Metal-Template-Directed Synthesis of Diphosphorus Compounds through Intramolecular Phosphinidene Additions

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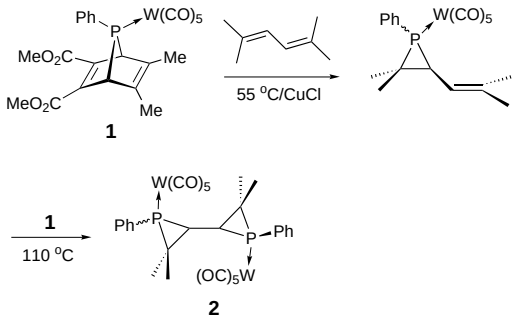
Abstract: Heating the nonchelating *cis*-bis-7-phosphanorbornadiene-[$Mo(CO)_4$] complex (**13**) results in the thermal decomposition of one of the 7-phosphanorbornadiene groups. The phosphinidene thus generated adds *intra*molecularly to a C=C bond of the other ligand to give the novel diphosphorus complex **14**. This reaction constitutes a metal-template-directed synthesis. Likewise, the intramolecular phosphinidene addition to the C=C bond of a Mo-phospholene ligand affords the diphos complex **18**. Its crystal structure exhibits an extremely small P-Mo-P bite-angle for a five-membered chelate ring. The similar intramolecular 1,2-addition to a C=C bond of a phosphole ligand gives a highly strained, unstable intermediate product. Scission of its P–Mo bond generates a free coordination site, which is then occupied by either CO or a phosphole to yield complexes **22** and **23**, respectively. The analogous *inter*molecular addition of [$PhPW(CO)_5$] to a [phosphole-$W(CO)_5$] complex gives the di-[$W(CO)_5$] complexed adduct **28**. The directing effect of the metal on the *intra*- and *inter*molecular additions is discussed.

Keywords: cage compounds · molybdenum · P ligands · phosphinidene complexes · phosphorus heterocycles

Introduction

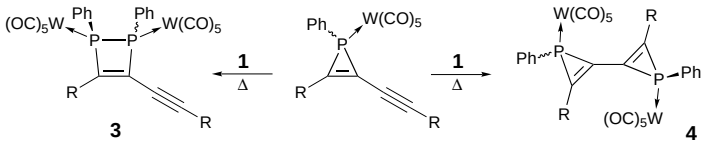
The first phosphorus analogues of carbenes were reported two decades ago. Mathey and Marinetti[1] demonstrated that the transition metal group [$M(CO)_5$] (M = W, Mo, Cr) stabilizes the phosphinidenes RP to provide viable synthons. The electrophilic reactivity of these transient species, which are generated in situ from 7-phosphanorbornadienes (**1**), has been amply demonstrated. Most prominent are the additions to C=C and C≡C bonds. The key question we address in this paper is whether phosphinidenes can also be used to generate new diphosphorus compounds (Scheme 1).

Multiple [$RPM(CO)_5$] additions are possible, but they are rare. Only selected dienes and diynes yield the corresponding bisphosphiranes (**2**)[2] and bisphosphirenes (**4**).[3] More typical is a P–C insertion of the second complexed phosphinidene into a phosphirene ring, formed by the first [$RPM(CO)_5$] addition, to give expanded four-membered 1,2-dihydro-1,2-diphosphete rings (**3**) (Scheme 2).



Scheme 1. Synthesis of new diphosphorus compounds.

Multiple [$RPM(CO)_5$] additions from a single source precursor are also known, but these are rare as well. In a very recent study, Huy et al.[4] explored precursor **5**, in which the two P centers are separated by a 2-butene chain (Scheme 3).



Scheme 2. Typical P–C insertion to expanded four-membered 1,2-dihydro-1,2-diphosphete rings and C≡C addition to bisphosphirenes.

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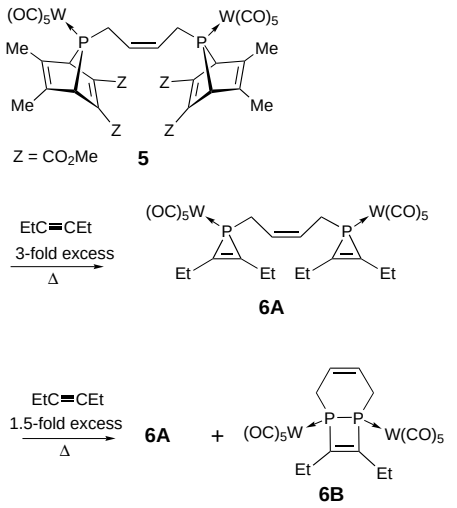
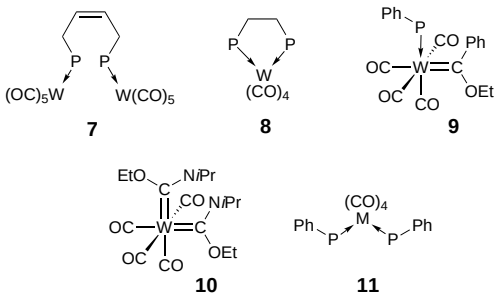


Scheme 3. Multiple $[RPM(CO)_5]$ additions investigated by Huy et al.[4]

Both phosphinidene centers add sequentially and only *inter*molecularly to C=C and C≡C bonds to give, for example, **6** in the case of 3-hexyne. Although Yoshifuji et al. reported on an intramolecular coupling of two uncomplexed phosphinidenes,[5] such P=P bond formation has not been observed on heating **5** in the absence of trapping reagents. Whereas formal P=P addition products, such as **6B**, have been observed to result from **5**, a stepwise mechanism was considered more plausible.[4]

Thus, no hard evidence was found for the intermediacy of bisphosphinidene **7**, which would result if both phosphanorbornadiene tails were to undergo cheletropic elimination simultaneously. Earlier, Mathey's group reported their investigations of chelating bisphosphinidenes.[6] For example, transient **8** was considered to be generated from the corresponding bis-P-norbornadiene precursor because trapping with simple alkenes, alkynes, methanol, and amines gave the corresponding di-adducts. However, these di-adducts can be equally well explained to result from the consecutive formation and reaction of the two phosphinidene centers. The same researchers also reported on mixed carbene-phosphinidene complexes.[7] These transient species **9** could be trapped with methanol and aniline, but not with alkynes. Clearly, the



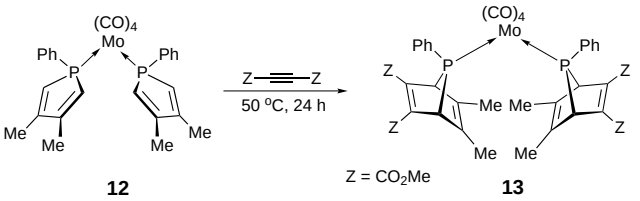
phosphinidene center dominates the stability and reactivity of **9**. Stable *cis*- and *trans*-biscarbene-$[M(CO)_4]$ complexes (M = W, Mo, Cr)[8] have been known for some time as well. Illustrative is an early X-ray crystal structure of *cis*-$[(OC)_4W[C(NiPr_2)OEt]_2]$ (**10**) by Fischer and co-workers.[8b] In contrast, we consider the corresponding *cis*-bisphosphinidene complexes $[(RP)_2M(CO)_4]$ (**11**) to be an unlikely synthon. Instead, we anticipate that the two phosphinidene centers will be generated consecutively at best; however, no attempts have been reported to demonstrate this so far.

