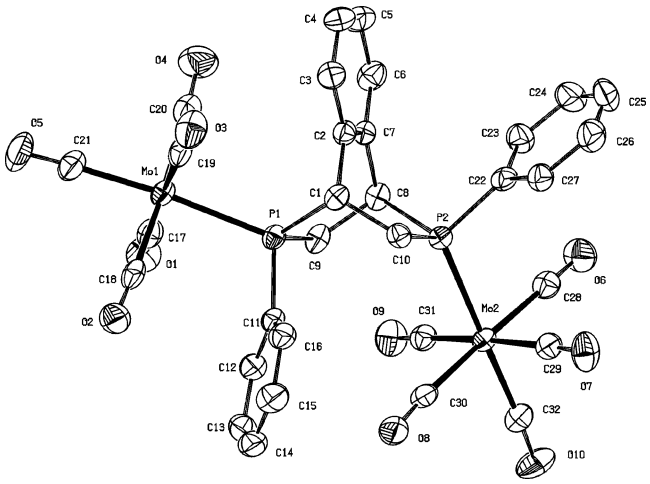


Figure 2. Displacement ellipsoid plot (50% probability level) of *meso*-**10b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): P1−Mo1, 2.5099(9); P2−Mo2, 2.5237(9); P1−C11, 1.826(3); P2−C22, 1.830(4); P1−C1, 1.850(4); P2−C8, 1.861(3); P1−C9, 1.855(4); P2−C10, 1.863(4); C1−C10, 1.533(5); C1−C2, 1.515(5); C2−C7, 1.396(5); C2−C3, 1.393(5); P1−C1−C2, 104.4(2); C2−C1−C10, 112.6(3); Mo1−P1−C1, 119.35(11); Mo2−P2−C8, 116.53(11); P1−C1−C2−C3, 116.2(3).

Application of the benzeno-1,4-diphosphinane frame, be it decomplexed, can be envisioned both as a novel ligand system and as a supramolecular building block. Its formation can be explained by successive attacks of two phosphide complexes on diethynylbenzene **2**. The yields increased with an excess of the phosphine complex. The first phosphide attacks a terminal acetylenic carbon in either an anti (a) or syn (b) fashion (Scheme 5). Route b gives a *cis*-vinylphosphide complex that undergoes intramolecular hydrophosphination to form benzophosphepine **1**. Anti attack leads to a *trans*-olefin that cannot undergo ring-closure and is therefore subject to attack by a second phosphide complex, either before or after protonation. When this occurs in a syn fashion ring-closure at the benzylic carbon will give the Markovnikov addition product, and subsequent protonation allows the other phosphorus atom to perform a similar addition to yield 1,4-diphosphinane **10**. When the second phosphide enters in an anti-fashion, which may even be sterically preferred, the resulting bis(*trans*-vinylphosphide) is unable to ring-close and may lead to polymeric structures and loss of material.

The uncatalyzed reaction of phosphine complexes **3** with 1,2-diethynylbenzene **2** (method B) is truly remarkable because so far all reported hydrophosphinations that used complexed phosphines required heat, base, and/or radical initiators,[7,26] except for a report on the room-temperature reaction of ethylene with a Pd−phosphine complex[9] and the facile reaction of a bridged phosphine diiron complex with phenylacetylene.[27]

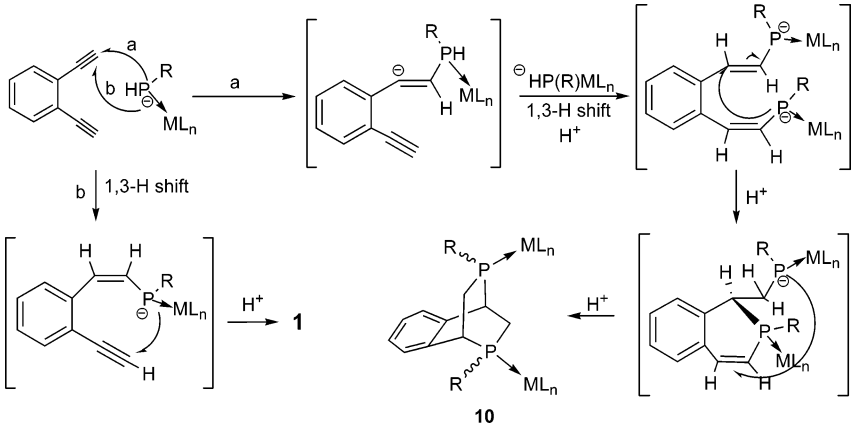
The first part of the explanation became apparent on mixing equimolar amounts of $PhPH_2-W(CO)_5$ and $PhPD_2-W(CO)_5$ in anhydrous THF. ^{31}P NMR monitoring showed slow H−D exchange, forming $PhPHD-W(CO)_5$ with a characteristic triplet at −90 ppm, which signifies phosphine disproportionation. The second indicator is the deshielded ^1H NMR chemical shift of the 1,2-diethynylbenzene **2** (3.33 ppm, ≡CH), which suggests an activated acetylenic group similar to benzoylacetylene (3.44 ppm),[28] which readily undergoes phosphine catalyzed additions.[29] Under the same experimental conditions, phenylphosphine **3a** reacted hardly with phenylacetylene (3.03 ppm), giving <1% of vinylphosphine, while *p*-diethynylbenzene (3.27 ppm) was only slightly less reactive than **2**. The third, important lead was the NMR identification of vinylphosphine **11d** in the reaction of $PhPH_2-Cr(CO)_5$ with **2** (Scheme 4), even though it could not be obtained free of benzophosphepine complex **1d**. The olefinic protons showed a NOE interaction and a coupling constant (12.5 Hz) that are consistent with a cis olefin. The ^{31}P NMR chemical shift at 4.3 ppm is similar to the radical-initiated hydrophosphination product (+3.4, $^1J_{PH} = 356$ Hz) of $PhPH_2-Cr(CO)_5$ (**3d**) with phenylacetylene, which reportedly has a cis configuration ($^3J_{HH} = 13$ Hz).[8] Further, ^{31}P NMR monitoring of the reaction of **3d** with **2** in the presence of the radical initiator AIBN showed conversion of the phosphine (**3d**) to vinylphosphine **11d**. Some benzophosphepine **1d** [$\delta(^{31}P)$ 23.1] was also formed, but it was not stable at the temperatures required for radical formation (50−60 °C). Finally, ^{31}P NMR monitoring of the deuteriophosphination of **2** with $PhPD_2-W(CO)_5$ (**3h**) (with incomplete conversion) showed the formation of only two D-containing products, 1,5-dideuteriophosphepine **1h** (−14.8 ppm, 95% D-label, 14% isolated yield) and a product with a chemical shift at −43.9 ppm (t, $^1J_{PD}$ 55 Hz) that we assign to **11h**.

Consequently, we surmise that the hydrophosphination in THF starts by some disproportionation of phosphine complex **3** into **12** and **13** of which the phosphide anion attacks the activated acetylenic carbon of **2** to form vinyl anion **14** that is then protonated (by **12**) to give *cis*-vinylphosphine **11** (Scheme 6). The fact that the phenylphosphine complexes give better yields than the alkylphosphines (Table 1) supports the disproportionation mechanism as the phenyl group stabilizes the charged phosphorus center better.

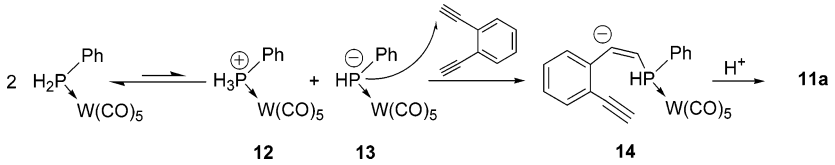
Reactivity and Kinetics of Benzophosphepines. All the benzophosphepine complexes **1** are phosphinidene precursors, as shown by their reaction at 80−85 °C (120 °C for **1f**) with diphenylacetylene and *trans*-stilbene that afforded the expected phosphirenes **15** and phosphiranes **16**, respectively, in (very)

(26) (a) Kalinina, I.; Donnadieu, B.; Mathey, F. *Organometallics* **2005**, *24*, 696. (b) Huttner, G.; Müller, H.-D.; Friedrich, P.; Kölle, U. *Chem. Ber.* **1977**, *110*, 1254.
(27) Sugiura, J.; Kakizawa, T.; Hashimoto, H.; Tobita, H.; Ogino, H. *Organometallics* **2005**, *24*, 1099.
(28) Noro, M.; Masuda, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1994**, *116*, 6179.
(29) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535.

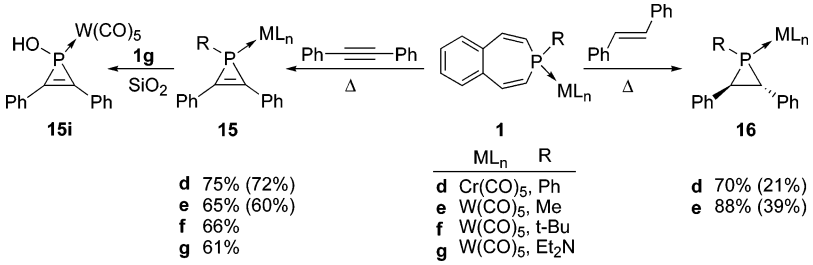
Scheme 5. Proposed Mechanism for the Formation of Diphoshabicyclo[2.2.]octanes **10**



Scheme 6. Proposed Mechanism for the Uncatalyzed Formation of Vinylphosphine Complexes



Scheme 7. Phosphinidene Addition Reactions for **1** with Yields in Parentheses for Those Using **6**



good yields (Scheme 7). The values in parentheses refer to the reported yields for the reaction with phosphanorbornadiene complex **6**.[18,30]

Particularly complexed aminobenzophosphepines are interesting precursors to aminophosphinidene complexes, which could be trapped upon thermolysis of aminophosphirane complexes in high yields.[17c] The amine group in these trapping products is easily replaced, as has been shown, for example, for the corresponding amino phosphirene that converts to the chloro derivative on treatment with dry HCl.[31] We found an unexpected functionalization of the known[32] aminophosphirene **15g** during its purification over silica, on which it partially converted to the yet unknown hydroxyphosphirene complex **15i**. This yellow solid (mp 122−124 °C) has a rather shielded ^{31}P NMR chemical shift at −78.1 ppm with a large $^{1}J_{PW}$ of 319.6 Hz.

The reaction of the benzophosphepine complexes **1** with phenylacetylene in toluene is a first-order process for the release of the phosphinidene moiety from **1** that depends more on the substituent than on the transition-metal group. The half-life times, summarized in Table 2, are at 75 °C, similar for the phenyl derivatives **1a**, **b**, **d**; the $t_{1/2}$ for Mn complex **1c** could not be determined accurately due to the broadness of the NMR signals, but the onset of the reaction starts similarly to **1a** at about 50 °C. Methyl substitution (**1e**) increases the half-life time by more than 3 times, and that for the *tert*-butyl derivative **1f** is about twice as much at the higher temperature of 115 °C. The kinetics was determined by ^{31}P NMR for methyl derivative **1e** at four different temperatures (Table 2) from which an activation energy is derived of 27.0 ± 0.3 kcal/mol, which is 6 kcal/mol less than for the related decomposition of 7-phenyl-7-phosphanorbornadiene complex **6**.[33] The activation enthalpy is calculated to be 26.3 ± 0.3 kcal/mol, with a small entropy of activation of −5.1 ± 0.9 eu. The rate constants were independent of either the concentration (5.1, 2.6, or 1.0 equiv) or the nature of the substrate (phenylacetylene, *trans*-stilbene, or aniline) in the reaction mixture as graphically shown in Figure 3. This behavior is similar to that reported for **6**.[30,34]

Table 2. Half-life Times of Benzophosphepines **1** in the Presence of Diphenylacetylene and the Rate Constants for the Decomposition of **1e** in the Presence of Diphenylacetylene

half-life determination			rate constant determination for **1e**	
phosphepine **1**	T (°C)	$t_{1/2}$ (min)	T (°C)	k (10^{-5} L mol^{-1} s^{-1})
a	75	203	70	1.00
b	75	111	80	3.18
d	75	142	90	9.45
e	75[a]	633	100	24.9
f	115	344	E_a (kcal/mol)	26.3 ± 0.3

[a] Derived from an Arrhenius plot.

(30) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.
(31) Deschamps, B.; Mathey, F. *Synthesis* **1995**, 941.
(32) Deschamps, B.; Mathey, F. *New J. Chem.* **1988**, *12*, 755.
(33) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

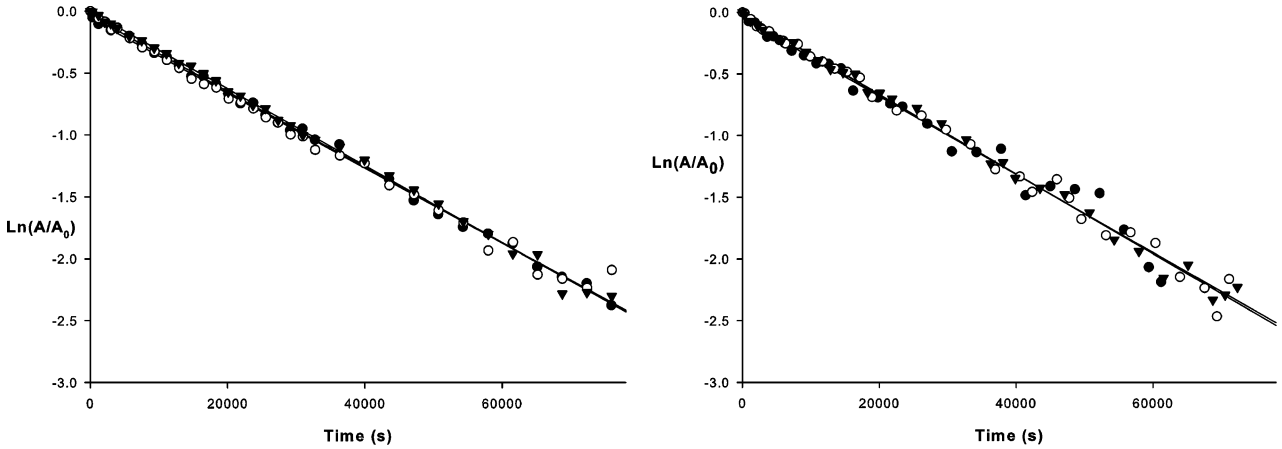


Figure 3. Kinetic plots of the decomposition of **1e** at 80 °C in the presence of (left) aniline (●), or 5.1 (○) or 2.6 (▼) equiv of stilbene, or (right) 5.1 (●), 2.6 (▼), or 1.0 (○) equiv of diphenylacetylene.

Table 3. B86-P88/*TZP* Energies (in kcal/mol) Relative to eq-**I**

entry	ML_n	R	annelated	syn-**II**	synTS	ax-**I**	TS-flip	eq-**I**	antiTS	anti-**II**
1	−	H	−	−4.2	10.6	0.0	6.3	0.0	9.7	−4.7
2	$Cr(CO)_5$	H	−	4.4	15.5	1.3	5.9	0.0	13.6	3.1
3	$W(CO)_5$	H	−	3.0	15.1	1.5	6.2	0.0	13.7	2.3
4	$Cr(CO)_5$	Ph[a]	−	2.8	13.5	2.0	5.5[c]	0.0	d	2.0
5	$Cr(CO)_5$	Ph[b]	−	3.3	15.3	0.9	4.1[c]	3.7[c]	21.4[c]	7.2
6	−	H	yes	9.6	19.3	−1.3	2.7	0.0	18.0	8.5
7	$Cr(CO)_5$	H	yes	19.1	26.1	0.4	2.8	0.0	24.1	17.6

[a] Perpendicular to the P−W bond. [b] Parallel to the P−W bond; values relative to eq-**I**, entry 4. [c] No frequencies. [d] No convergence.

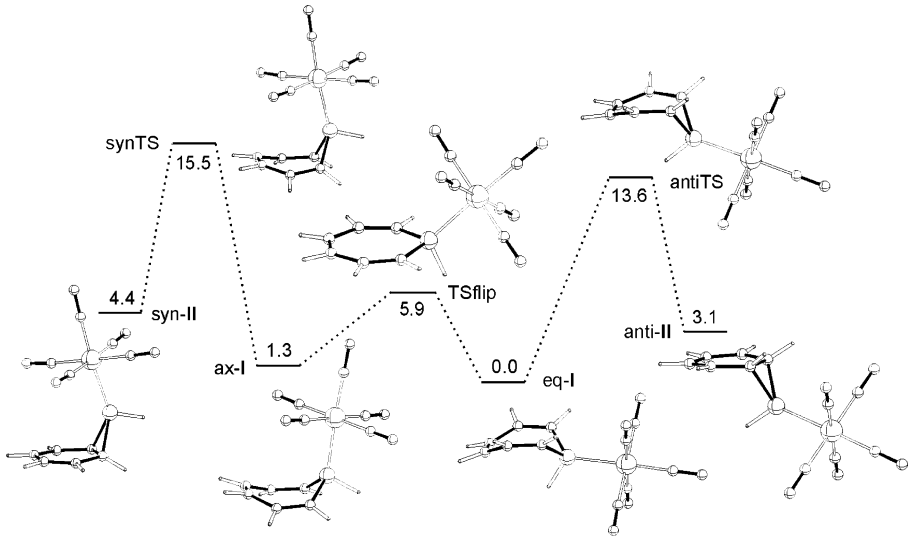


Figure 4. Energy diagram for the relationship of phosphine−$Cr(CO)_5$ (**I**) and phosphanorcaradiene−$Cr(CO)_5$ (**II**).

To better understand the relationship between the benzophosphepine and 7-phosphanorbornadiene complexes, we used density functional theory (B86-P88) for several parent phosphinidene complexes. Their energetic data are summarized in Table 3. The relationship is graphically depicted in Figure 4 for the parent phosphepine−$Cr(CO)_5$ (labeled **I**). Its two conformations with the transition metal group in either an axial (ax) or equatorial position (eq) interconvert via a ring-flip with a small energy barrier of only 5.9 kcal/mol. Each rearranges in a symmetry-allowed disrotatory process to the corresponding *syn*- or *anti*-phosphanorcaradiene complex (labeled **II**), but these processes are endothermic by about 3 kcal/mol with barriers of nearly 14 kcal/mol. The higher barrier for *ax*-**I** → *syn*-**II** may stem from steric interactions between the metal group and the cyclohexadiene ring.

The influence of the transition group on the energy profile is important but does not discriminate between the metals (entries 2 and 3 of Table 3). Complexation destabilizes norcaradiene **II** with respect to phosphepine **I** and to a smaller extent the transition state for the electrocyclization. Thus, whereas the rearrangement is exothermic for the uncomplexed phosphepine (entry 1), which is indeed an elusive species,[12,20,35] metal complexation results in an endothermic rearrangement. The

(34) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

(35) (a) Märkl, G.; Schubert, H. *Tetrahedron Lett.* **1970**, 1273. (b) Märkl, G.; Burger, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 894.

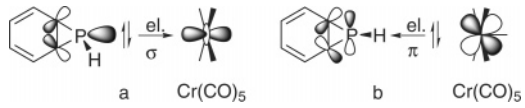
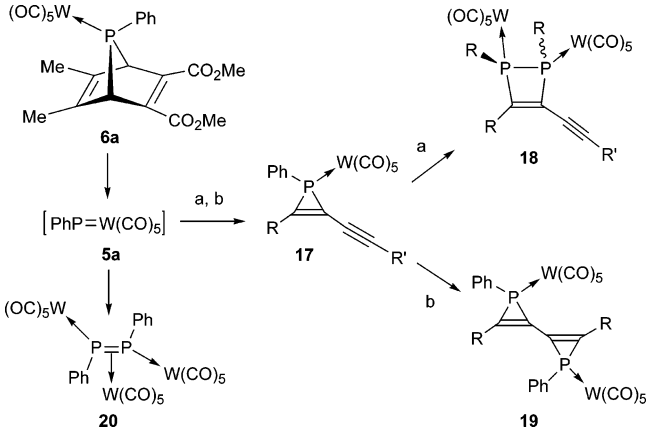


Figure 5. Schematic representation of the interaction of the Walsh orbitals of phosphanorcaradiene **II** with the orbitals of chromium−pentacarbonyl group.

Scheme 8. Reaction of Phosphinidene 5**a** with Diphenyldiacetylene at (a) 55 °C with Cu^{I}Cl and (b) 110 °C



influence of the transition metal is evident. Coordination of the phosphorus atom to the transition metal results in strong σ-bonding with electron transfer from the ligand to the metal together with weaker π-back-bonding due to electron donation of the metal into the unoccupied orbitals of the ligand.[36] The P-metal σ-bond diminishes the strength of the phosphirane C−C bonding orbital (Figure 5a), while π-back-donation enhances the antibonding nature of the distal C−C bond (Figure 5b). Both effects stabilize the phosphepine over the norcaradiene structure.[37]

Substituting hydrogen for a phenyl group decreases the barrier for electrocyclization slightly (≤1.0 kcal/mol, entries 4 and 5). The phenyl group can adopt two conformations, either perpendicular or parallel to the P−W bond, the latter of which is found in the crystal structure of W(CO)$_5$−benzophosphepine **1a**, but the difference is marginal for *ax*-**I** and *syn*-**II**; for the equatorial/anti pair, a parallel orientation results in an unfavorable interaction of the phenyl group with the phosphepine ring, leading to considerably higher energies. The effect of benzannellation is far more pronounced, raising the cyclization barrier by about 10 to 26.1 kcal/mol for forming *syn*-benzo-**II** from *ax*-benzo-**I** (entry 6, Table 3), because benzophosphanorcaradiene benefits far less from electron delocalization than benzophosphepine. Dissociation of *syn*-benzo-**II** into Cr(CO)$_5$−phosphinidene and naphthalene is endothermic by 14.9 kcal/mol, but is likely more favorable when the entropy term is included.[38] Recent DFT calculations on W(CO)$_5$−complexed phosphinidenes suggest a small barrier for this process (6.7 kcal/mol).[19]

In summary, ring-closure of metal-complexed benzophosphepine **I** appears to be the rate-determining step, which is in compliance with the kinetic data and with the experimental activation energy of 27.0 kcal/mol for reaction of the W(CO)$_5$−

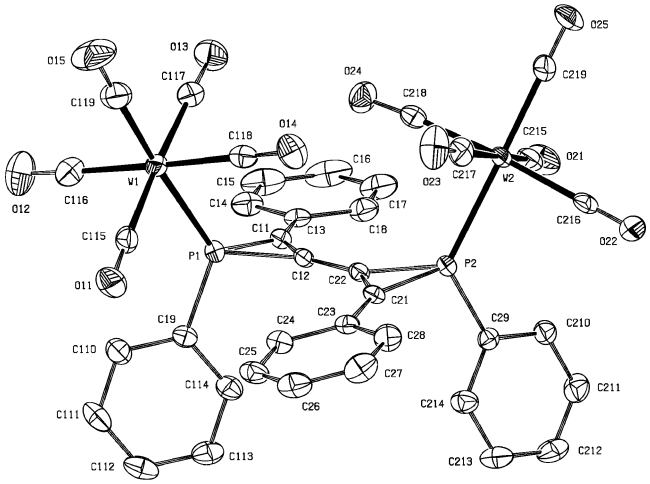


Figure 6. Displacement ellipsoid plot (50% probability level) of *rac*-**19**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): W1−P1, 2.4905(11); W2−P2, 2.4765(10); P1−C11, 1.803(4); P1−C12, 1.799(4); C11−C12, 1.325(6); C21−C22, 1.326(6); C12−C22, 1.423(6); C11−P1−C12, 43.18(18); C21−P2−C22, 43.27(18); C11−C12−C22−C21, −176.1(6); C12−C11−C13−C18, −3.2(9); C22−C21−C23−C28, −178.6(6).

complex **1e**. This is also consistent with the observation that the decomposition of **1e** is neither catalyzed by metals ($PdCl_2$, Pd/C, $CuSO_4$) nor by (Lewis) bases (KOH, Et_3N, BPh_3).

Addition to Diynes. Next to turn to is the window within (some of) the benzophosphepines complexes **1** are usable. After all, the electrophilic phosphinidene complexes may add to the C=C bonds that **1** possesses and to the C≡CH bonds of their starting material (**2**). We address these aspects starting with a 1,3-diyne. It has been shown that the "classical" 7-phosphanorbornadiene complex **6a** gives different products depending on the manner in which it is used (Scheme 8). At ca. 55 °C, using Cu(I)Cl as catalyst,[18] [1 + 2]-adduct **17** is the primary product. In selected cases, depending on the substituents R and R′, a second [PhPW(CO)$_5$] inserts into a C−P bond to give 1,2-diphosphetes **18**.[39] Instead, without using a catalyst (110 °C), a second alkyne addition takes place and gives bisphosphirenes **19**.[40] Diphosphene complex **20** is typically observed as a byproduct, resulting from the decomposition of **6a**.[33]

Benzophosphepines **1a** (2.2 equiv) reacted at 60 °C with diphenyl-1,3-butadiyne to give the *rac*-bis-phosphirene **19a** (δ ^{31}P −137.3 ppm) as orange needles in 11% yield, a trace of the meso-isomer (δ^{31}P −137.1 ppm), and 28% of monoadduct **17**[39a] (28%). The low yield of the diadduct is likely due to steric hindrance, which is evident from the single X-ray crystal structure analysis of the rac-isomer (Figure 6). In the crystal, the molecule of **19** has only C_1 symmetry. Conjugation of the two phosphirene double bonds is apparent from the short connecting C12−C22 bond [1.423(6) Å], similar to that reported for the di-SiMe$_3$ derivative.[40] In **19** conjugation is extended to the phenyl substituents, which lie almost in the same plane as the two phosphirene rings [torsion angles of −3.2(9)° and −178.6(6)°].

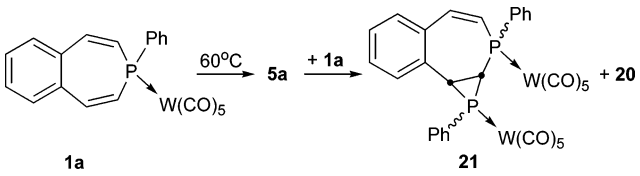
The question arises of the fate of the reactive phosphinidene in the absence of a substrate. For precursor **6a** this results mostly

(36) Goumans, T. P. M.; Ehlers, A. W.; van Hemert, M. C.; Rosa, A.; Baerends, E.-J.; Lammertsma, K. *J. Am. Chem. Soc.* **2003**, *125*, 3558.
(37) Günther, H. *Tetrahedron Lett.* **1970**, 5173.
(38) Bulo, R. E. Ph.D. thesis, Vrije Universiteit, Amsterdam (NL), The Netherlands, 2004.
(39) (a) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 4501. (b) Wang, B.; Nguyen, K. A.; Srinivas, N.; Watkins, C. L.; Menzer, S.; Spek, A. L.; Lammertsma, K. *Organometallics* **1999**, *18*, 796.
(40) Tran Huy, N. H.; Ricard, L.; Mathey, F. *J. Chem. Soc., Dalton Trans.* **1999**, 2409−2410.