In this paper we report on the behavior of **13**, which must be considered to be a potential precursor for a bisphosphinidene. We will show, in fact, that only one transient P center is generated, which subsequently undergoes a rapid *intra*molecular cycloaddition. This chemistry, the *intra*molecular cycloaddition between two P ligands, is then further explored with the aim of generating novel diphosphorus compounds.

Results and Discussion

In our approach we make use of i) the 7-phosphanorbornadiene unit, which is a convenient precursor for phosphinidenes, and ii) the $[Mo(CO)_4]$ group, because of the facile synthesis of *cis*-$[Mo(CO)_4L_2]$ complexes.[9]

A *cis*-bis-7-phosphanorbornadiene-[Mo(CO)$_4$] complex: As a starting point, we chose the known *cis*-bis-η^1-3,4-dimethylphosphole-$[Mo(CO)_4]$ complex (**12**) and performed a double Diels–Alder reaction with dimethylacetylene dicarboxylate to obtain the desired *cis*-bis-7-phosphanorbornadiene complex **13** in high yield (90%) as a single isomer (Scheme 4). The *cis*-configuration of **13** is evident from i) its IR carbonyl frequencies at $\tilde{\nu} = 2027$, 1927, and 1902 cm^{-1}, ii) its ^{13}C NMR carbonyl resonances at $\delta = 213.4$ and 207.5, and iii) its characteristic ^{31}P NMR singlet at $\delta = 246.0$.



Scheme 4. Double Diels–Alder reaction with **12**.

The single-crystal X-ray analysis of **13** (Figure 1) shows that the dimethylacetylene dicarboxylate has, as usual, approached both phospholes from the sterically least hindered side, namely, *anti* from the transition metal group. In solution, this is reflected in the small $^2J(P,C)$ coupling of ≈ 3.1 Hz of the CCO_2Me carbons.[4, 10] In the crystal, the octahedral geometry of the molybdenum atom in **13** is slightly distorted with a normal P1-Mo1-P2 angle of 89.231(17)°; however, it has a somewhat deviating C39-Mo1-C40 angle of 173.05(9)°. The P–C, C–C, and C=C bond lengths in the 7-phosphanorbornadiene units are almost identical to those reported for a $[Cr(CO)_5]$-complexed 7-phosphanorbornadiene.[9] It is noteworthy that crystals of **13** were enantiomerically pure. The 7-phosphanorbornadiene ligands are *meso*-ligands; however, because the rotations around the Mo–P bonds are "frozen" in the crystal, the complex becomes chiral. Since **13** is obtained from nonchiral building blocks, a racemic mixture of crystals must result.

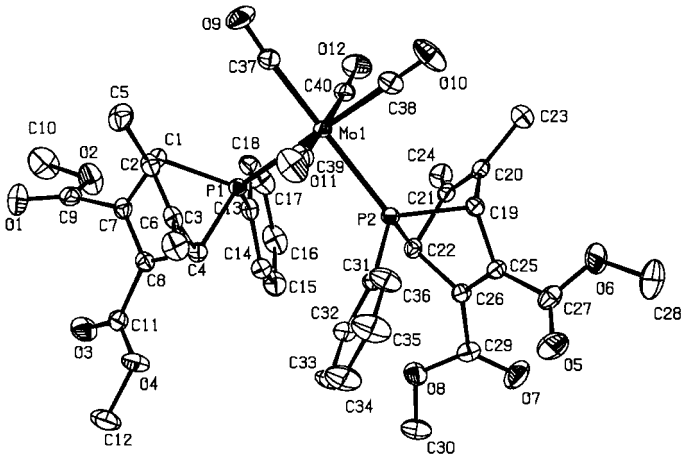
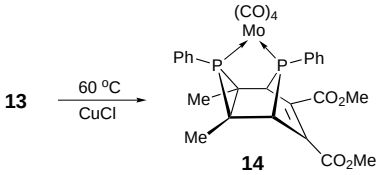


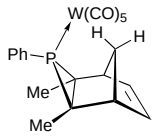
Figure 1. Displacement ellipsoid plot of **13** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–P1 2.5038(5), Mo1–P2 2.4844(5), P1–C1 1.8872(19), P2–C19 1.881(2), P1–C4 1.886(2), P2–C22 1.879(2), P1–C13 1.8242(19), P2–C31 1.827(2), C1–C2 1.536(3), C19–C20 1.537(3), C3–C4 1.533(3), C21–C22 1.534(3), C2–C3 1.338(3), C20–C21 1.332(3), C1–C7 1.523(3), C19–C25 1.520(3), C4–C8 1.521(3), C22–C26 1.520(3), C7–C8 1.344(3), C25–C26 1.339(3), P1-Mo1-P2 89.231(17), P1-Mo1-C38 179.09(6), P2-Mo1-C37 177.37(6), C39-Mo1-C40 173.05(9), Mo1-P1-C13 114.96(6), Mo1-P2-C31 114.80(6), C1-P1-C4 78.60(9), C19-P2-C22 78.58(9), P1-C1-C2 96.24(12), P2-C19-C20 96.94(12), P1-C4-C3 96.55(13), P2-C22-C21 97.05(12), P1-C1-C7 100.65(12), P2-C19-C25 101.29(13), P1-C4-C8 101.21(13), P2-C22-C26 101.08(13), C1-C2-C3 110.42(17), C19-C20-C21 109.46(17), C2-C3-C4 109.65(18), C20-C21-C22 110.47(17), C1-C7-C8 109.91(17), C19-C25-C26 109.88(17), C4-C8-C7 110.26(17), C22-C26-C25 110.18(17).

Thermal decomposition of complex **13** in toluene at 60 °C in the presence of olefins or alkynes, such as *trans*-stilbene, phenylacetylene, and diphenylacetylene, with CuCl as a catalyst did not give any complexed (bis)phosphirane nor (bis)phosphirene. Instead, *intra*molecular addition results to give **14** as sole product in 73% isolated yield (Scheme 5). The same product is obtained even when the decomposition

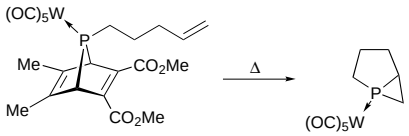


Scheme 5. Compound **14** as sole product of the Cu-catalyzed intramolecular addition.

is conducted with an olefin as the solvent. Thus, in 2,3-dimethyl-1,4-butadiene more than 60% of **13** is converted to **14**, as evidenced by ^{31}P NMR spectroscopy. The ^{31}P NMR resonance at $\delta = 159.7$ is characteristic for a chelating 7-phosphanorbornene,[11] while that at $\delta = -79.7$ is at rather low field for a phosphirane compared to those for other [Mo(CO)$_5$]-complexed phosphiranes ($\delta = -115$ to -135).[12] However, similar deshieldings have been observed for related phosphiranes, such as **15** obtained from the addition of [PhPW(CO)$_5$] to norbornadiene.[13] This effect has been attributed to negative hyperconjugation between the phosphorus group and the C=C bond. Complex **14** is remarkably stable. Heating at 110 °C in toluene in the presence of dppe for 10 hours does not result in decomplexation nor in any significant degradation. Evidently, **14** is a rather strong chelating complex in which the cheletropic formation of the "second" phosphinidene center does not occur.

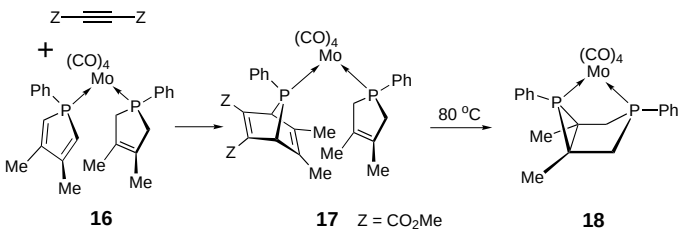


The formation of **14** is remarkable for two reasons. Firstly, *inter*molecular addition of a phosphinidene to the C=C bond of the generally employed 7-phosphanorbornadiene complex **1** has never been observed. Instead, formation of phosphinidene dimers, trimers, and higher oligomers occurs when [RPM(CO)$_5$] is generated in the absence of substrates.[14] Secondly, an *intra*molecular reaction with another ligand of the same complexing metal group has not been reported as yet. So far, only *intra*molecular addition to a C=C bond within the phosphinidene substituent is known (Scheme 6).[15] The ease by which **14** is formed encouraged us to further investigate the applicability of phosphinidene chemistry in metal-template-directed synthesis. All that may be needed is the correct ligand substitution of [Mo(CO)$_6$]. We pursue two cases: both contain the 7-phosphanorbornadiene ligand to generate the phosphinidene, while the other is a C=C-containing ligand for which we chose a phospholene and a phosphole.



Scheme 6. Intramolecular addition to a C=C bond within the phosphinidene substituent.

A *cis*-7-phosphanorbornadiene phospholene-[Mo(CO)$_4$] complex: We started our approach by simplifying one of the 7-phosphanorbornadiene ligands of **13** for a phospholene. That is, if the reaction proceeds in a similar manner to that described for **13** → **14**, this should result in a simplified diphos "basket". Starting material **17** was generated from a Diels–Alder reaction of dimethylacetylene dicarboxylate with **16**, which was obtained from *cis*-[{bis(piperidine)}Mo(CO)$_4$] by successive exchange of the piperidine ligands for 1-phenyl-3,4-dimethylphospholene and 1-phenyl-3,4-dimethylphosphole (Scheme 7). Heating a toluene solution of **17** at 80 °C gives the desired *intra*molecular addition product **18** in 54% isolated yield. This reaction is equally remarkable as that



Scheme 7. Preparation of diphos "basket" **18**.

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described for **13**. Interestingly, *inter*molecular addition of [PhPW(CO)$_5$] to a [phospholene-W(CO)$_5$] complex is sluggish at best, while reaction with an uncomplexed phospholene only results in the transfer of the [W(CO)$_5$] group.[16] The chelating complex **18** is very stable. Even attempts to chemically liberate its metal complex were not successful, neither by reaction with sulfur[11a] nor by iodine oxidation followed by ligand exchange.[17]

Similar to **14**, the phosphirane phosphorus of complex **18** has a relatively low-field ^{31}P NMR resonance at $\delta = -101.7$, although it is deshielded to a smaller extend because of the absence of the C=C bond and hence the lack of negative hyperconjugation. However, a downfield shift is generally also observed for five-membered chelates in [M(L$_2$)(CO)$_4$] complexes (M = W, Mo, Cr).[18]

A single crystal X-ray structure determination (Figure 2) provided conclusive structural characterization of this new ligand system. The octahedral Mo-coordination of **18** is

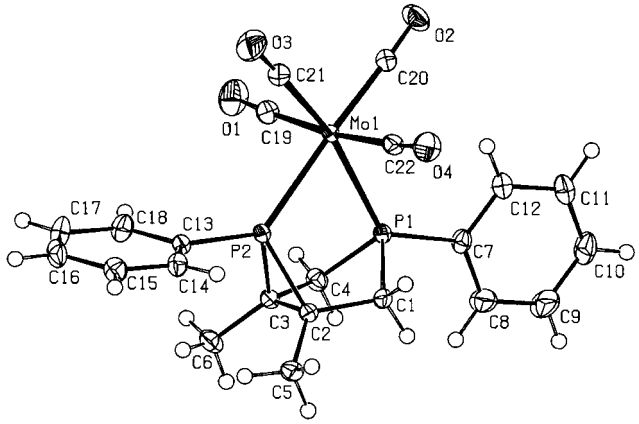
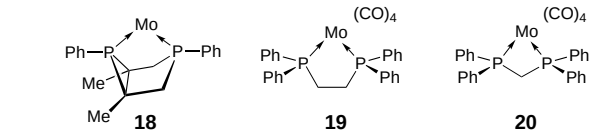


Figure 2. Displacement ellipsoid plot of **18** drawn at the 50% probability level. Selected bond lengths [Å], angles and torsion angles [°]: Mo1–P1 2.5030(5), Mo1–P2 2.4958(5), P1–C1 1.856(2), P1–C4 1.847(2), P2–C2 1.8596(19), P2–C3 1.8696(19), C1–C2 1.531(2), C2–C3 1.533(3), C3–C4 1.523(3), P1-Mo1-P2 69.732(16), P1-Mo1-C20 102.52(6), P1-Mo1-C19 96.03(6), P1-Mo1-C22 89.06(6), P2-Mo1-C21 94.22(6), P2-Mo1-C19 88.32(6), P2-Mo1-C22 95.88(6), Mo1-P1-C7 129.11(7), Mo1-P2-C13 132.57(6), C1-P1-C4 89.42(9), C2-P2-C3 48.53(8), P2-C2-C3 66.08(10), P2-C3-C2 65.39(10), P2-C2-C1 109.19(13), P2-C3-C4 112.76(13), C1-C2-C3-P2 –102.78(14), P2-C2-C3-C4 106.23(15), P1-C1-C2-P2 –41.80(14), P2-C3-C4-P1 37.02(16).

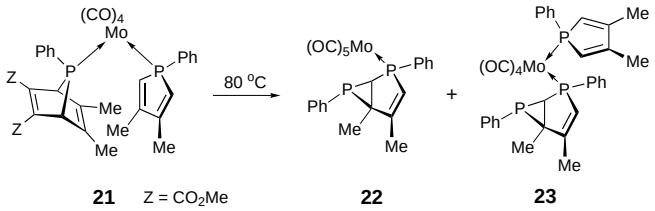
significantly distorted. The P1-Mo-P2 bond angle of 69.732(16)° is very small for a five-membered chelate ring, as compared to the 80.2(1)° for [(dppe)Mo(CO)$_4$] (**19**),[19] and



is only 2.4° larger than for the four-membered chelate ring of [(dppm)Mo(CO)$_4$] (**20**).[20] Consequently, both *cis*-P-Mo-C angles are significantly widened: the P1-Mo-C20 angle (102.52(6)°) is much larger than the P2-Mo-C21 angle (94.22(6)°). The two P1–Mo and P2–Mo bond lengths of 2.5030(5) and 2.4958(5) Å, respectively, are almost identical.

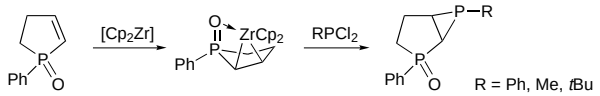
A *cis*-7-phosphanorbornadiene phosphole-[Mo(CO)$_4$] complex: Can the metal-template-directed reaction also be employed for the synthesis of other diphosphorus compounds that are even more strained than the five-membered chelates **14** and **18**? A logical and simple approach to verify this is to replace the phospholene in **17** for a phosphole, if indeed the phosphinidene center will react with one of its C=C bonds.

Precursor complex **21** is easily obtained by following the same procedure as that described for the synthesis of **13**, but with a reduced reaction time of 10 hours; this illustrates that the Diels–Alder cycloadditions occur sequentially. Much to our surprise, thermal decomposition of **21** at 80 °C yielded a 4:1 ratio of the products **22** and **23**, in which an additional CO and a phosphole ligand, respectively, are incorporated into the formal 1,2-adduct (Scheme 8).