Table 4. ^{31}P NMR Chemical Shifts (ppm), Assignments, and Intensities of the Isomers of **21**

21	δ	$^3J_{PP}$ (Hz)	W(CO)$_5$P2	W(CO)$_5$P1	rel int
a	−8.4, −126.9	14.7	endo	endo	0.46
b	−6.6, −118.8	11.7	endo	exo	1.00
c	−15.5, −123.4	11.4	exo	exo	0.59
d	−16.4, −127.9	14.6	exo	endo	<0.1

Scheme 9. Reaction of Phosphinidene **5a** in the Presence of **1a** at 60 °C



in diphosphene **20**, which often is also a byproduct of the addition reactions. Monitoring by ^{31}P NMR the decomposition of benzophosphepine **1a** in toluene at 60 °C for 3 days likewise resulted in the formation of **20** (10% by ^{31}P NMR), confirming the intermediacy of the same reagent, but in addition gave other products (70% by ^{31}P NMR) that were also observed in the reaction with diphenyldiacetylene. Analysis of the reaction mixture (see the Experimental Section) showed the presence of the four isomers of phosphirane complex **21** (characteristics are summarized in Table 4) that must result from addition of [PhPW(CO)$_5$] to one of the double bonds of phosphepine **1a** (Scheme 9). The addition underscores the olefinic nature of the phosphepine ring of **1a** as additions to aromatic rings are rare.[41]

Characteristic in the ^{31}P NMR spectrum of the major isomer **21b** are the double doublets at −6.6 and −118.8 ppm with a $^3J_{PP}$ coupling constant of 11.7 Hz, which enables the assignment of the other isomers as they have different ^{31}P NMR chemical shifts (Table 4). The fact that both the endo and exo orientations of the W(CO)$_5$P2 moiety are observed is in accord with the calculated modest energy barrier between the axial and equatorial conformations of benzophosphepine complexes. The assignment of **21b** was confirmed by a single-crystal X-ray structure determination, which is shown in Figure 7. The W(CO)$_5$ moiety of the phosphepine ring is positioned axially, just as in **1a**, and that of the phosphirane is exo-substituted. The P-phenyl substituent is parallel to the almost planar seven-membered ring, thereby rotated by about 90° from its perpendicular position in **1a**. The P−C bond lengths [1.840(2) and 1.839(2) Å] and the C1−P−C2 bond angle [48.74(9)°] for the phosphirane ring are in the expected range.[42]

To further establish the reaction window within which the benzophosphepine complexes can be used, it is of interest to verify to what extent they can react with their precursor, 1,2-diethynylbenzene **2**. For this purpose we applied the molybdenum complex **1b** that gave both the monoadduct **22** (49%) and the diadduct **23** (40%) in modest yields (Scheme 10), which in part is due to the limited stability of **2** at elevated temperatures. For **23** steric hindrance plays a role. The X-ray crystal structure of *rac*-**23** shows a slightly deformed Mo(CO)$_5$ moiety (Figure 8). The C═C bonds of the phosphirenes are conjugated with each other via the connecting benzene ring, as signified by the small dihedral angles and the short C1−C7 [1.456(3) Å] and C2−C9 [1.457(3) Å] bonds. Still, steric bulk prevents the benzene and phosphirene rings to lie in the same plane, causing the P1-phosphirene ring to be tilted by 20°. The other characteristic data of *rac*-**23** in solution (^{31}P δ -135.5 ppm) resemble those of a similar phosphirene molybdenum complex.[43]

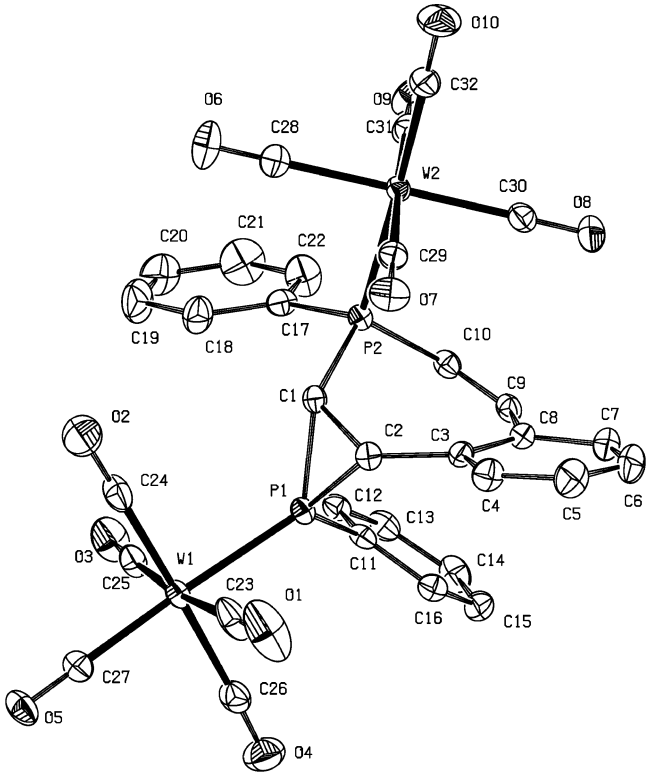


Figure 7. Displacement ellipsoid plot (50% probability level) of **21b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): W1−P1, 2.4681(5); W2−P2, 2.4960(5); P1−C1, 1.840(2); P2−C1, 1.814(2); P1−C2, 1.860(2); P2−C10, 1.799(2); C3−C8, 1.412(3); C1−P1−C2, 48.74(9); C1−P2−C10, 106.17(10); P1−C1−P2, 128.77(12); P1−C2−C3, 130.22(16); C11−P1−C1−P2, 11.47(18); P2−C1−C2−P1, −122.23(16); C8−C9−C10−P2, 4.4(4); P2−C1−C2−C3, 0.4(3); C28−W2−P2−C17, 46.02(11); C23−W1−P1−C11, 122.53(12).

Reactivity of a Manganese Phosphinidene. So far we discussed the benzophosphepines **1** as precursors for electrophilic phosphinidenes, such as [RPM(CO)$_5$], but because of its convenient synthesis, access to species with other philicities can be envisioned. We will elaborate on this aspect for manganese benzophosphepine **1c**, on which we reported only briefly in an earlier communication.[11] Presumably [Ph−P═Mn(CO)$_2$Cp] (**5c**) has strongly reduced electrophilic character, since the philicity of a phosphinidene complex [RP═ML$_n$] is known to change profoundly on replacing electron-withdrawing (e.g. CO) for electron-donating ligands, such as the cyclopentadienyl ring (Cp).[44] In fact, a number of very stable, highly nucleophilic phosphinidene complexes with rather limited reactivity have

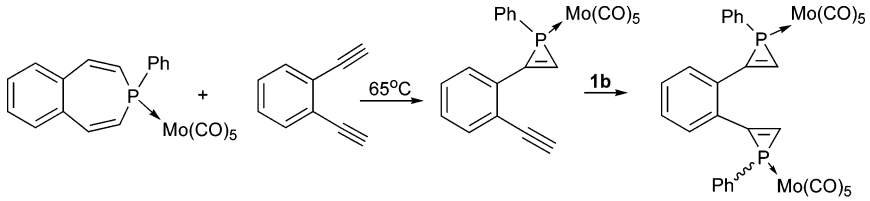
(41) (a) Bulo, R. E.; Trion, L.; Ehlers, A. W.; de Kanter, F. J. J.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2004**, *10*, 5332. (b) Bulo, R. E.; Ehlers, A. W.; de Kanter, F. J. J.; Wang, B.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2004**, *10*, 2732. (c) van Eis, M. J.; Komen, C. M. D.; de Kanter, F. J. J.; de Wolf, W. H.; Lammertsma, K.; Bickelhaupt, F.; Lutz, M.; Spek, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1547. (d) Svara, J.; Mathey, F. *Organometallics* **1986**, *5*, 1159.

(42) Mathey, F.; Regitz, M. Three-membered rings. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Elsevier: Oxford; 2001; p 17−55.

(43) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.

(44) Ehlers, A. W.; Baerends, E. J.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2831.

Scheme 10. Reaction of Benzophosphepine **1b** with 1,2-Diethynylbenzene



been reported.[45] Because both CO and Cp ligands are present in **5c**, it is of interest to explore its reactivity.

Phosphinidene complex **5c** was found to be not nucleophilic enough to react with benzophenone to form a phosphaalkene[46] nor to be electrophilic enough to yield a P−O ylide either.[47] And although reaction with *trans*-stilbene did not take place, addition to phenylacetylene did occur to give the first manganese-complexed phosphirene (**24**) in 81% yield (Scheme 11). The increased electron donation from the transition metal fragment of the yellow product (mp 105 °C) is apparent from the ^{31}P NMR chemical shift at −59.0 ppm, which is significantly deshielded from that for the phosphirene−M(CO)$_5$ (M = W, Mo) complexes. Phosphirene **24** shows a doublet for its olefinic proton at 8.52 ppm with a large $^2J_{HP}$ of 19.3 Hz. An X-ray crystal structure (Figure 9) supports the formation of the phosphirene, which has a Mn−P bond length [2.1961(6) Å] similar to that of the benzophosphepine complex **1c**[11] and likewise has its P-phenyl group oriented parallel to this bond. The phosphirene bond lengths and angles are in the expected range.[42] Conjugation between the C1-phenyl group and the phosphirene ring is suggested by the small torsion angle of 5.6(3)°.

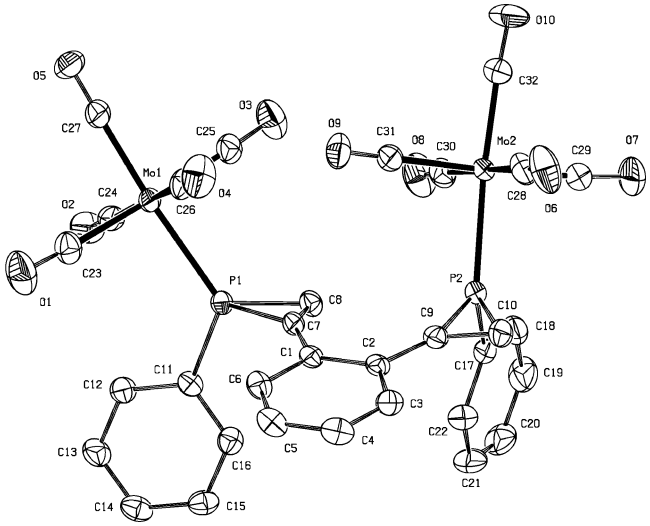
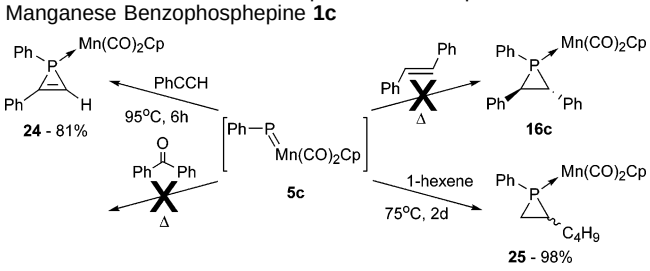


Figure 8. Displacement ellipsoid plot (50% probability level) of *rac*-**23**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): Mo1−P1, 2.5180(6); Mo2−P2, 2.4885(7); P1−C7, 1.808(2); P1−C8, 1.795(3); P2−C9, 1.808(3); P2−C10, 1.781(3); C7−C8, 1.311(4); C9−C10, 1.311(4); C1−C7, 1.456(3); C1−C2, 1.416(3); C2−C9, 1.457(3); C2−C3, 1.398(3); C7−P1−C8, 42.66(11); C9−P2−C10, 42.85(12); C2−C1−C7, 123.7(2); C2−C9−C10, 139.6(2); P2−C9−C2, 152.85(19); C2−C1−C7−P1, 177.1(2); C2−C1−C7−C8, 21.2(6); C7−C1−C2−C9, 5.1(4); C1−C2−C9−C10, 177.2(3); C1−C2−C9−P2, −5.0(6); C23−Mo1−P1−C11, 42.02(12); C31−Mo2−P2−C17, 122.98(12).

Scheme 11. Reactions of Phosphinidene **5c** Expelled from Manganese Benzophosphepine **1c**



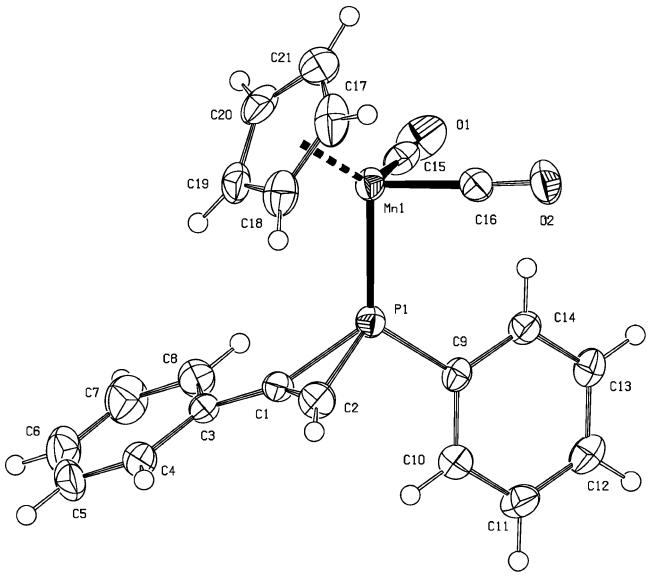


Figure 9. Displacement ellipsoid plot (50% probability level) of **24**. Selected bond distances (Å), angles (deg), and torsion angles (deg): Mn1−P1, 2.1961(5); P1−C1, 1.7896(16); P1−C2, 1.7781(18); C1−C2, 1.310(2); Mn−C15, 1.7691(18); Mn−C16, 1.7633(18); C15−O1, 1.157(2); C1−P1−C2, 43.08(8); Mn1−P1−C1, 125.48(5); C16−Mn1−P1−C9, −47.71(8); C2−C1−C3−C4, 5.6(3).