Scheme 8. Thermal decomposition of compound **21**.

The ^{31}P NMR spectrum of complex **22** shows a characteristic AX pattern with resonances at $\delta = -138.7$ and 41.7 for the phosphirane and phospholene phosphorus, respectively, with a ^2J(P,P) coupling constant of 64.8 Hz. The absence of $^{95/97}$Mo,^{31}P couplings at the higher field resonance indicates that the three-membered ring phosphorus is not coordinated to the molybdenum. Moreover, the carbonyl resonances in the ^{13}C NMR spectrum at $\delta = 210.2$ and 206.0 and their IR frequencies at $\tilde{\nu} = 2071$ and 1944 cm^{-1} show that the molybdenum carries five CO ligands. Recently, saturated analogues of **22** have been obtained as phospholane oxides by a zirconocene-mediated synthesis (Scheme 9). The ^{31}P NMR chemical shifts for its phosphirane ring range from $\delta = -175$ to -192.[21]

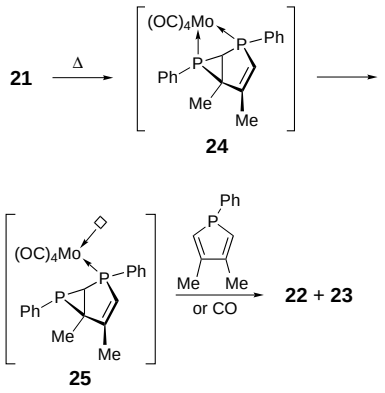


Scheme 9. Zirconocene-mediated synthesis of phospholane oxides.

Complex **23** is readily characterized by the three ^{31}P NMR resonances at $\delta = -140.0$, 33.4, and 43.1 with coupling patterns typical for an AMX system. The *cis*-configuration is evident from its ^{13}C NMR spectrum (four CO resonances) and the IR frequencies at $\tilde{\nu} = 2020$, 1909, and 1880 cm^{-1}. Compared to other uncomplexed phosphiranes, which generally oxidize rapidly upon contact with air, the insensitivity of

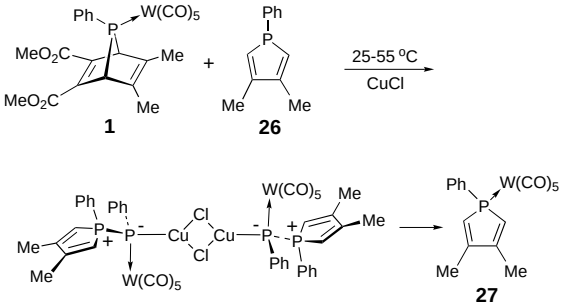
compounds **22** and **23** toward oxidation is startling. Both are air stable in solution for days and in the solid state for months.

The formation of **22** and **23** can be rationalized by an *intra*molecular addition to one of the C=C bonds of **21** to furnish the highly strained **24** (Scheme 10). Because of the unfavorable overlap between the phosphorus lone-pair and the d orbitals of molybdenum, the Mo–phosphirane bond breaks. The resulting free Mo coordination site is subsequently occupied by either a carbon monoxide or a phosphole, which may be present in solution from the decomposition of **21**, **24**, or **25**, to give products **22** and **23**, respectively. Hence, a more selective reaction is expected when one of the ligands is present in excess. Indeed, thermal decomposition of **21** in the presence of additional phosphole gives **23** as the sole product in 48% yield.



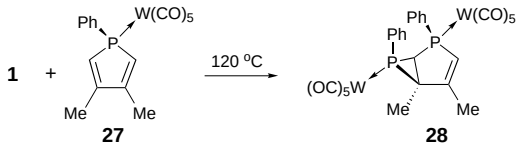
Scheme 10. Mo-mediated conversion of **21**.

Interestingly, the analogous *inter*molecular reaction with 1-phenyl-3,4-dimethylphosphole (**26**) follows a different path: [PhPW(CO)$_5$], generated in situ from complex **1**,[10] adds to the phosphole phosphorus instead of to one of its C=C bonds, to give the [W(CO)$_5$]-complexed phosphole **27** via a dimeric phosphoranylidene phosphine complex and elimination of [PhP-CuCl] (Scheme 11).[16] This reaction looks deceptively simple, as if only a [W(CO)$_5$] transfer has taken place.



Scheme 11. Cu-catalyzed synthesis of [W(CO)$_5$]-complexed phosphole **27**.

This complementary finding suggests that *inter*molecular addition to the C=C bonds of phospholes may be achieved only when the phosphorus center is blocked, for example, by a bulky complexing group. To test this, we reacted the [PhPW(CO)$_5$] precursor **1** with the [W(CO)$_5$]-complexed phosphole **27** (Scheme 12). Indeed, the 1,2-addition product



Scheme 12. Intermolecular addition to the C=C bonds of phospholes as a result of a blocked phosphorus center to yield **28**.

28 was obtained in 17% isolated yield. Compared with complexes **22** and **23**, the ^{31}P NMR resonance of the phosphirane ring of **28** at $\delta = -89.5$ is deshielded by $\approx$49 ppm and shows a very small ^2J(P,P) coupling of only 16 Hz with the phospholene phosphorus at $\delta = 41.2$.

The structural assignment of **28** has been ascertained by a single-crystal X-ray structure determination (Figure 3). As expected, the phosphinidene is added to the sterically least-hindered side of the [W(CO)$_5$]-complexed phosphole. In contrast to **22** and **23**, the phenyl group of **28** is located above

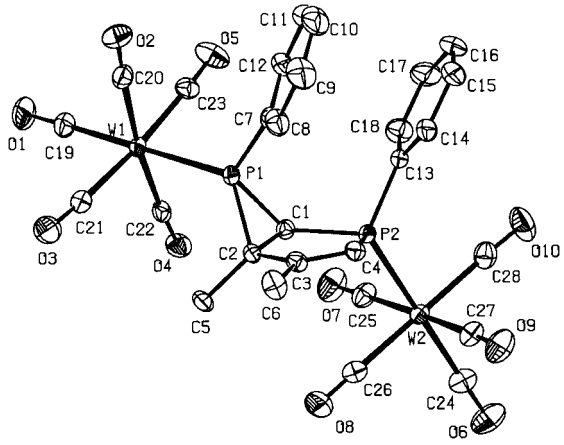


Figure 3. Displacement ellipsoid plot of **28** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–P1 2.4964(9), W2–P2 2.4960(9), P1–C1 1.845(4), P1–C2 1.853(3), P1–C7 1.823(4), C1–C2 1.540(5), P2–C1 1.823(3), P2–C4 1.804(4), P2–C13 1.812(3), C2–C3 1.492(4), C3–C4 1.332(5), C1-P1-C2 49.23(14), P1-C1-C2 65.64(18), P1-C2-C1 65.13(18), C1-P2-C4 91.70(16), C1-P1-C7 112.50(15), C2-P1-C7 113.10(16), W1-P1-C7 118.77(11), W2-P2-C13 116.02(12), C1-P2-C13 108.52(16).

the ring at the side opposite to the phospholene [M(CO)$_5$] group. The two phenyl groups are virtually periplanar to each other. The structure has two equivalent phosphirane P–C bonds of 1.845(4) Å for P1–C1 and 1.853(3) Å for P1–C2, which are similar to those of the 1,2-addition adduct of cyclopentene.[22] The steric congestion is reflected in the relatively large C1-P1-C7 and C2-P1-C7 angles of 112.50(15) and 113.10(16)°, respectively, which are usually not larger than 110°.[23] The C1–C2 bond length of 1.540(5) Å and the C1-P1-C2 bond angle of 49.23(14)° are as expected.