The reduced reactivity of [Ph−P═Mn(CO)$_2$Cp] (**5c**) is reminiscent to that of [*i*-Pr$_2$N−P═Fe(CO)$_4$], which adds to alkynes and to terminal olefins, but not to di- or higher substituted ones.[17a−c] Reaction of benzophosphepine **1c** in 1-hexene at 70 °C gave nearly quantitatively (98%) in a 1:1.4 mixture the *anti-:syn*-phosphirane complexes **25** as a yellow oil (Scheme 11). The ^{31}P NMR chemical shifts of **23** (−77.5/−

(45) For examples: (a) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (b) Ho, J.; Rousseau, R.; Stephan, D. W. *Organometallics* **1994**, *13*, 1918. (c) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed.* **1993**, *32*, 756. (d) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643. (e) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846. (f) Termaten, A. T.; Nijbacker, T.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Organometallics* **2002**, *21*, 3196. (g) Termaten, A. T.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2003**, *9*, 3577. (h) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 13350. (i) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Baik, M. H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 1924.
(46) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914. The high reactivity of the Zr-complex may be due to loss of a ligand (16-electron species) and/or oxophilicity of the Zr-center.
(47) Streubel, R.; Ostrowski, A.; Wilkens, H.; Ruthe, F.; Jeske, J.; Jones, P. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2427.

72.7 ppm) are at distinctly higher field than that of phosphirene complex **24** (−59.0 ppm), while the phosphorus in a phosphirene is usually more deshielded than in a less condensed phosphirane. The $Mn(CO)_2Cp$-complexed phosphiranes **25** are stable at room temperature, which differs from the $Fe(CO)_4$-complexed ones that are amenable to retroaddition of the phosphinidene.[17a−c] It is evident that **5c** still shows electrophilic behavior, albeit less than **1a,b**.

Conclusion

We have demonstrated the accessibility of 3*H*-benzophosphepine complexes for a variety of metals and substituents under mild conditions in acceptable yields. As side products in the synthesis of benzophosphepines, novel benzeno-1,4-diphosphinanes were isolated. All of the benzophosphepine complexes eliminate electrophilic phosphinidene complexes at elevated temperatures, as demonstrated by trapping experiments and kinetic analysis and as confirmed by calculations on the proposed mechanism. Compared to others, the lower reaction temperature of this method to generate phosphinidenes enabled the synthesis of a delicate diphosphirene complex. Decomposition of benzophosphepines **1** in the absence of a substrate present results in addition of the phosphinidene complex to the a C═C bond of another phosphepine molecule. Currently, we are exploring the use of phosphepines, complexed with other transition-metal groups and Lewis acids, to enlarge their scope and applicability.

Experimental Section

Calculations. All geometry optimizations were performed with the ADF[48] program, using a triple ζ basis set with polarization functions, the local density approximation (LDA) in the Vosko−Wilk−Nusair parametrization[49] with nonlocal corrections for exchange (Becke88)[50] and correlation (Perdew86)[51] included in a self-consistent manner, and the analytical gradient method of Versluis and Ziegler.[52] Minima were confirmed to have only a positive force constant and the transition structures to have only one imaginary value using the Gaussian98 program package,[53] using geometries optimized with the BP86 exchange-correlation potentials and the LANL2DZ basis set for chromium or tungsten and 6-31G(d) for all other elements.

Synthesis. All experiments were performed under an atmosphere of dry nitrogen. All solvents were distilled from $LiAlH_4$ (pentane, diethyl ether), sodium benzophenone (THF), or P_2O_5 (dichloromethane) before use. Diisopropylamine was distilled from KOH. $W(CO)_5(MePH_2)$, $W(CO)_5tBuPH_2$, and $Cr(CO)_5(PhPH_2)$ were synthesized according to literature procedures.[54] The synthesis of $W(CO)_5(Et_2NPH_2)$ (**3g**) has been described briefly before.[55] All other compounds were purchased and used as such. NMR spectra were recorded on Bruker AC 200 (^1H, ^{13}C), Bruker WM 250 (^1H, ^{13}C, ^{31}P), and Bruker MSL 400 MHz (^1H, ^{13}C) spectrometers, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 900 spectrometer. NMR chemical shifts are internally referenced to the solvent for ^1H ($CDCl_3$, 7.25 ppm; C_6D_6, 7.15 ppm) and ^{13}C ($CDCl_3$, 77.0 ppm; C_6D_6, 128 ppm) and externally for ^{31}P to 85% H_3PO_4.

1,2-Bis(2′,2′-dibromoethenyl)benzene (8). Triphenylphosphine (27.52 g, 104.9 mmol) was added portionwise to a cold (0 °C) solution of tetrabromomethane (17.39 g, 52.4 mmol) in 250 mL of dichloromethane. The resulting orange-red solution was stirred at room temperature for 20 min. After cooling to 0 °C a solution of 3.07 g (22.8 mmol) of *o*-phthaldialdehyde in 100 mL of dichloromethane was added slowly and the mixture was stirred in the dark at room temperature for 2 h. The reaction mixture was extracted with distilled water (2 × 100 mL) and the water layers washed with dichloromethane (2 × 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Pentane (7 × 150 mL) was added and the resulting suspension was decanted after stirring. After addition of another 150 mL of pentane to the suspension it was filtered and all pentane fractions were combined, concentrated, and purified by column chromatography (SiO_2, 1% Et_2O in pentane, $R_f = 0.5$), yielding a yellow oil (9.85 g, 22.1 mmol, 97%). ^{13}C NMR ($CDCl_3$): δ 135.4 (CH═), 134.58 (*ipso*-ArC), 128.8 (*o*-ArC), 128.4 (*m*-ArC), 93.1 (═CBr_2). ^1H NMR ($CDCl_3$): δ 7.47−7.56 (m, 2H, *o*-ArH), 7.42 (s, 2H, CH═), 7.35−7.39 (m, 2H, *m*-ArH). HRMS Calcd for $C_{10}H_6{}^{79}Br_2{}^{81}Br_2$: 445.716 20. Found: 445.717 01. MS *m/z* (%): 446 (5) [M^+], 367 (20) [$M^+ - Br$], 286 (100) [$M^+ - {}^{81}Br - {}^{79}Br$], 126 (38) [$M^+ - Br_4$].

1,2-Diethynylbenzene (2). *n*-BuLi (48.8 mL, 78.1 mmol, 1.6 M in hexanes) was added to a cold (−78 °C) solution of 10.3 mL (78.1 mmol) of diisopropylamine in 250 mL of THF. After warming up to room temperature the solution was added carefully to a cold (−78 °C), well-stirred solution of 5.82 g (13.0 mmol) of **8** in 50 mL of THF. After 20 min of stirring at −78 °C, the reaction was quenched with 130 mL of sat. aq. $(NH_4)_2SO_4$ and stirred for 2 h at room temperature. The reaction mixture was poured out in 200 mL of pentane, the organic layer was separated and washed with water, dried ($MgSO_4$), concentrated, and purified using column chromatography (SiO_2, 1% Et_2O in pentane, $R_f = 0.42$), yielding a colorless liquid (1.54 g, 12.2 mmol, 94%). ^1H NMR ($CDCl_3$): δ 7.48−7.54 (m, 2H, *o*-ArH), 7.27−7.34 (m, 2H, *m*-ArH), 3.33 (s, 2H, CH).

1,2-Bis(bromoethynyl)benzene (9). To a cold (−78 °C) solution of **8** (0.3 mmol) in THF (3 mL) was added KO-*t*-Bu (0.5 g, 5.3 mmol). After 5 min, brine (3.8 mL) was added and the solution was allowed to warm to room temperature. The organic layer was separated and the water layer extacted with diethyl ether (3 × 5 mL). The combined organic layers were dried (Na_2SO_4), and after evaporation of the solvent, the crude product was purified by filtration over a short silica plug, eluting with 1% Et_2O in pentane, yielding a clear oil (0.084 g, 0.3 mmol, ∼100%). ^{13}C NMR ($CDCl_3$): δ 132.8 (s, ArC), 128.7 (s, ArC), 126.2 (s, *ipso*), 78.8 (s, Ar−C≡), 54.5 (s, ≡CBr).^1H NMR ($CDCl_3$): δ 7.37−7.41 (m, 2H, ArH), 7.21−7.25 (m, 2H, ArH).

(*N*,*N*-Diethylamino)phosphine Pentacarbonyltungsten(0) (3g). To a solution of dichloro(*N*,*N*-diethylamino)phosphine[56] (1.76 g, 10.1 mmol) in THF (80 mL) was added a mixture of $W(CO)_5AcCN$ and $W(CO)_5NMe_3$ (3.75 g, 10.0 mmol). The resulting green solution was protected from light and stirred for 3 days at 45 °C. The mixture was concentrated and filtered over a short silica plug, eluting with diethyl ether. Evaporation gave a yellow powder (3.57 g, 7.5 mmol, 75%). ^{31}P NMR ($CDCl_3$): δ 124.01 ($^1J_{PW} = 378.5$ Hz). ^1H NMR ($CDCl_3$): δ 3.44−3.59 (m, 4H, CH_2N), 1.25 (m, 6H, CH_3).

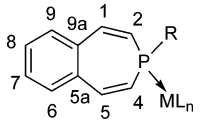
To a cold (0 °C), stirred suspension of $LiAlH_4$ (0.58 g, 15.3 mmol) in diethyl ether (20 mL) was carefully added a solution of dichloro(*N*,*N*-diethylamino)phosphine pentacarbonyltungsten(0) (3.64 g, 7.3 mmol) in diethyl ether (24 mL). After 1 h of stirring at room temperature, acrylonitrile was added (1.0 mL), the suspension was filtrated, and the solvent was evaporated, yielding a yellow oil (1.76 g, 4.1 mmol, 56%), which was immediately dissolved in diethyl ether. ^{31}P NMR (Et_2O): δ −12.1 ($^1J_{PW} = 245.0$ Hz)

(48) ADF program, version 2003.01: (a) te Velde, G.; Bickelhaupt F. M.; Baerends, E. J.; Fonseca-Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (b) Fonseca-Guerra, C.; Visser, O.; Snijders, J. G.; Baerends, E. J. In *METECC-95;* Clementi, E., Corongiu, C., Eds.; STEFF; Cagliari, Italy, 1995; p 307.
(49) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys*. **1992**, *99*, 84.
(50) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(51) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(52) (a) Fan, L.; Versluis, L.; Ziegler, T.; Baerends, E. J.; Raveneck, W. *Int. J. Quantum. Chem.; Quantum. Chem. Symp*. **1988**, *S22*, 173. (b) Versluis, L.; Ziegler, T. J. *J. Chem. Phys*. **1988**, *322*, 88.
(53) Frisch, M. J.; et al. *Gaussian 98*, Revision A.3, 1998.
(54) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.
(55) Mercier, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1984**, 782.
(56) Perich, J. W.; Johns, R. B. *Synthesis* **1988**, 142.

***P,P*-Dideuteriophenylphosphine Pentacarbonyltungsten(0) (3h).** Compound **3a** (0.71 g, 1.6 mmol) was dissolved in THF (3 mL), D_2O (1.8 mL) was added, and the resulting mixture was stirred well. THF was evaporated, pentane added, and the D_2O layer separated. ^{31}P NMR analysis of the pentane layer showed incomplete conversion, so pentane was evaporated and the procedure repeated twice. Upon complete conversion the pentane layer was filtered over little Na_2SO_4 and concentrated. At −20 °C light yellow plates were formed (0.52 g, 1.2 mmol, 72%). Mp: 47−48 °C. ^{31}P NMR (C_6D_6): δ −89.6 (q, $^1J_{PD}$ = 52.9 Hz, $^1J_{PW}$ = 220.5 Hz, int 100, PD_2), −88.9 (t, $^1J_{PD}$ = 52.9 Hz, int 4, PHD). ^{13}C NMR (C_6D_6): δ 198.4 (d, $^2J_{CP}$ = 21.8 Hz, CO_{ax}), 195.8 (d, $^2J_{CP}$ = 6.9 Hz, $^1J_{CW}$ = 125.0 Hz, CO_{eq}), 132.7 (d, $^2J_{CP}$ = 11.4 Hz, *o*-ArC), 130.5 (d, $^4J_{CP}$ = 2.3 Hz, *p*-ArC), 129.0 (d, $^3J_{CP}$ = 10.4 Hz, *m*-ArC), 125.3 (d, $^1J_{CP}$ = 48.1 Hz, *ipso*-ArC). ^{1}H NMR (C_6D_6): δ 6.94−7.05 (m, 2H, *o*-H), 6.86−6.91 (m, 3H, *m*+*p*-H), 4.73 (dm, $^1J_{HP}$ = 344.1 Hz, rel int 0.02, PHD). IR (KBr): ν = 2076.6 (m), 1996.6 (m), 1949.7 (s), 1913.7 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{11}H_5D_2O_5PW$: 435.966 39. Found: 435.967 26. MS *m/z* (%): 436 (48) [M^+], 380 (52) [M^+ − 2CO], 350 (92) [M^+ − 3CO − D], 348 (100) [M^+ − 3CO − D_2], 320 (50) [M^+ − 4CO − D_2], 292 (70) [M^+ − 5CO − D_2].

General Synthesis of 3*H*-3-Benzophosphepine Complexes 1. Method A (with Base). The appropriate phosphine complex (1 mmol) and 1,2-diethynylbenzene (1.5 mmol) were dissolved in THF (11.75 mL) followed by addition of freshly ground KOH (79 mg). Almost immediately a color change took place, and after completion of the reaction, the mixture was filtered over a short silica column, the solvent was evaporated, and the excess 1,2-diethynylbenzene distilled off at 50 °C/1 mmHg. The crude product was purified by column chromatography (toluene:pentane = 1:4) and subsequently crystallized from diethyl ether:pentane = 1:4 at −20 °C.

Method B (without Initial Base). The appropriate phosphine complex (1 mmol) and 1,2-diethynylbenzene (1.3 mmol) were dissolved in THF (11.75 mL). After 2−3 h freshly ground KOH (50 mg) was added. Workup was as above.



3-Phenyl-3*H*-3-benzophosphepine Pentacarbonylchromium(0) (1d) was synthesized according to the general synthesis, with 10 min of stirring, to give yellow plates (37%). Mp: 114 °C (dec). ^{31}P NMR ($CDCl_3$): δ 23.1. ^{13}C NMR ($CDCl_3$): δ 221.6 (d, $^2J_{CP}$ = 7.4 Hz, CO_{ax}), 216.3 (d, $^2J_{CP}$ = 13.6 Hz, CO_{eq}), 141.0 (d, $^2J_{CP}$ = 3.4 Hz, C1, C5), 136.6 (d, $^3J_{CP}$ = 4.4 Hz, C5a, C9a), 135.8 (d, $^1J_{CP}$ = 41.5 Hz, *ipso*-ArC), 132.4 (d, $^4J_{CP}$ = 0.8 Hz, C6, C9), 131.1 (d, $^2J_{CP}$ = 11.0 Hz, *o*-ArC), 129.7 (d, $^4J_{CP}$ = 2.2 Hz, *p*-ArC), 128.4 (d, $^3J_{CP}$ = 9.6 Hz, *m*-ArC), 128.1 (s, C7, C8), 126.6 (d, $^1J_{CP}$ = 32.6 Hz, C2, C4). ^{1}H NMR ($CDCl_3$): δ 7.56−7.64 (m, 2H, *o*-ArH), 7.14−7.37 (m, 5H, *m*+*p*-ArH+H1+H5), 7.29 (s, 4H, H(C6−C9)), 6.18 (dd, $^2J_{HP}$ = 24.1 Hz, $^3J_{HH}$ = 12.4 Hz, 2H, H2+H4). IR (KBr): ν = 2063.9 (s), 1924.0 (s), 1898.7 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{21}H_{13}CrPO_5$, 427.9906. Found 427.9886. MS *m/z* (%): 428 (16) [M^+], 288 (100) [M^+ − 5CO], 160 (55) [M^+ − 5CO − $C_{10}H_8$], 128 (16) [$C_{10}H_8^+$].

3-Methyl-3*H*-3-benzophosphepine Pentacarbonyltungsten(0) (1e) was synthesized according to the general synthesis, but with 2 equiv of 1,2-diethynylbenzene and 10 min of stirring, to give large light yellow needles (47%). Mp: 105−106 °C (dec). ^{31}P NMR ($CDCl_3$): δ −34.2 ($^1J_{PW}$ = 231.3 Hz). ^{13}C NMR ($CDCl_3$): δ 199.8 (d, $^2J_{CP}$ = 19.6 Hz, CO_{ax}), 196.3 (d, $^2J_{CP}$ = 7.1 Hz, CO_{eq}), 140.1 (s, C1, C5), 136.7 (d, $^3J_{CP}$ = 5.6 Hz, C5a, C9a), 132.4 (s, C6, C9), 128.0 (s, C7, C8), 129.8 (d, $^1J_{CP}$ = 35.9 Hz, C2, C4), 18.7 (d, $^1J_{CP}$ = 33.9 Hz, CH_3P). ^{1}H NMR ($CDCl_3$): δ 7.33 (s, 4H, H6−H9), 7.06 (ddd, $^3J_{HP}$ = 33.8 Hz, $^3J_{HH}$ = 12.7 Hz, $^4J_{HH}$ = 2.3 Hz, 2H, H1+H5), 5.93 (dd, $^2J_{HP}$ = 18.7 Hz, $^3J_{HH}$ = 12.7 Hz, 2H, H2+H4), 1.91 (d, $^2J_{HP}$ = 7.4 Hz, 3H, CH_3P). IR (KBr): ν = 2067.8 (s), 1913.5 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{16}H_{11}O_5PW$: 497.9853, found: 497.9839. MS *m/z* (%): 498 (57) [M^+], 414 (100) [M^+ − 3CO], 356 (85) [M^+ − H_2 − 5CO], 128 (17) [$C_{10}H_8^+$].

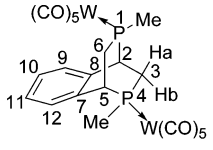
3-*t*-Butyl-3*H*-3-benzophosphepine Pentacarbonyltungsten(0) (1f) was synthesized according to the general synthesis, with 1.75 h of stirring, to give orange plates (41%). Mp: 95 °C. ^{31}P NMR ($CDCl_3$): δ 10.5 ($^1J_{PW}$ = 233.4 Hz). ^{13}C NMR ($CDCl_3$): δ 199.8 (d, $^2J_{CP}$ = 20.4 Hz, CO_{ax}); 197.0 (d, $^2J_{CP}$ = 6.8 Hz, CO_{eq}), 140.9 (d, $^2J_{CP}$ = 3.9 Hz, C1, C5), 136.5 (d, $^3J_{CP}$ = 3.6 Hz, C5a, C9a), 133.7 (s, C6, C9), 128.6 (s, C7, C8), 123.2 (d, $^1J_{CP}$ = 31.5 Hz, C2, C4), 33.6 (d, $^1J_{CP}$ = 26.6 Hz, CMe_3), 26.6 (d, $^2J_{CP}$ = 5.1 Hz, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.26−7.34 (m, 4H, H(C6−C9)), 7.03 (ddd, $^3J_{HP}$ = 31.2 Hz, $^3J_{HH}$ = 13.6 Hz, $^5J_{HH}$ = 2.9 Hz, 2H, H1+H5), 5.92 (dd, $^2J_{HP}$ = 19.4 Hz, $^3J_{HH}$ = 13.6 Hz, 2H, H2+H4), 1.34 (d, $^3J_{HP}$ = 14.9 Hz, 9H, CH_3). IR (KBr): ν = 2068.0 (s), 1995.4 (s), 1981.6 (s), 1944.7 (s), 1920.6 (sh), 1904.5 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{19}H_{17}WPO_5$: 540.032 35. Found: 540.031 04.

3-Diethylamino-3*H*-3-benzophosphepine Pentacarbonyltungsten(0) (1g). A solution of **3g** (0.33 mmol, 1.3 mL, 0.25 M in Et_2O) was added slowly with stirring to a solution of **2** (25 mg, 0.20 mmol) in THF (0.4 mL) at room temperature. The reaction mixture was stirred overnight, freshly ground KOH (30 mg) was added, and after 2.25 h filtered over a short silica plug. After evaporation the crude product was purified by column chromatography (SiO_2, 1:4 = toluene:pentane) and crystallization (Et_2O:pentane = 1:4) to give yellow blocks (40%). Mp: 97 °C (dec). ^{31}P NMR ($CDCl_3$): δ 56.8 ($^1J_{PW}$ = 261.0 Hz). ^{13}C NMR ($CDCl_3$): δ 200.3 (d, $^2J_{CP}$ = 21.2 Hz, CO_{ax}), 196.6 (d, $^2J_{CP}$ = 7.2 Hz, $^1J_{CW}$ = 126.2 Hz, CO_{eq}), 137.4 (s, C1, C5), 136.3 (d, $^3J_{CP}$ = 3.8 Hz, C5a, C9a), 133.5 (s, C6, C9), 130.8 (d, $^1J_{CP}$ = 38.9 Hz, C2, C4), 128.3 (s, C7, C8), 42.7 (d, $^2J_{CP}$ = 5.8 Hz, CH_2), 14.6 (d, $^3J_{CP}$ = 2.8 Hz, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.24−7.28 (m, 4H, H(C6−C9)), 6.83 (ddd, $^3J_{HP}$ = 35.0 Hz, $^3J_{HH}$ = 13.2 Hz, $^4J_{HH}$ = 3.1 Hz, 2H, H1+H5), 5.87 (dd, $^2J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 13.2 Hz, 2H, H2+H4), 3.30 (dq, $^3J_{HP}$ = 11.9 Hz, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 1.15 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3). IR (KBr): ν = 2071.2 (m), 1986.7 (s), 1938.7 (sh), 1917.7 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{19}H_{18}NO_5P^{182}W$: 553.040 51. Found: 553.040 61. Calcd for $C_{19}H_{18}NO_5P^{186}W$: 557.04666. Found: 557.04644. MS *m/z* (%): 555 (48) [M^+], 471 (100) [M^+ − 3CO], 415 (50) [M^+ − 5CO], 128 (72) [$C_{10}H_8^+$].

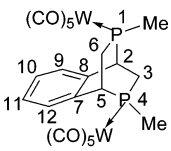
3-Phenyl-1,5-dideuterio-3*H*-benzophosphepine Pentacarbonyltungsten(0) (1h). To a solution of **3h** (135 mg, 0.31 mmol) in THF (5.7 mL) was added 1,2-diethynylbenzene (0.8 mL, 0.5 M in THF, 0.4 mmol). The mixture was stirred for 1 day at room temperature and 7 h at 35 °C, followed by filtration over a silica plug and purification by column chromatography (1:4 = toluene:pentane, then 2:3 = toluene:pentane). **1h** was obtained in pure form by crystallization (−20 °C) from 1:4 = Et_2O:pentane to give light yellow plates (25 mg, 0.044 mmol, 14%, >94% D_2). Mp: 110 °C (dec). ^{31}P NMR ($CDCl_3$): δ −14.8 ($^1J_{PW}$ = 236.8 Hz). ^{13}C NMR ($CDCl_3$): δ 199.6 (d, $^2J_{CP}$ = 20.5 Hz, CO_{ax}), 196.4 (d, $^2J_{CP}$ = 7.0 Hz, $^1J_{CW}$ = 126.0 Hz, CO_{eq}), 140.3 (t, $^1J_{CD}$ = 24 Hz, C1, C5), 136.4 (d, $^3J_{CP}$ = 4.7 Hz, C5a, C9a), 135.5 (d, $^1J_{CP}$ = 46.2 Hz, *ipso*-C), 132.7 (s, C6, C9), 132.2 (d, $^2J_{CP}$ = 12.2 Hz, *o*-ArC), 130.2 (d, $^4J_{CP}$ = 2.1 Hz, *p*-ArC), 128.6 (d, $^3J_{CP}$ = 10.0 Hz, *m*-ArC), 128.1 (s, C7, C8), 127.3 (d, $^1J_{CP}$ = 36.6 Hz, C2, C4). ^{1}H NMR ($CDCl_3$): δ 7.70−7.75 (m, 2H, *o*-ArH), 7.37−7.47 (m, 3H, *m*+*p*-ArH), 7.31 (s, 4H, H6−H9), 6.10 (d, $^2J_{HP}$ = 21.3 Hz, 2H, H2+H4). IR (KBr): ν = 2069.2 (m), 1948.0 (s), 1928 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{21}H_{11}D_2O_5WP$: 562.013 34. Found: 562.013 59. MS *m/z* (%): 562 (35) [M^+], 478 (100) [M^+ − 3CO], 420 (100) [M^+ − 5CO − D/H_2], 130 (100) [$C_{10}H_6D_2^+$].

1,4-Dimethyl-2,5-[1,2]benzeno-1,4-diphosphinane Bis(pentacarbonyltungsten(0)) (10e). Compounds **3e** (185 mg, 0.497 mmol) and **2** (50 mg, 0.4 mmol) were dissolved in THF (5.8 mL). Freshly ground KOH (70 mg) was added, and the solution turned immediately red. After stirring overnight the red and cloudy solution was filtered over silica, eluted with THF, and concentrated. The residue was purified by

column chromatography (toluene:pentane:THF = 17:66:1), yielding several fractions. The first fraction (R_f = 0.57) contained benzophosphepine **1e** (50.3 mg, 25%). Fraction 2 (R_f = 0.36) contained mainly (~75%) *meso*-**10e**, part of which could be obtained pure after succesive crystallizations from hexane/dichloromethane. Fraction 3 (R_f = 0.13) was *rac*-**10e** (54.1 mg, 14%). Small, yellowish needles could be obtained from chloroform or diethyl ether.



meso-**10e**



rac-**10e**

***meso*-10e:** Mp: 174−175 °C. ^{31}P NMR ($CDCl_3$): δ -15.0 (d, $^3J_{PP}$ = 17.4 Hz, $^1J_{PW}$ = 246.9 Hz), −16.6 (d, $^3J_{PP}$ = 17.4 Hz, $^1J_{PW}$ = 235.0 Hz). ^{13}C NMR ($CDCl_3$): δ 198.6 (d, $^2J_{CP}$ = 23.5 Hz, CO_{ax}), 197.6 (d, $^2J_{CP}$ = 22.2 Hz, CO_{ax}), 196.7 (d, $^2J_{CP}$ = 6.7 Hz, $^1J_{CW}$ = 118.1 Hz, CO_{eq}), 196.0 (d, $^2J_{CP}$ = 7.1 Hz, $^1J_{CW}$ = 132.6 Hz, CO_{eq}), 135.8 (m, C7), 134.3 (dd, $^2J_{CP}$ = 6.6 Hz, $^3J_{CP}$ = 1.8 Hz, C8), 129.0−129.2 (m, C9−C11), 128.0 (t, $^3J_{CP}$ = $^4J_{CP}$ = 3.2 Hz, C12), 39.1 (dd, $^1J_{CP}$ = 20.4 Hz, $^2J_{CP}$ = 5.7 Hz, C5), 38.5 (dd, $^1J_{CP}$ = 19.8 Hz, $^2J_{CP}$ = 5.8 Hz, C2), 30.0 (dd, $^1J_{CP}$ = 26.9 Hz, $^2J_{CP}$ = 6.0 Hz, C6), 29.1 (dd, $^1J_{CP}$ = 21.6 Hz, $^2J_{CP}$ = 5.5 Hz, C3), 22.1 (d, $^1J_{CP}$ = 28.7 Hz, CH_3P4), 19.9 (d, $^1J_{CP}$ = 18.4 Hz, CH_3P1). ^{1}H NMR ($CDCl_3$): δ 7.37−7.43 (m, 3H, H9−H11), 7.19−7.21 (m, 1H, H12), 3.67 (dddd, $^2J_{HP}$ = 19.9 Hz, $^3J_{HP}$ = 5.0 Hz, $^3J_{HH}$ = 5.1, $^3J_{HH}$ = 2.1 Hz, 1H, H2), 3.40 (ddm, $^2J_{HP}$ = 19.9 Hz, $^3J_{HH}$ = 4.1 Hz, H5), 2.77 (dddm, $^3J_{HP}$ = 7.5 Hz, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 2.1 Hz, 1H, H3a), 2.61 (dm, $^3J_{HH}$ = 4.1 Hz, 2H, H6a−b), 2.07 (d, $^2J_{HP}$ = 6.1 Hz, 3H, CH_3P1), 1.98 (ddm, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, H3b), 1.04 (d, $^2J_{HP}$ = 5.9 Hz, 3H, CH_3P4). IR (KBr): ν = 2068.0 (s), 1982.0 (s), 1952.3 (sh), 1939.6 (sh), 1921.3 (sh), 1910.6 (sh), 1899.9 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{22}H_{16}W_2P_2O_{10}$, 869.9237. Found 869.92623. MS *m/z* (%): 870 (100) [M$^+$], 786 (92) [M$^+$ − 3CO], 758 (52) [M$^+$ − 4CO].