Conclusions

Thermally induced cheletropic elimination occurs for only one of the reactive centers of *cis*-bis-7-phosphanorbornadiene **13**, rather than giving a double elimination to a bis-phosphi-

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nidene complex. The thus-generated single phosphinidene center only adds *intra*molecularly to the remaining 7-phosphanorbornadiene unit to give the chelating diphos-[Mo(CO)$_4$] complex **14**. This reaction constitutes a *metal-template-directed synthesis* with one ligand of the *cis*-[Mo(CO)$_4$L$_2$] complex reacting with another ligand. *Intra*molecular 1,2-addition to a *cis*-phospholene ligand likewise results in the formation of the very stable chelating complex **18**, which has an extremely small P-Mo-P bite-angle of 69.732(16)°. *Intra*-molecular reaction with a *cis*-phosphole ligand gives a transient 1,2-adduct. Scission of one of its P–Mo bonds, on account of a too small bite angle, results in a free Mo coordination site, which is occupied by either CO or a phosphole to yield complexes **22** and **23**, respectively.

Albeit in lower yield and with a different configuration, the 1,2-adduct **28** is obtained from the *inter*molecular addition of [PhPW(CO)$_5$] to a [W(CO)$_5$]-complexed phosphole. However, *inter*molecular addition of [PhPW(CO)$_5$] to uncomplexed phospholenes and phospholes occurs only with a net transfer of the [W(CO)$_5$] group, while no addition (*exo* nor *endo*) to any complexed 7-phosphanorbarnadiene complexes has been observed to our knowledge.

The difference between intra- and intermolecular additions of the phosphinidene illustrates that the metal is not necessarily an innocent, stabilizing bystander. Rather, it can participate in the reaction, acting as a template that brings the reactants in close vicinity, thereby enabling selective additions. It can do so by the correct use of its coordination sphere. As a result, we have been able to synthesize novel bidentate diphosphorus ligands with extremely small P-M-P bite-angles. The use of other metals, which are more easily expelled, can expand this work to novel free diphos ligands, which can readily be made chiral by the correct substitution.

Experimental Section

General remarks: All experiments were performed under an atmosphere of dry nitrogen. Solvents were used as purchased, except for toluene which was distilled over sodium. 1-Phenyl-3,4-dimethylphospholene,[24] 1-phenyl-3,4-dimethylphosphole (**26**),[25] *cis*-[{bis-(piperidine)}Mo(CO)$_4$],[9] and *cis*-[{bis(1-phenyl-3,4-dimethylphosphole)}Mo(CO)$_4$][11a] (**12**) were prepared according to literature procedures. NMR spectra were recorded on a Bruker AC200 (^{1}H, ^{13}C) and Avance 250 spectrometers (^{31}P) with SiMe$_4$ (^{1}H, ^{13}C) and 85% H$_3$PO$_4$ (^{31}P) as external standards. IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) on a Finnigan Mat 90 spectrometer.

Synthesis of *cis*-bis-7-phosphanorbornadiene complex 13: A mixture of complex **12** (0.97 g, 1.7 mmol) and dimethylacetylene dicarboxylate (3.1 mL, 25 mmol) was allowed to stand at room temperature for 25 d. Chromatography (silica gel, i) dichloromethane (to regenerate excess dimethylacetylene dicarboxylate), ii) dichloromethane/diethylacetate 9:1) gave complex **13** (1.25 g, 86%) as a yellow solid. (The reaction time can be reduced to 24 h by stirring complex **12** and a large excess dimethylacetylene dicarboxylate at 50 °C with only a slight decrease in yield.) M.p. 149–150 °C (decomp.); ^{31}P NMR (CDCl$_3$): $\delta = 246.0$; ^{1}H NMR (CDCl$_3$): $\delta = 1.67$ (s, 12H; CCH$_3$), 3.54 (s, 4H; CH), 3.57 (s, 12H; OCH$_3$), 7.05–7.42 (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta = 15.5$ (s; *C*CH$_3$), 52.0 (s; O*C*H$_3$), 59.7 (m, $^{(1+3)}J$(P,C) = 17.2 Hz; *C*H), 127.7–129.1 (m; Ar), 137.5 (m; *ipso*-Ph), 141.9 (m, $^{(2+4)}J$(P,C) = 2.1 Hz; C*C*H$_3$), 145.8 (m, $^{(2+4)}J$(P,C) = 1.6 Hz; C*C*O$_2$CH$_3$), 165.0 (m, $^{(3+5)}J$(P,C) = 3.1 Hz; *C*O$_2$CH$_3$), 207.5 (t, ^2J(P,C) = 9.5 Hz; *C*O$_{ax}$), 213.2 (m; *C*O$_{eq}$); IR (CH$_2$Cl$_2$): $\tilde{\nu}$(CO) = 2027 (m), 1927 (s), 1902 (sh) cm^{-1}.

Synthesis of 14 by thermal decomposition of 13: A solution of complex **13** (0.19 g, 0.22 mmol) in toluene (3 mL) with CuCl as the catalyst was stirred at 60 °C for 45 min. Evaporation to dryness and chromatography (silica gel, dichloromethane) gave complex **14** (0.10 g, 73%) as a yellow solid. M.p. 145–146 °C (decomp.); ^{31}P NMR (CDCl$_3$): $\delta = -79.7$ (s; phosphirane P), 159.7 (s; phosphanorbornene P); ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (d, ^3J(P,H) = 8.81 Hz, 6H; CCH$_3$), 3.63 (s, 6H; OCH$_3$), 3.75 (s, 2H; CH), 7.18–7.43 (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta = 15.1$ (d, ^2J(P,C) = 6.6 Hz; C*H*$_3$), 41.0 (dd, ^{1+2}J(P,C) = 11.9 Hz, ^2J(P,C) = 8.5 Hz; *C*CH$_3$), 52.4 (s; O*C*H$_3$), 61.4 (dd, ^1J(P,C) = 21.7 Hz, ^2J(P,C) = 10.2 Hz; P*C*H), 128.5–132.7 Ar, 142.5 (dd, ^2J(P,C) = 8.8 Hz, ^3J(P,C) = 1.0 Hz; *C*CO$_2$Me), 164.6 (d, ^3J(P,C) = 1.9 Hz; *C*O$_2$Me), 206.1 (dd, ^2J(P,C) = 9.2 Hz, ^2J(P,C) = 11.4 Hz; *C*O$_{ax}$), 214.8 (dd, ^2J(P,C) = 8.6 Hz, ^2J(P,C) = 30.5 Hz; *C*O$_{eq}$), 215.7 (dd, ^2J(P,C) = 9.9 Hz, ^2J(P,C) = 24.2 Hz; *C*O$_{eq}$); HR-MS: calcd for C$_{28}$H$_{24}$O$_8$P$_2$Mo: 648.00016; found: 648.00117 ($\delta = 3 \times 10^{-3}$); IR (CH$_2Cl_2$): $\tilde{\nu}$(CO) = 2025 (m), 1917 (s) cm^{-1}.

Synthesis of complex 16: A mixture of *cis*-[{bis(piperidine)}Mo(CO)$_4$] (0.62 g, 1.6 mmol) and 1-phenyl-3,4-dimethylphospholene (0.31 g, 1.6 mmol) was stirred in refluxing dichloromethane (20 mL) for 10 min. 1-Phenyl-3,4-dimethylphosphole (0.31 g, 1.6 mmol) was added and the mixture was stirred at reflux for an additional 3 h. Evaporation to dryness and chromatography (silica gel, pentane/dichloromethane 4:1) gave complex **16** (0.86 g, 90%) as a yellow solid. M.p. 113–114 °C; ^{31}P NMR (CH$_2$Cl$_2$): $\delta = 33.0$ (d, ^2J(P,P) = 23.2 Hz; phosphole-P), 18.0 (d, ^2J(P,P) = 23.2 Hz; phospholene-P); ^{1}H NMR (CDCl$_3$): $\delta = 1.66$ (s, 6H; phospholene-CH$_3$), 2.03 (s, 6H; phosphole-CH$_3$), 2.34–2.94 (m, 4H; CH$_2$), 6.31 (d, ^1J(P,H) = 36.2 Hz; PCH), 7.23–7.49 (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): δ = 16.2 (d, ^3J(P,C) = 6.7 Hz; phospholene-*C*H$_3$), 17.2 (d, ^3J(P,C) = 10.0 Hz; phosphole-*C*H$_3$), 44.2 (dd, ^3J(P,C) = 2.0 Hz, ^1J(P,C) = 21.2 Hz; *C*H$_2$), 128.2 (d, ^1J(P,C) = 17.6 Hz; *C*H),128.8–131.3 (m; Ar), 129.5 (d, ^2J(P,C) = 3.0 Hz; CH$_2$*C*CH$_3$), 132.7 (dd, ^3J(P,C) = 2.4 Hz, ^1J(P,C) = 33.2 Hz; phosphole *ipso*-Ph), 139.5 (dd, ^3J(P,C) = 1.5 Hz, ^1J(P,C) = 24.5 Hz; phospholene *ipso*-Ph), 148.6 (d, ^2J(P-C) = 7.8 Hz; CH*C*CH$_3$), 209.5 (dd, ^2J(P,C) = 9.0 Hz, ^2J(P,C) = 9.6 Hz; *C*O$_{ax}$), 214.5 (dd, ^2J(P,C) = 1.3 Hz, ^2J(P,C) = 9.1 Hz; *C*O$_{eq}$), 214.9 (dd, ^2J(P,C) = 3.0 Hz, ^2J(P,C) = 9.1 Hz; *C*O$_{eq}$); HR-MS: calcd for C$_{28}$H$_{28}$O$_4$P$_2$Mo: 588.051797; found: 588.052260 ($\delta = 2 \times 10^{-3}$); IR (CH$_2Cl_2$): $\tilde{\nu}$(CO) = 2020 (m), 1908 (s), 1883 (sh) cm^{-1}.

Synthesis of complex 17: A mixture of complex **16** (0.86 g, 1.5 mmol) and dimethylacetylene dicarboxylate (2.0 mL, 16 mmol) was stirred at 45 °C for 24 h. Chromatography (silica gel, starting with pentane and gradual change to pure dichloromethane) gave recovered dimethylacetylene dicarboxylate followed by **17** (0.54 g, 50%) as a yellow oil. Recrystallization (dichloromethane/hexane) gave yellow crystals. M.p. 123–124 °C; ^{31}P NMR (CDCl$_3$): $\delta = 19.6$ (d, ^2J(P,P) = 26.4 Hz; phospholene-P), 252.0 (d, ^2J(P,P) = 26.4 Hz; phosphanorbornadiene-P); ^{1}H NMR (CDCl$_3$): $\delta = 1.65$ (s, 6H; phospholene-CH$_3$), (d, ^3J(P,H) = 0.86 Hz, 6H; phosphanorbornadiene-CH$_3$), 2.84 (m, 4H; CH$_2$), 3.53 (d, ^2J(P,H) = 3.15 Hz, 2H; CH), 3.59 (s, 6H; OCH$_3$), 6.93–7.48 (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta = 15.7$ (d, ^3J(P,C) = 2.0 Hz; phosphanorbornadiene-*C*H$_3$), 16.1 (d, ^3J(P,C) = 6.8 Hz; phospholene-*C*H$_3$), 44.0 (dd, ^3J(P,C) = 1.9 Hz, ^1J(P,C) = 21.8 Hz; *C*H$_2$), 51.9 (s; O*C*H$_3$), 59.7 (dd, ^3J(P,C) = 2.1 Hz, ^1J(P,C) = 14.5 Hz; *C*H), 127.7–129.4 (m; Ar), 129.5 (s; CH$_2$*C*CH$_3$), 137.3 (d, ^1J(P,C) = 17.3 Hz; phosphanorbornadiene *ipso*-Ph), 140.1 (dd, ^3J(P,C) = 1.7 Hz, ^1J(P,C) = 24.9 Hz; phospholene *ipso*-Ph), 141.9 (d, ^2J(P,C) = 3.7 Hz; CH*C*CH$_3$), 145.8 (d, ^2J(P,C) = 3.5 Hz; *C*CO$_2$CH$_3$),165.1 (d, ^3J(P,C) = 2.3 Hz; *C*O$_2$CH$_3$), 208.6 (dd, ^2J(P,C) = 8.1 Hz, ^2J(P,C) = 10.0 Hz; *C*O$_{ax}$), 214.0 (dd, ^2J(P,C) = 9.0 Hz, ^2J(P,C) = 21.3 Hz; *C*O$_{eq}$), 214.5 (dd, ^2J(P,C) = 10.0 Hz, ^2J(P,C) = 16.3 Hz; *C*O$_{eq}$); IR (CH$_2$Cl$_2$): $\tilde{\nu}$(CO) = 2023 (m), 1915 (s), 1891 (sh) cm^{-1}.

Synthesis of 18 by thermal decomposition of 17: A solution of **17** (0.35 g, 0.48 mmol) in toluene (3 mL) was stirred at 80 °C for 3 h. Evaporation to dryness and chromatography (silica gel, dichloromethane/pentane 2:1) followed by recrystallization from dichloromethane/hexane gave **18** (0.13 g, 54%) as colorless crystals. M.p. 134–136 °C (decomp.); ^{31}P NMR (CDCl$_3$): $\delta = -101.7$ (d, ^2J(P,P) = 8.1 Hz; phosphirane-P), 15.4 (d, ^2J(P,P) = 8.1 Hz; phospholane-P); ^{1}H NMR (CDCl$_3$): $\delta = 1.49$ (d, ^3J(P,H) = 8.83 Hz, 6H; CH$_3$), 2.28–2.67 (m, 4H; CH$_2$), 7.24–7.80 (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta = 16.5$ (dd, ^3J(P,C) = 1.6 Hz, ^2J(P,C) = 8.9 Hz; *C*H$_3$), 36.2 (dd, ^2J(P,C) = 5.7 Hz, ^{1+2}J(P,C) = 10.9 Hz; *C*CH$_3$), 45.5 (dd, ^2J(P,C) = 10.5 Hz, ^1J(P,C) = 26.1 Hz; *C*H$_2$), 128.7–133.9 (m; Ar), 208.0 (dd, ^2J(P,C) = 9.3 Hz, ^2J(P,C) = 11.6 Hz; *C*O$_{ax}$), 216.1 (dd, ^2J(P,C) = 9.2 Hz, ^2J(P,C) = 22.9 Hz; *C*O$_{eq}$), 217.5 (dd, ^2J(P,C) = 8.9 Hz, ^2J(P,C) = 31.5 Hz; *C*O$_{eq}$); HR-MS: calcd for C$_{22}$H$_{20}$O$_4$P$_2$Mo: 507.98907; found: 507.99067 ($\delta = 1.6 \times 10^{-2}$); IR (CH$_2Cl_2$): $\tilde{\nu}$(CO) = 2020 (m), 1904 (s) cm^{-1}.