***rac*-10e:** Mp: 170 °C (dec). ^{31}P NMR ($CDCl_3$): δ -15.7 ($^1J_{PW}$ = 249.2 Hz). ^{13}C NMR ($CDCl_3$): δ 198.7 (m, CO_{ax}), 196.0 (m, CO_{eq}), 136.0 (m, C7, C8), 129.6 (m, C10, C11), 129.1 (m, C9, C12), 38.4 (m, C2, C5), 28.6 (m, C3, C6), 19.0 (m, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.40 (s, 4H, H9−H12), 3.64 (ddd, $^2J_{HP}$ = 22.7 Hz, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 2.1 Hz, 2H, H2, H5), 2.67 (ddm, $^2J_{HH}$ = 14.9 Hz, $^3J_{HH}$ = 2.1 Hz, 2H, H3a, H6a), 2.54 (ddm, $^2J_{HH}$ = 14.9 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, H3b, H6b). 2.07 (d, $^2J_{HP}$ = 6.1 Hz, 6H, CH_3P). IR (KBr): ν = 2068.1 (m), 1985.4 (m), 1926.4 (s), 1909.8 (s), 1895.0 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{22}H_{16}W_2P_2O_{10}$: 869.9238. Found: 869.9254. MS *m/z* (%): 870 (<1) [M$^+$], 590 (<1) [M$^+$ − 10CO], 472 (20) [M$^+$ − 10CO − CH_3 − C_8H_7], 430 (100) [$W_2P_2^+$].

1,4-Diphenyl-2,5-[1,2]benzeno-1,4-diphosphinane Bis(pentacarbonylmolybdenum(0)) (10b). To a suspension of KOH (0.24 g) in THF (16.0 mL) was added simultaneously a solution of **2** (0.85 mmol, 0.5 M in THF, 1.7 mL) and **3b** (1.47 mmol, 0.49 M in THF, 3.0 mL). The solution turned red immediately and was stirred overnight at room temperature. After filtration over a short silica plug and evaporation of the solvent, the crude product mixture was separated by column chromatography (Et_2O:pentane = 1:4), yielding several fractions. The first fraction (R_f = 0.57) contained mostly benzophosphepine **1b**, which was purified by crystallization (43.1 mg, 0.091 mmol, 11%). The second fraction (R_f = 0.43, 106 mg) was a mixture of the benzophosphepine (5%) and the two isomers of **10b** (*rac*, 67%; *meso*, 29%). *rac*-**10b** could be isolated in pure form after fractional crystallization from DCM/pentane. *meso*-**10b** could be obtained almost pure (>95%), also by crystallization from DCM/pentane.

***meso*-10b:** Colorless blocks. Mp: 163 °C (dec). ^{31}P NMR ($CDCl_3$): δ 27.2 (d, $^3J_{PP}$ = 11.7 Hz), 25.1 (d, $^3J_{PP}$ = 11.7 Hz). ^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$ = 25.2 Hz, CO_{ax}), 208.9 (d, $^2J_{CP}$ = 24.0 Hz, CO_{ax}), 205.0 (d, $^2J_{CP}$ = 8.8 Hz, CO_{eq}), 204.5 (d, $^2J_{CP}$ = 9.1 Hz, CO_{eq}), 138.0 (d, $^1J_{CP}$ = 24.6 Hz, *ipso*-C), 136.7 (d, $^1J_{CP}$ = 32.8 Hz, *ipso*-C), 136.4 (m, C7), 133.0 (d, $^2J_{CP}$ = 7.0 Hz, C8), 128.1−129.8 (m, C9−12 + ArC), 38.1 (dd, $^1J_{CP}$ = 13.5 Hz, $^2J_{CP}$ = 5.2 Hz, C5), 36.6 (dd, $^1J_{CP}$ = 14.3 Hz, $^2J_{CP}$ = 6.0 Hz, C2), 27.0 (dd, $^1J_{CP}$ = 20.0 Hz, $^2J_{CP}$ = 9.1 Hz, C6), 26.1 (dd, $^1J_{CP}$ = 15.3 Hz, $^2J_{CP}$ = 5.6 Hz, C3). ^{1}H NMR ($CDCl_3$): δ 6.79−7.60 (m, 14H, H9−H12 + ArH), 4.12−4.21 (m, 1H, H2), 3.85 (ddm, $^2J_{HP}$ = 19.9 Hz, $^3J_{HH}$ = 6.4 Hz, H5), 3.29 (ddm, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, H3a), 2.89 (ddm, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, H3b), 2.72−2.84 (m, 2H, H6a−b). IR (KBr): ν = 2071.0 (m), 1991.2 (m), 1930.1 (s), 1914.1 (s) (C≡O) cm^{-1}. MS *m/z* (%): 822 (18) [M$^+$], 738 (30), [M$^+$ − 3CO], 444 (50) [M$^+$ − $Mo(CO)_{10}$], 346 (100) [M$^+$ − $Mo_2(CO)_{10}$], 149 (100) [$C_9H_{10}P^+$].

***rac*-10b:** Mp: 116 °C (dec). ^{31}P NMR ($CDCl_3$): δ 19.7 ($^1J_{PMo}$ = 26.2 Hz).^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$ = 24.8 Hz, CO_{ax}), 204.5 (m, CO_{eq}), 136.8 (d, $^1J_{CP}$ = 25.0 Hz, *ipso*-ArC), 135.8 (t, $^2J_{CP}$ = $^3J_{CP}$ = 3.3 Hz, C7, C8), 129.6 (s, C10, C11), 128.5−129.2 (m, C9, C12, *o*+*m*+*p*-ArC), 37.5 (m, C2, C5), 27.4 (m, C3, C6). ^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$ = 24.8 Hz, CO_{ax}), 204.5 (m, CO_{eq}), 136.8 (d, $^1J_{CP}$ = 25.0 Hz, *ipso*-ArC), 135.8 (t, $^2J_{CP}$ = $^3J_{CP}$ = 3.3 Hz, C7, C8), 129.6 (s, C10, C11), 128.5−129.2 (m, C9, C12, *o*+*m*+*p*-ArC), 37.5 (m, C2, C5), 27.4 (m, C3, C6). ^{1}H NMR ($CDCl_3$): δ 7.45−7.57 (m, 4H, H9−H12), 7.20−7.27 (m, 6H, *m*+*p* ArH), 6.95−7.00 (m, 4H, *o*-ArH), 4.14 (ddd, $^2J_{HP}$ = 22.3 Hz, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 2.3 Hz, 2H, H2, H5), 3.11 (ddd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HP}$ = 3.3 Hz, $^3J_{HH}$ = 2.3 Hz, 2H, H3a, H6a), 2.53 (ddd, $^2J_{HP}$ = 21.8 Hz, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, H3b, H6b). IR (KBr): ν = 2070.3 (s), 1988.6 (sh), 1939.9 (m), 1916.1 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{32}H_{20}O_{10}P_2Mo_2$, 821.8640. Found 821.8803. MS *m/z* (%): 822 (50) [M$^+$], 738 (72) [M$^+$ − 3CO], 682 (60) [M$^+$ − 5CO], 542 (15) [M$^+$ − 10CO], 444 (50) [M$^+$ − $Mo(CO)_{10}$], 346 (100) [M$^+$ − $Mo_2(CO)_{10}$].

11d: Isolated with phosphepine **1d**. Data obtained from differential spectra. ^{31}P NMR ($CDCl_3$): δ 4.3 (d, $^1J_{PH}$ = 348 Hz). ^{1}H NMR ($CDCl_3$): δ 7.50 (ddm, $^3J_{HP}$ = 28.9 Hz, $^3J_{HH}$ = 12.8 Hz, 1H, Ar−CH═), 7.27−7.57 (m, 9H, ArH), 6.29 (ddd, $^2J_{HP}$ = 25.7 Hz, $^3J_{HH(C)}$ = 12.8 Hz, $^3J_{HH(P)}$ = 11.2 Hz, 1H, ═CH−P), 6.17 (ddd, $^1J_{HP}$ = 347.7 Hz, $^3J_{HH}$ = 11.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, PH), 3.27 (s, 1H, CCH). IR (KBr): ν = 3301.06 (w), 2957.6 (w), 2942.6 (w), 2863.3 (w), 2063.4 (m, C≡O), 1983.5 (sh, C≡O), 1937.4 (s, C≡O), 1260.5 (w), 1093.9 (br, m), 1022.3 (br, m), 799.6 (m), 762.3 (w), 627.0 (s), 650.9 (s, CCH) cm^{-1}.

Evidence for Disproportionation of 3a. A mixture of **3a** (10.5 mg, 0.024 mmol) and **3h** (10.9 mg, 0.025 mmol) was dissolved in THF (0.5 mL). The resulting solution was monitored by ^{31}P NMR. Alongside the signals attributed to **3a** (−89.4 ppm, s) and **3h** (−90.6, q, $^1J_{PD}$ = 53.7 Hz) the signal of PhPHD−W(CO)$_5$ grew in: −90.0 (t, $^1J_{PD}$ = 53.7 Hz). After 2 h an equilibrium is reached, with the following intensities: PH_2:PHD:PD_2 = 1.0:0.4:0.7.

General Procedure for Phosphinidene Reactions. The benzophosphepine complex and substrate were dissolved in dry toluene (20 mL/mmol) and placed in an oil bath at the reaction temperature until completion. The solvent was evaporated, followed by sublimation of naphthalene at 60 °C/1−2 mmHg. The residue was purified by column chromatography (pentane, then pentane:Et_2O = 1:4) when necessary and/or crystallization (pentane, −20 °C).

15d:[18] 1.5 equiv of tolane and 11 h at 85 °C gave yellow crystals (75%). ^{31}P NMR ($CDCl_3$): δ −109.2.^{13}C NMR ($CDCl_3$): δ 220.3 (d, $^2J_{CP}$ = 5.8 Hz, CO_{ax}), 216.3 (d, $^2J_{CP}$ = 16.4 Hz, CO_{eq}), 138.7 (d, $^1J_{CP}$ = 1.9 Hz, *ipso*-ArP), 130.9 (d, $^2J_{CP}$ = 14.4 Hz, *o*-ArP), 130.6 (s, *p*-ArC), 130.4 (d, $^3J_{CP}$ = 5.0 Hz, *o*-ArC), 130.3 (d, $^4J_{CP}$ = 2.3 Hz, *p*-ArP), 129.3 (d, $^1J_{CP}$ = 12.4 Hz, C═), 129.3 (d, $^4J_{CP}$ = 0.7 Hz, *m*-ArC), 128.6 (d, $^3J_{CP}$ = 9.7 Hz, *m*-ArP), 127.4 (d, $^2J_{CP}$ = 6.9 Hz, *ipso*-ArC). ^{1}H NMR ($CDCl_3$): δ 7.88−7.92 (m, 4H, ArH), 7.45−7.58 (m, 8H, ArH), 7.27−7.35 (m, 3H, ArH).

16d:[30] 2.9 equiv of *trans*-stilbene and 11 h at 85 °C gave a light-yellow solid (~100%), which after crystallization became yellow

needles (70%). ^{31}P NMR ($CDCl_3$): δ −72.5. ^{1}H NMR ($CDCl_3$): δ 6.98−7.50 (m, 15H, ArH), 3.97 (dd, $^3J_{HH}$ = 10.0 Hz, $^2J_{HP}$ = 8.1 Hz, 1H, H(trans-Cr)), 3.55 (d, $^3J_{HH}$ = 10.0 Hz, 1H, H(cis-Cr)).

15e:[18] 1.1 equiv of diphenylacetylene and 24 h at 80 °C gave small, light yellow crystals (65%). ^{31}P NMR ($CDCl_3$): δ −167.9 ($^1J_{PW}$ = 261.2 Hz).^{1}H NMR ($CDCl_3$): δ 7.85−7.89 (m, 4H, *o*-ArH), 7.50−7.57 (m, 6H, *m*+*p*-ArH), 1.70 (d, $^2J_{HP}$ = 5.6 Hz, 3H, CH_3P).

16e:[30] 2.9 equiv of *trans*-stilbene and 26 h at 85 °C gave a light yellow oil (89%). ^{31}P NMR ($CDCl_3$): δ −138.8 ($^1J_{PW}$ = 261 Hz). ^{1}H NMR ($CDCl_3$): δ 7.28−7.41 (m, 10H, ArH), 3.45 (d, $^3J_{HH}$ = 9.5 Hz, 1H, CH), 3.34 (dd, $^3J_{HH}$ = 9.5 Hz, $^2J_{HP}$ = 8.0 Hz, 1H, CH), 1.25 (d, $^2J_{HP}$ = 6.4 Hz, 3H, Me).