Synthesis of complex 21: A mixture of complex **12** (3.00 g, 5.2 mmol) and dimethylacetylene dicarboxylate (12.5 mL, 0.1 mol) was stirred at 50 °C for 9 h. Chromatography (silica gel, starting with pentane and gradual change to pure dichloromethane) gave recovered dimethylacetylene dicarboxylate followed by **21** (1.92 g, 52 %) as yellow crystals and complex **13** (0.61 g, 14 %). M.p. 107 – 108 °C; ^{31}P NMR (CH_2Cl_2): $\delta = 33.2$ (d, ^2J(P,P) = 19.8 Hz; phosphole-P), 249.8 (d, ^2J(P,P) = 19.8 Hz; phosphanorbornadiene-P); ^{1}H NMR ($CDCl_3$): $\delta = 1.90$ (s, 6H; phosphanorbornadiene-CH_3), 2.12 (s, 6H; phosphole-CH_3), 3.55 (m, 8H; OCH_3, phosphanorbornadiene-CH), 6.37 (d, ^2J(P,H) = 36.4 Hz, 2H; phosphole-CH), 6.94 – 7.41 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 15.7$ (d, ^3J(P,C) = 1.7 Hz; phosphanorbornadiene-*C*H$_3$), 17.4 (d, ^3J(P,C) = 10.0 Hz; phosphole-*C*H$_3$), 51.9 (s; O*C*H$_3$), 59.4 (dd, ^3J(P,C) = 1.7 Hz, ^1J(P,C) = 14.8 Hz; phosphanorbornadiene-*C*H), 127.6 – 131.2 (m; Ar), 131.6 (d, ^1J(P,C) = 35.4 Hz; phosphole-*C*H), 137.2 (d, ^1J(P,C) = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 142.0 (d, ^2J(P,C) = 3.7 Hz; phosphanorbornadiene CH*C*CH$_3$), 145.7 (d, ^2J(P,C) = 3.6 Hz; *C*CO$_2$CH$_3$), 148.6 (d, ^2J(P,C) = 7.9 Hz; phosphole CH*C*CH$_3$), 165.1 (d, ^3J(P,C) = 2.3 Hz; *C*O$_2$CH$_3$), 208.4 (dd, ^2J(P,C) = 8.0 Hz, ^2J(P,C) = 9.3 Hz; *C*O$_{ax}$), 213.6 (m; *C*O$_{eq}$); HR-MS: calcd for $C_{34}H_{32}O_8P_2Mo$: 728.063217; found: 728.062755 ($\delta = 2 \times 10^{-3}$); IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 2025 (m), 1919 (s), 1894 (sh) cm^{-1}.

Synthesis of complexes 22 and 23 by thermal decomposition of 21: A solution of **21** (0.40 g, 0.55 mmol) in toluene (5 mL) was stirred at 80 °C for 5 h. Evaporation to dryness and chromatography (silica gel, dichloromethane/pentane 3:1) gave **22** (77 mg, 26 %) as a white solid and **23** (25 mg, 7 %) as a yellow solid. Both products were recrystallized from dichloromethane/hexane.

Compound 22: M.p. 147 – 148 °C (decomp.), colorless crystals; ^{31}P NMR ($CDCl_3$): $\delta = -138.7$ (d, ^2J(P,P) = 64.8 Hz; phosphirane-P), 41.7 (d, ^2J(P,P) = 64.8 Hz; phospholene-P); ^{1}H NMR ($CDCl_3$): $\delta = 1.23$ (d, ^4J(P,H) = 4.04 Hz, 3H; C=CCH$_3$), 2.11 (s, 3H; PCCH$_3$), 2.80 (d, ^2J(P,H) = 8.8 Hz, 1H; PCH), 5.65 (d, ^2J(P,H) = 39.0 Hz, 1H; C=CH), 7.24 – 7.62 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 16.7$ (d, ^3J(P,C) = 2.6 Hz; C=*C*CH$_3$), 17.4 (^2J(P,C) = 9.7 Hz; PC*C*H$_3$), 40.0 (dd, ^1J(P,C) = 26.8 Hz, ^1J(P,C) = 40.0 Hz; P*C*P), 51.6 (dd, ^2J(P,C) = 6.5 Hz, ^{1+2}J(P,C) = 40.5 Hz; P*C*CH$_3$), 120.7 (dd, ^3J(P,C) = 8.2 Hz, ^1J(P,C) = 37.9 Hz; P*C*=C), 128.5 – 136.3 (m; Ar), 159.6 (dd, ^2J(P,C) = 3.5 Hz, ^2J(P,C) = 10.4 Hz; PC=*C*), 206.0 (dd, ^2J(P,C) = 1.8 Hz, ^2J(P,C) = 9.5 Hz; *C*O$_{ax}$), 210.2 (d, ^2J(P,C) = 23.4 Hz; *C*O$_{eq}$); HR-MS calcd for $C_{23}H_{18}O_5P_2Mo$: 533.96832; found: 533.96756 ($\delta = 6 \times 10^{-3}$); IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 2071 (w), 1944 (s) cm^{-1}.

Compound 23: M.p. 79 – 80 °C, yellow crystals; ^{31}P NMR ($CDCl_3$): $\delta = -140.0$ (d, ^2J(P,P) = 63.3 Hz; phosphirane-P), 33.4 (d, ^2J(P,P) = 24.3 Hz; phosphole-P), 43.1 (dd, ^2J(P,P) = 63.3 Hz, ^2J(P,P) = 24.3 Hz; phospholene-P); ^{1}H NMR ($CDCl_3$): δ 1.14 (d, ^3J(P,H) = 4.0 Hz, 3H; PCCH$_3$), 1.96 (s, 6H; C=CCH$_3$), 2.04 (s, 3H; C=CCH$_3$), 2.62 (d, ^2J(P,H) = 8.7 Hz, 1H; PCH), 5.26 (d, ^2J(P,H) = 38.1 Hz, 1H; C=CH), 6.33 (dd, ^2J(P,H) = 36.0 Hz, ^4J(P,H) = 20.8 Hz, 2H; C=CH), 7.24 – 7.52 (m, 15H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 16.6$ (d, ^2J(P,C) = 2.6 Hz; PC*C*H$_3$), 17.2 (d, ^3J(P,C) = 10.0 Hz; C=*C*CH$_3$), 17.5 (d, ^3J(P,C) = 9.3 Hz; C=*C*CH$_3$), 41.1 (ddd, ^4J(P,C) = 3.6 Hz, ^2J(P,C) = 24.3 Hz, ^2J(P,C) = 44.3 Hz; P*C*P), 51.1 (dd, ^2J(P,C) = 6.9 Hz, ^{1+2}J(P,C) = 39.9 Hz; P*C*CH$_3$), 121.4 (ddd, ^3J(P,C) = 1.3 Hz, ^3J(P,C) = 8.1 Hz, ^1J(P,C) = 34.2 Hz; P*C*=C), 128.2 – 133.4 (m; Ar), 131.6 (dd, ^3J(P,C) = 2.1 Hz, ^1J(P,C) = 35.4 Hz; PC=*C*), 136.5 (dd, ^3J(P,C) = 4.7 Hz, ^1J(P,C) = 50.1 Hz; *ipso*-Ph), 141.0 (dd, ^3J(P,C) = 4.7 Hz, ^1J(P,C) = 15.2 Hz; *ipso*-Ph), 148.5 (dd, ^2J(P,C) = 7.9 Hz, ^4J(P,C) = 16.1 Hz; PC=*C*), 158.4 (dd, ^2J(P,C) = 3.0 Hz, ^4J(P,C) = 10.2 Hz; PC=*C*), 209.2 (ddd, ^4J(P,C) = 2.8 Hz, ^2J(P,C) = 9.1 Hz, ^2J(P,C) = 18.4 Hz; *C*O$_{ax}$), 210.1 (dd, ^2J(P,C) = 8.1 Hz, ^2J(P,C) = 9.1 Hz; *C*O$_{ax}$), 214.7 (dd, ^2J(P,C) = 8.2 Hz, ^2J(P,C) = 26.0 Hz; *C*O$_{eq}$), 215.0 (ddd, ^4J(P,C) = 2.1 Hz, ^2J(P,C) = 9.8 Hz, ^2J(P,C) = 21.4 Hz; *C*O$_{eq}$); IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2020 (w), 1909 (s), 1880 (sh) cm^{-1}.

Thermal decomposition of 21 in the presence of 27: A solution of **21** (0.64 g, 0.88 mmol) and **26** (0.24 g, 1.28 mmol) in toluene (5 mL) was stirred at 80 °C for 5.5 h. Evaporation to dryness and chromatography (silica gel, dichloromethane/pentane 4:1) gave **23** (0.30 g, 48 %) as a yellow solid.

Synthesis of complex 28: A solution of complex **1** (0.64 g, 1.0 mmol) and a fivefold excess of complex **27** in toluene was heated at 120 °C for 3 h. Excess **27** was separated from the product by chromatography (hexane). Elution with hexane/dichloromethane 4:1 followed by crystallization from hexane gave **28** (0.16 g, 17 %) as colorless crystals. M.p. 110 – 111 °C; ^{31}P NMR ($CDCl_3$): $\delta = -89.5$ (d, ^2J(P,P) = 16 Hz, ^1J(W,P) = 262 Hz; phosphirane-P), 41.2 (d, ^2J(P,P) = 16 Hz, ^1J(W,P) = 231 Hz; phospholene-P); ^{1}H NMR ($CDCl_3$): $\delta = 1.81$ (d, ^3J(P,H) = 17.6 Hz, 3H; PC=CCH$_3$), 2.16 (s, 3H; PCCH$_3$), 2.41 (dd, ^2J(P,H) = 7.1 Hz, ^2J(P,H) = 17.1 Hz, 1H; C-CH), 5.72 (d, ^2J(P,H) = 35.1 Hz, 1H; C=CH), 6.4 – 7.3 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 18.5$ (d, ^2J(P,C) = 11.4 Hz; PC*C*H$_3$), 20.2 (dd, ^3J(P,C) = 7.2 Hz, ^3J(P,C) = 1.9 Hz; PC=C*C*H$_3$), 36.2 (dd, ^1J(P,C) = 26.8 Hz, ^1J(P,C) = 21.7 Hz; P*C*P), 49.5 (dd, ^{1+2}J(P,C) = 16.9 Hz, ^2J(P,C) = 4.3 Hz; P*C*CH$_3$), 120.4 (dd, ^1J(P,C) = 40.7 Hz, ^3J(P,C) = 2.7 Hz; C=*C*H), 127.7 – 131.8 (m; Ar), 129.4 (dd, ^1J(P,C) = 25.6 Hz, ^3J(P,C) = 3.5 Hz; *ipso*-Ph), 136.9 (dd, ^1J(P,C) = 40.7 Hz, ^3J(P,C) = 2.7 Hz; *ipso*-Ph), 150.9 (dd, ^2J(P,C) = 7.7 Hz, ^2J(P,C) = 5.6 Hz; C=*C*CH$_3$), 195.2 (d, ^2J(P,C) = 7.9 Hz, CO$_{eq}$),196.5 (d, ^2J(P,C) = 6.7 Hz, CO$_{eq}$), 197.6 (d, ^2J(P,C) = 31.6 Hz, CO$_{ax}$), 200.2 (d, ^2J(P,C) = 20.3 Hz, CO$_{ax}$); elemental analysis calcd (%) for $C_{28}H_{18}P_2W_2O_{10}$: C 35.62, H 1.92; found: C 35.64, H 1.93.

Crystal structure determinations: X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode ($Mo_{K\alpha}$, λ = 0.71073 Å) at a temperature of 150 K. The structures were solved with automated Patterson methods with the program DIRDIF 97[26] and refined with the program SHELXL 97[27] against F^2 for all reflections. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON.[28]

Complex 13: $C_{40}H_{38}MoO_{12}P_2$, *Fw* = 868.58, yellow needle, 0.60 × 0.15 × 0.12 mm^3, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.0822(1)$, $b = 13.2106(1)$, $c = 25.2055(2)$ Å, $V = 4023.13(6)$ Å^3, $Z = 4$, $\rho = 1.434$ g cm^{-3}. Of the 74068 reflections measured, 9238 were unique ($R_{int} = 0.068$). The absorption correction was based on multiple measured reflections (program PLATON,[28] routine MULABS, $\mu = 0.47$ mm^{-1}, 0.80 – 0.95 transmission), 648 refined parameters, no restraints. Flack *x* parameter: −0.031(16). *R* values [$I > 2\sigma(I)$]: $R1 = 0.0253$, w$R2 = 0.0524$. *R* values [all refl.]: $R1 = 0.0337$, w$R2 = 0.0548$. GoF = 1.036. Residual electron density between −0.26 and 0.41 e Å^3.

Complex 18: $C_{22}H_{20}MoO_4P_2$, Fw = 506.26, colorless cube, 0.48 × 0.48 × 0.42 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 9.6689(1)$, $b = 13.4545(2)$, $c = 18.6736(2)$ Å, $\beta = 115.8894(6)°$, $V = 2185.45(5)$ Å^3, $Z = 4$, $\rho = 1.539$ g cm^{-3}. Of the 36380 reflections measured, 4996 were unique ($R_{int} = 0.046$). The absorption correction was based on multiple measured reflections (program PLATON,[28] routine MULABS, $\mu = 0.77$ mm^{-1}, 0.58 – 0.68 transmission), 342 refined parameters, no restraints. *R* values [$I > 2\sigma(I)$]: $R1 = 0.0240$, w$R2 = 0.0619$. *R* values [all refl.]: $R1 = 0.0248$, w$R2 = 0.0623$. GoF = 1.247. Residual electron density between −0.43 and 0.34 e Å^3.

Complex 28: $C_{28}H_{18}O_{10}P_2W_2$, *Fw* = 944.06, colorless block, 0.60 × 0.39 × 0.30 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 10.8278(1)$, $b = 12.1630(1)$, $c = 24.1488(2)$ Å, $\beta = 106.4655(3)°$, $V = 3049.94(5)$ Å^3, $Z = 4$, $\rho = 2.056$ g cm^{-3}. Of the 44378 reflections measured, 6973 were unique ($R_{int} = 0.067$). The absorption correction was based on multiple measured reflections (program PLATON,[28] routine MULABS, $\mu = 7.70$ mm^{-1}, 0.05 – 0.09 transmission), 389 refined parameters, no restraints. *R* values [$I > 2\sigma(I)$]: $R1 = 0.0257$, w$R2 = 0.0630$. *R* values [all refl.]: $R1 = 0.0285$, w$R2 = 0.0641$. GoF = 1.148. Residual electron density between −2.17 and 1.35 e Å^3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-172780 (complex **13**), 172781 (complex **18**), and 172782 (complex **28**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax. (+44) 1223-336-033; e-mail: deposit@ccdc.am.ac.uk).

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