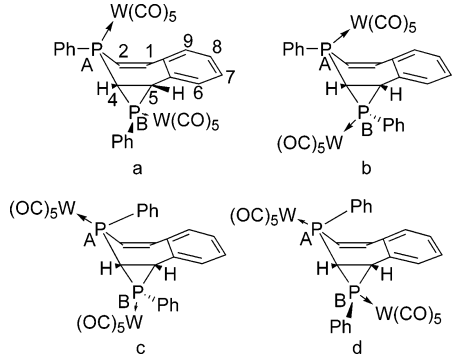
15f: 1.5 equiv of diphenylacetylene and 26 h at 120 °C gave orange crystals (66%). Mp: 110 °C (dec). ^{31}P NMR ($CDCl_3$): δ −125.7 ($^1J_{PW}$ = 247.1 Hz). ^{13}C NMR ($CDCl_3$): δ 198.0 (d, $^2J_{CP}$ = 29.3 Hz, CO_{ax}), 196.5 (d, $^2J_{CP}$ = 7.9 Hz, CO_{eq}), 130.6 (d, $^1J_{CP}$ = 12.8 Hz, C═), 130.4 (s, *p*-ArC), 130.1 (d, $^3J_{CP}$ = 4.6 Hz, *o*-ArC), 129.3 (d, $^4J_{CP}$ = 0.4 Hz, *m*-ArC), 128.5 (d, $^2J_{CP}$ = 7.2 Hz, *ipso*-ArC), 37.7 (d, $^1J_{CP}$ = 2.9 Hz, CP), 28.3 (d, $^2J_{CP}$ = 8.9 Hz, CH_3).^{1}H NMR ($CDCl_3$): δ 7.84−7.88 (m, 4H, *o*-ArH), 7.48−7.55 (m, 6H, *m*+*p*-ArH), 1.14 (d, $^3J_{HP}$ = 17.4 Hz, 9H, CH_3). IR (KBr): ν = 2067.6 (w), 1980.9 (w), 1927.2 (s), 1917.4 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{23}H_{19}WPO_5$: 590.0479. Found: 590.0458. MS *m/z* (%): 590 (49) [M^+], 449 (100) [M^+ − 5CO − H], 393 (39) [M^+ − 5CO − C_4H_9].

15g:[32] 1.6 equiv of diphenylacetylene and 11.5 h at 85 °C gave yellow crystals (61%). ^{31}P NMR ($CDCl_3$): δ −100.8 ($^1J_{PW}$ = 299.7 Hz). ^{1}H NMR ($CDCl_3$): δ 7.83 (d, $^3J_{HH}$ = 7.0 Hz, 4H, *o*-ArH), 7.43−7.57 (m, 6H, *m*+*p*-ArH), 2.90−3.04 (m, 4H, NCH_2), 0.98 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3).

15i: Chromatography of **15g** over SiO_2 eluting with THF gave a yield that depends on the time on the column. Crystallization from pentane yielded yellow blocks. Mp: 122−124 °C. ^{31}P NMR ($CDCl_3$): δ −78.1 ($^1J_{PW}$ = 319.6 Hz). ^{13}C NMR ($CDCl_3$): δ 198.3 (d, $^2J_{CP}$ = 38.4 Hz, CO_{ax}), 195.2 (d, $^2J_{CP}$ = 9.8 Hz, CO_{eq}), 147.7 (d, $^1J_{CP}$ = 15.0 Hz, C═), 131.1 (s, *p*-ArC), 129.9 (d, $^3J_{CP}$ = 5.7 Hz, *o*-ArC), 129.4 (s, *m*-ArC), 127.7 (d, $^2J_{CP}$ = 4.9 Hz, *ipso*-ArC). ^{1}H NMR ($CDCl_3$): δ 7.89−7.92 (m, 4H, *o*-ArH), 7.49−7.58 (m, 6H, *m*+*p*-ArH), 2.60 (s, broad, 1H, OH). IR (KBr): ν = 3524.8 (w), 3461.5 (m) (OH), 2074.5 (m), 1988.8 (m), 1933.9 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{19}H_{11}WPO_6$: 549.9803. Found: 549.98002. MS *m/z* (%): 550 (30) [M^+], 410 (100) [M^+ − 5CO], 209 (86) [PhCC(P)Ph$^+$], 178 (63) [PhCCPh$^+$].

rac-19: A mixture of **1a** (70.3 mg, 0.304 mmol) and diphenyldiacetylene (28.5 mg, 0.141 mmol) in toluene (2.9 mL) was heated at 60 °C for 3 days. The solvent was evaporated, naphthalene sublimed (50 °C, 1−2 mmHg), and the crude product purified by chromatography (SiO_2, dichloromethane:pentane = 1:9). The monoadduct elutes first, followed by the main isomer, to yield 16.1 mg (0.015 mmol, 11%) as yellow needles. Mp: 152 °C (dec). ^{31}P NMR ($CDCl_3$): δ −137.3 ($^1J_{PW}$ = 274 Hz).^{13}C NMR ($CDCl_3$): δ 197.1 (d, $^2J_{CP}$ = 32.5 Hz, CO_{ax}), 195.3 (pseudo-t, $^2J_{CP}$ = 4.0 Hz, CO_{eq}), 137.0 (m, C3,C3′), 134.0 (m, *ipso*-ArP), 132.1 (s), 131.3−131.7 (m), 129.6 (s), 129.0 (m), 126.5 (pseudo-t, $^2J_{CP}$ = 3.2 Hz *ipso*-ArC), 115.3 (m, C2,C2′). ^{1}H NMR ($CDCl_3$): 7.80−7.86 (m, 4H, *o*-ArH), 7.38−7.58 (m, 16H, ArH). IR (KBr): ν = 2073.3 (m), 1995.7 (m), 1986.8 (m), 1924.5 (s) (C≡O) cm^{-1}. MS: MS *m/z* (%): 1066 (3) [M^+], 870 (3) [M^+ − 7CO], 786 (5) [M^+ − 10CO], 352 (67) [$W(CO)_6^+$], 296 (48) [$W(CO)_4^+$], 268 (100) [$W(CO)_3^+$], 184 (20) [W^+].

21: A solution of **1a** (84.1 mg, 0.150 mmol) in toluene (1.4 mL) is heated at 60 °C for 64 h. After evaporation of the solvent the crude mixture is separated by column chromatography (SiO_2, 30 g, starting with 5% Et_2O in pentane, increasing to 10%). 4% of benzophosphepine **1a** is regenerated (R_f = 0.37).



21a: 6.9 mg, 5%. R_f = 0.24, crystals from Et_2O:pentane, −20 °C. Mp: 153−158 °C (dec).[57] ^{31}P NMR ($CDCl_3$): δ -8.4 (d, $^3J_{PP}$ = 14.7 Hz, $^1J_{PW}$ = 239 Hz, P_A), −126.9 (d, $^3J_{PP}$ = 14.7 Hz, $^1J_{PW}$ = 263 Hz, P_B). ^{13}C NMR ($CDCl_3$): δ 198.6 (d, $^2J_{CP}$ = 21 Hz, $CO_{ax}{}^A$), 197.4 (d, $^2J_{CP}$ = 34 Hz, $CO_{ax}{}^B$), 196.2 (d, $^2J_{CP}$ = 6.8 Hz, $CO_{eq}{}^A$), 195.3 (d, $^2J_{CP}$ = 7.4 Hz, $CO_{eq}{}^B$), 143.2 (pseudo-s, C1), 141−1−141.4 (m, *ipso*-Ar^A), 135.6−135.9 (m, C5a, C9a), 134.8 (pseudo-s, C9), 134.2 (d, $^3J_{CP}$ = 4.0 Hz, C6), 130.9−131.1 (m), 130.5 (s), 130.1 (d, $^3J_{CP}$ = 10.6 Hz, *m*-Ar^B), 129.2−129.4 (m), 127.6 (d, $^5J_{CP}$ = 2.3 Hz, C8), 124.1 (dd, $^1J_{CP}$ = 37.5 Hz, $^3J_{CP}$ = 4.7 Hz, C2), 43.0 (m, C4), 36.7 (d, $^1J_{CP}$ = 16.5 Hz, C5). ^{1}H NMR ($CDCl_3$): δ 7.99−8.03 (m, 2H, *o*-ArP^A), 7.64−7.68 (4H, *m*+*p*Ar^A, H6), 7.32−7.42 (m, 8H, Ar^BH, H7−H9), 7.08 (dd, $^3J_{HP}$ = 35.6 Hz, $^3J_{HH}$ = 13.7 Hz, 1H, H1), 6.35 (m, 1H, H2), 3.71−3.83 (m, 1H, H5), 3.02−3.10 (m, 1H, H4). IR (KBr): ν = 2066.7 (m), 1990.5 (m), 1948.14 (s), 1929.4 (s), 1912.4 (sh) (C≡O) (cm^{-1}). HRMS Calcd for $C_{32}H_{18}O_{10}P_2W_2$: 991.939 38. Found: 991.9394. MS *m/z* (%): 992 (3) [M^+], 712 (12) [M^+ − 10CO], 558 (37) [M^+ − $PhPH_2W(CO)_5$], 476 (78) [M^+ − 3CO−PhPW$(CO)_5$], 418 (80) [M^+ − 5CO−$PhPH_2W(CO)_5$], 128 (100) [$C_{10}H_8^+$].

The third fraction (R_f = 0.16, 10%) gave 25.2 mg (17%) of a mixture of **21b**−**c**. Colorless blocks of **21b** from Et_2O:pentane = 1:4.

21b: mp 158−160 °C (dec).[57] ^{31}P NMR ($CDCl_3$): δ -6.6 (d, $^3J_{PP}$ = 11.7 Hz, $^1J_{PW}$ = 235 Hz, P_A), −118.8 (d, $^3J_{PP}$ = 11.7 Hz, $^1J_{PW}$ = 263 Hz, P_B). ^{13}C NMR ($CDCl_3$): δ 199.3 (d, $^2J_{CP}$ = 21.1 Hz, $CO_{ax}{}^A$), 197.5 (d, $^2J_{CP}$ = 32.6 Hz, $CO_{ax}{}^B$), 196.3 (d, $^2J_{CP}$ = 6.6 Hz, $CO_{eq}{}^A$), 195.3 (d, $^2J_{CP}$ = 7.9 Hz, $CO_{eq}{}^B$), 139.9 (pseudo-s, C1), 137.3 (d, $^1J_{CP}$ = 45.6 Hz, *ipso*-Ar^A), 135.0 (m, C5a, C9a), 134.4−134.5 (m, C6,C9), 131.5 (d, $^2J_{CP}$ = 11.0 Hz, *o*-Ar^B), 131.1 (*ipso*-Ar^B),[58] 130.8 (d, $^4J_{CP}$ = 2.0 Hz, *p*-Ar^B), 130.4 (d, $^4J_{CP}$ = 2.1 Hz, *p*-Ar^A), 129.5 (d, $^3J_{CP}$ = 9.2 Hz, *m*-Ar^A), 129.4 (s, C7), 128.8 (d, $^3J_{CP}$ = 9.9 Hz, *m*-Ar^B), 128.5 (d, $^2J_{CP}$ = 9.7 Hz, *o*-Ar^A), 127.4 (d, $^5J_{CP}$ = 2.8 Hz, C8),123.3 (dd, $^1J_{CP}$ = 37.5 Hz, $^3J_{CP}$ = 2.9 Hz, C2), 45.9 (dd, $^1J_{CP}$ = 27.1 Hz, $^1J_{CP}$ = 15.0 Hz, C4), 37.9 (d, $^1J_{CP}$ = 16.0 Hz, C5). ^{1}H NMR ($CDCl_3$): δ 7.79−7.85 (m, 2H, *o*-Ar^A), 7.72 (d, $^3J_{HH}$ = 8.0 Hz, H6), 7.64−7.69 (m, 2H, *m*-Ar^A), 7.56−7.58 (m, 1H, *p*-Ar^A), 7.35−7.38 (m, 1H, H7), 7.20−7.28 (m, 2H, 8+*p*-Ar^B), 7.00−7.02 (m, 2H, *m*-Ar^A), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, H9), 6.51−6.55 (m, 2H, *o*-Ar^B), 5.90 (dd, $^3J_{HP}$ = 36.6 Hz, $^3J_{HH}$ = 13.9 Hz, 1H, H1), 5.60 (ddd, $^2J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 13.9 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, H2), 3.64−3.70 (m, $^3J_{HH}$ = 12.9 Hz, 1H, H5), 3.19−3.22 (m, $^3J_{HH}$ = 12.9 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, H4). IR (KBr): ν = 2067.9 (m), 1998.8 (w), 1979.4 (m), 1932.9 (s), 1922.8 (s), 1906.2 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{32}H_{18}O_{10}P_2W_2$: 991.939 38. Found: 991.939 54. MS *m/z* (%): 992 (3) [M^+], 964 (34) [M^+ − CO], 476 (96) [M^+ − 3CO −PhPW$(CO)_5$], 418 (100) [M^+ − 5CO − $PhPH_2W(CO)_5$].

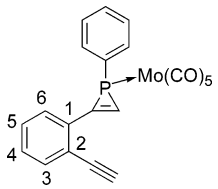
21c: ^{31}P NMR ($CDCl_3$): δ −15.5 (d, $^3J_{PP}$ = 11.4 Hz, $^1J_{PW}$ = 247 Hz, P_A), −123.4 (d, $^3J_{PP}$ = 11.3 Hz, $^1J_{PW}$ = 268 Hz, P_B).

The fourth fraction gave 6.0 mg of impure **21d.** ^{31}P NMR ($CDCl_3$): δ −16.4 (d, $^3J_{PP}$ = 14.6 Hz, P_A), −127.9 (d, $^3J_{PP}$ = 14.6 Hz, P_B).

(57) The crystals of **21a,b** shrink upon slowly heating to 125 °C, but do not melt or turn black. Above the mentioned temperature they turn black. Melting occurs on more rapid heating (>145 °C), but without a defined temperature rage.

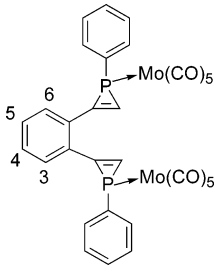
(58) This *ipso*-carbon was only seen in the HMBC spectrum, because it is very small and obscured by neighboring signals.

22: **2** (1.4 mmol) and **1b** (199.5 mg, 0.422 mmol) were heated in toluene (10 mL) at 75 °C for 17 h. The solvent was evaporated and



the crude residue purified by column chromatography (SiO_2, 1% Et_2O in pentane, 20% Et_2O in pentane). Crystallization from pentane (−20 °C) yielded red needles (97 mg, 0.206 mmol, 49%). Mp: 65 °C. ^{31}P NMR ($CDCl_3$): δ −131.3. ^{13}C NMR ($CDCl_3$): δ 208.8 (d, $^2J_{CP}$ = 33.6 Hz, CO_{ax}), 205.0 (d, $^2J_{CP}$ = 11.2 Hz, CO_{eq}), 138.9 (d, $^1J_{CP}$ = 2.2 Hz, *ipso*-ArC), 135.6 (d, $^1J_{CP}$ = 13.6 Hz, C*C*═), 133.9 (d, $^4J_{CP}$ = 0.5 Hz, C3), 131.3 (d, $^3J_{CP}$ = 4.0 Hz, C6), 131.3 (d, $^2J_{CP}$ = 17.0 Hz, *o*-ArC), 130.6 (s, *p*-ArC), 130.4 (d, $^4J_{CP}$ = 2.5 Hz, C5), 129.3 (d, $^5J_{CP}$ = 0.7 Hz, C4), 128.4 (d, $^3J_{CP}$ = 10.2 Hz, *m*-ArC), 127.5 (d, $^2J_{CP}$ = 6.9 Hz, C1), 123.7 (d, $^3J_{CP}$ = 3.8 Hz, C2), 120.7 (d, $^1J_{CP}$ = 12.4 Hz, ═CH), 83.9 (s, C*C*H), 81.5 (−*C*CH). ^{1}H NMR ($CDCl_3$): δ 8.56 (d, $^2J_{HP}$ = 22.3 Hz, 1H, ═CH), 7.62−7.70 (m, 2H, H3+H6), 7.37−7.49 (m, 7H, ArH), 3.38 (s, 1H, CCH). IR (KBr): ν = 2073.5 (m), 1994.0 (m), 1920.3 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{21}H_{11}MO_5P$: 471.939 82. Found: 471.940 52. MS *m/z* (%): 472 (10) [M^+], 332 (100) [M^+ − 5CO], 126 (46) [$C_{10}H_6^+$].

23: To a solution of **22** (97 mg, 0.206 mmol) in toluene (4.0 mL) was added **1b** (117.0 mg, 0.248 mmol, 1.2 eq) and the resulting mixture



was heated at 65 °C for 24 h. The solvent was evaporated and the crude product purified by chromatography (1:4 = Et_2O:pentane). The combined yield of both isomers was 86 mg (43%). The rac-compound could be obtained pure after crystallization from Et_2O/pentane (yellowish plates). *rac*-**22**: 15%. Mp: 133 °C (dec). ^{31}P NMR ($CDCl_3$): δ −135.5. ^{13}C NMR ($CDCl_3$): δ 208.3 (d, $^2J_{CP}$ = 34.0 Hz, CO_{ax}), 204.8 (d, $^2J_{CP}$ = 11.1 Hz, CO_{eq}), 137.9 (d, $^1J_{CP}$ = 2.6 Hz, *ipso*-ArC), 135.6 (d, $^1J_{CP}$ = 15.5 Hz, C-C═), 133.3 (d, $^3J_{CP}$ = 5.3 Hz, C3+C6), 131.7 (s, *p*-ArC), 131.5 (d, $^2J_{CP}$ = 17.2 Hz, *o*-ArC), 130.8 (d, $^4J_{CP}$ = 2.4 Hz, C4+C5), 128.6 (d, $^3J_{CP}$ = 10.3 Hz, *m*-ArC), 126.8−127.0 (m, C1+C2), 121.5 (d, $^1J_{CP}$ = 12.1 Hz, ═CH). ^{1}H NMR ($CDCl_3$): δ 8.47 (d, $^2J_{HP}$ = 22.0 Hz, 2H, ═CH), 7.78−7.84 (m, 2H, H3+H6), 7.57−7.63 (m, 2H, H4+H5), 7.30−7.48 (m, 10H, ArH). IR (KBr): ν = 2073.4 (m), 1991.9 (m), 1925.1 (s) (C≡O) cm^{-1}. MS: 817 (<0.001) [M^+ − H], 266 (100) [M^+ − $Mo_2(CO)_{10}$ − C_6H_6]. Anal. Calcd (%) for $C_{32}H_{16}Mo_2O_{10}P_2$: C, 47.20; H, 1.98. Found: C, 46.27; H, 2.25.

24: 2.5 equiv of phenylacetylene and 6 h at 95 °C gave yellow blocks (81%). Mp: 105 °C. ^{31}P NMR ($CDCl_3$): δ −59.0. ^{13}C NMR ($CDCl_3$): δ 144.3 (s, = *C*Ph), 142.1 (s, *ipso*-ArP), 131.1 (d, $^2J_{CP}$ = 14.1 Hz, *o*-ArP), 130.6 (s, *p*-ArC), 129.8 (d, $^3J_{CP}$ = 4.1 Hz, *o*-ArC), 129.6 (d, $^4J_{CP}$ = 2.5 Hz, *p*-ArP), 129.1 (s, *m*-ArC), 128.0 (d, $^3J_{CP}$ = 10.0 Hz, *m*-ArP), 127.5 (d, $^2J_{CP}$ = 6.0 Hz, *ipso*-ArC), 124.1 (s, HC═), 81.7 (s, Cp). ^{1}H NMR ($CDCl_3$): δ 8.52 (d, $^2J_{HP}$ = 19.3 Hz, ═CH), 7.52−7.71 (m, 2H, ═C(*o*-ArH)), 7.41−7.52 (m, 5H, ArH), 7.29−7.32 (m, 3H, *m*+*p*-Ar(P)H), 4.51 (d, $^2J_{HP}$ = 2.4 Hz, 5H, Cp). IR (KBr): ν = 1932.6 (s), 1856.2 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{21}H_{16}MnPO_2$: 386.0268. Found: 386.0247. MS *m/z* (%): 386 (26) [M^+], 330 (100) [M^+ − 2CO], 264 (32) [M^+ − 2CO − C_5H_6], 228 (88) [M^+ − 2CO − PhCCH].

25: A solution of **1c** (50.4 mg, 0.122 mmol) in 1-hexene (1.0 mL) was heated under reflux at 75 °C for 2 days. After evaporation of the solvent the crude product was purified by chromatography (SiO_2, 1:4 = toluene:pentane) yielding a yellow oil (43.8 mg, 0.119 mmol, 98%). Data in square brackets refer to the minor anti-isomer. ^{31}P NMR (C_6D_6): δ −77.5 [−72.7]. ^{13}C NMR (C_6D_6): δ 231.3 (broad, CO), 140.8 [136.7] (d, $^1J_{CP}$ = 25.4 [24.7] Hz, *ipso*-C), 131.3 [132.7] (d, $^2J_{CP}$ = 11.3 [10.7] Hz, *o*-ArC), 129.1 [129.4] (d, $^4J_{CP}$ = 2.4 [2.3], *p*-ArC), 128.5 [128.4] (d, $^3J_{CP}$ = 9.5 [9.4] Hz, *m*-ArC), 81.4 [81.5] (s, Cp), 32.4 [32.3] (d, $^3J_{CP}$ = 7.6 [4.8] Hz, *C*H_2CH$_2$CHP), 31.1 [30.9] (d, $^2J_{CP}$ = 1.9 [4.7] Hz, *C*H_2CH$_3$), 24.2 [23.8] (d, $^1J_{CP}$ = 11.7 [13.1] Hz, CHP), 22.9 [22.6] (s, *C*H_2CH$_3$), 15.5 [13.9] (d, $^1J_{CP}$ = 11.6 [12.0] Hz, CH_2P), 14.3 [14.0] (s, CH_3). ^{1}H NMR (C_6D_6): δ 7.28−7.35 (m, 2H, *o*-ArH), 6.91−7.03 (m, 3H, *m*+*p*-ArH), 4.16 [4.10] (d, $^2J_{HP}$ = 2.0 [2.1] Hz, 5H, Cp), 1.01−1.44 (m, unresolved), 0.92 [0.71] (t, $^3J_{HH}$ = 7.1 [7.3] Hz, 3H, CH_3), 0.64 (t, $^3J_{HH}$ = 7.5 Hz, 1H, HC*H*P). IR (KBr): ν = 1935.7 (s), 1866.3 (s) (C≡O) cm^{-1}. HRMS Calcd for $C_{19}H_{22}MnPO_2$: 368.073 79. Found: 368.073 62. MS *m/z* (%): 368 (18) [M^+], 312 (48) [M^+ − 2CO], 228 (100) [M^+ − 2CO − C_6H_{12}].

X-ray Crystallography. Crystal Structure Determination of *rac*-10e. $C_{22}H_{16}O_{10}P_2W_2$, fw = 869.99, yellowish needle, 0.48 × 0.06 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 6.7509(4) Å, b = 14.9157(8) Å, c = 26.1982(13) Å, β = 92.038(2)°, V = 2636.3(2) Å^3, Z = 4, ρ = 2.192 g/cm^3. A total of 49 511 reflections up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 8.89 mm^{-1}, 0.19−0.59 correction range). There were 6046 unique reflections (R_{int} = 0.047). The structure was solved with automated Patterson methods[59] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined as rigid groups, and 327 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0176/0.0383. R1/wR2 [all refl]: 0.0226/0.0401. S = 1.115. Residual electron density was between −1.08 and 0.58 e/Å^3. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[61]

Crystal Structure Determination of *meso*-10b. $C_{32}H_{20}Mo_2O_{10}P_2$, fw = 818.30, colorless block, 0.21 × 0.12 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 9.0413(1) Å, b = 21.6707(3) Å, c = 17.8474(3) Å, β = 111.9773(5)°, V = 3242.75(8) Å^3, Z = 4, ρ = 1.676 g/cm^3. A total of 38 814 reflections up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.60 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 0.93 mm^{-1}, 0.87−0.95 correction range). There were 5864 unique reflections (R_{int} = 0.071). The structure was solved with direct methods[62] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C1, C8, C9, and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. A total of 439 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma$(I)]: 0.0326/0.0706. R1/wR2 [all refl]: 0.0596/0.0827. S = 1.051. Residual electron density was between −0.57

(59) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla C. *The DIRDIF99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
(60) Sheldrick G. M. *SHELXL-97. Program for crystal structure refinement;* Universität Göttingen: Germany, 1997.
(61) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.
(62) Sheldrick G. M. *SHELXS-97. Program for crystal structure solution;* Universität Göttingen: Germany, 1997.

and 0.69 e/Å^3. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[61]

Crystal Structure Determination of *rac*-19. $C_{38}H_{20}O_{10}P_2W_2$, fw = 1066.18, yellow needle, 0.39 × 0.06 × 0.06 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 8.0153(3) Å, b = 10.6946(4) Å, c = 22.3651(5) Å, α = 88.441(2)°, β = 83.323(2)°, γ = 79.194(1)°, V = 1870.34(10) Å^3, Z = 2, ρ = 1.893 g/cm^3. A total of 44 445 reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 6.29 mm^{-1}, 0.37−0.69 correction range). There were 8531 unique reflections (R_{int} = 0.045). The structure was solved with automated Patterson methods[59] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined as rigid groups and 469 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0295/0.0542. R1/wR2 [all refl]: 0.0463/0.0580. S = 1.200. Residual electron density was between −0.96 and 1.10 e/Å^3. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package.[61]

Crystal Structure Determination of 21b. $C_{32}H_{18}O_{10}P_2W_2$, fw = 992.10, colorless block, 0.42 × 0.24 × 0.18 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 10.4762(1) Å, b = 11.3603(1) Å, c = 14.8964(1) Å, α = 103.5604(4)°, β = 99.8561(5)°, γ = 103.9820(4)°, V = 1622.87(2) Å^3, Z = 2, ρ = 2.030 g/cm^3. A total of 47 067 reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 7.24 mm^{-1}, 0.15−0.27 correction range). There were 7450 unique reflections (R_{int} = 0.029). The structure was solved with automated Patterson methods[59] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C1, C2, C9, and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. A total of 431 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0155/0.0334. R1/wR2 [all refl]: 0.0173/0.0339. S = 1.105. Residual electron density between −0.61 and 0.89 e/Å^3. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package.[61]

Crystal Structure Determination of *rac*-23. $C_{32}H_{16}Mo_2O_{10}P_2$, fw = 814.27, yellowish plate, 0.42 × 0.33 × 0.06 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 9.2748(4) Å, b = 12.0660(6) Å, c = 15.2717(6) Å, α = 90.529(2)°, β = 98.060(1)°, γ = 104.808(2)°, V = 1634.16(12) Å^3, Z = 2, ρ = 1.655 g/cm^3. A total of 36 889 reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 0.92 mm^{-1}, 0.50−0.95 correction range). There were 7481 unique reflections (R_{int} = 0.049). The structure was solved with automated Patterson methods[59] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C8 and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. A total of 423 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0338/0.0873. R1/wR2 [all refl]: 0.0425/0.0935. S = 1.038. Residual electron density was between −1.36 and 1.10 e/Å^3. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[61]

Crystal Structure Determination of 24. $C_{21}H_{16}MnO_2P$, fw = 386.25, yellow block, 0.36 × 0.15 × 0.12 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 9.2488(1), b = 10.0296(1), c = 10.8435(2) Å, α = 110.0434(9), β = 95.2573(10), γ = 105.1996(8)°, V = 893.42(2) Å^3, Z = 2, ρ = 1.436 g/cm^3. A total of 16 043 reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.710 73 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied (μ = 0.84 mm^{-1}, 0.85−0.91 correction range). There were 4040 unique reflections (R_{int} = 0.047). The structure was solved with automated Patterson methods[59] and refined with SHELXL-97[60] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl H atoms were refined as rigid groups; all other H atoms were refined freely with isotropic displacement parameters. A total of 250 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0289/0.0680. R1/ wR2 [all refl]: 0.0380/0.0731. S = 1.038. Residual electron density was between −0.28 and 0.43 e/Å^3. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[61]

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Note Added after ASAP Publication: In the version published on the Internet November 10, 2005, there was an error in the caption for Figure 3. This has been corrected in the version published November 14, 2005, and in the print version.

Supporting Information Available: The calculated energies and *xyz*-coordinates of the species discussed and details of the single-crystal X-ray structure determinations (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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