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Notes

Phosphaspiropentene as a Transient Intermediate

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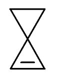
Summary: A phosphaspiropentene is the plausible kinetic product from the addition of dichlorocarbene to a phosphatriafulvene, which rearranges to a novel P-substituted triafulvene. The calculated barrier of 18.6 kcal mol^{-1} *for this process is consistent with the temperature of −40 °C at which this reaction proceeds.*

Introduction

Spiro-connected cycloalkenes exhibit intriguing bonding and electronic properties due to spiroconjugation.[1] Although the smallest of these highly strained hydrocarbons, spiropentene (**1**)[2] and spiropentadiene (**2**),[3] have been reported, spirenes with heteroatoms are extremely rare. Only recently, the thermally stable spiropentasiladiene **3** was reported.[4] Examples with other heteroatoms are limited to 1-oxaspiropent-4-enes, including the parent **4**,[5] and 1-azaspiropent-1-ene **5**,[6] but none with a phosphorus atom are known other than the 1-aza-2-phosphaspiro[2.2]pentene **6**, which may be a transient in the formation of 1*H*-2-iminophosphetes.[7] In contrast, P-containing spiranes carrying a transition-metal complex, e.g. the phosphaspiropentane **7**,[8] are stable, which is highlighted for the extended arrays[9] by a phospha[7]triangulane that consists of seven spiro-connected three-membered rings and has a melting point above 150 °C.[10]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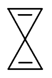
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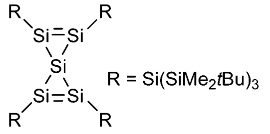

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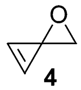

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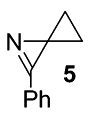

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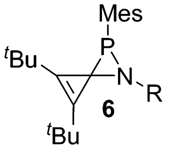

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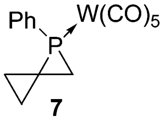

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Results and Discussion

Can a transition-metal complex likewise stabilize a P-containing spirene? To explore this, we examine the chemistry of 1-phosphaspiropent-4-ene. Access to this compound can be envisioned by addition of dichlorocarbene, generated in situ from *t*-BuOK/$CHCl_3$,[11] to the exocyclic P=C bond[12] of the phosphatriafulvene complex **8**[13] (0 °C, pentane). This reaction yielded, instead, the novel P-substituted triafulvene **10** (95%, colorless crystals) and showed no trace of phosphaspiropentene **9**, not even by ^{31}P NMR monitoring of the reaction at −40 °C (Scheme 1). Triafulvene **10** has distinctive resonances at $\delta(^{31}P)$ 110.0 (^1J(P,W) = 282.7 Hz) and $\delta(^{13}C)$ 86.6 (^1J(C,P) = 52.5 Hz), 135.2 (d, ^2J(C,P) = 9 Hz), 146.0 (s), and 147.4 (^3J(C,P) = 6.4 Hz).[14] P−C bond rotation of the mesityl group is hindered, causing a broad signal

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(1) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311−365.

(2) (a) Bloch, R.; Denis, J. M. *Angew. Chem.* **1980**, *92*, 969−970; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928−929. (b) Irngartinger, H.; Gries, S. *Angew. Chem.* **1991**, *103*, 595−596; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 565−566. (c) Wade, P. A.; Kondracki, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1263−1264.

(3) (a) Billups, W. E.; Haley, M. H. *J. Am. Chem. Soc.* **1991**, *113*, 5084−5085. (b) Saini, R. K.; Litosh, V. A.; Daniels, A. D.; Billups, W. E. *Tetrahedron Lett.* **1999**, *40*, 6157−6158.

(4) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504−506.

(5) (a) Billups, W. E.; Litosh, V. A.; Saini, R. K.; Daniels, A. D. *Org. Lett.* **1999**, *1*, 115−116. (b) Bickers, P. T.; Halton, B.; Kay, A. J.; Northcote, P. T. *Aust. J. Chem.* **1999**, *52*, 647−652. (c) Halton, B.; Cooney, M. J.; Wong, H. *J. Am. Chem. Soc.* **1994**, *116*, 11574−11575.

(6) (a) Irngartinger, H.; Gries, S. *Chem. Ber.* **1992**, *125*, 2513−2515. (b) A 1,2-diazaspiro[2.2]pent-1-ene was also reported: Patent, Bergwerksverband G.m.b.H., GB 1097238, 1965.

(7) Eisfeld, W.; Slany, M.; Bergsträsser, U.; Regitz, M. *Tetrahedron Lett.* **1994**, *35*, 1527−1530.

(8) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786−6790.

(9) Slootweg, J. C.; de Kanter, F. J. J.; Schakel, M.; Lutz, M.; Spek, A. L.; Kozhushkov, S. I.; de Meijere, A.; Lammertsma, K. *Chem., Eur. J.*, in press.

(10) Slootweg, J. C.; Schakel, M.; de Kanter, F. J. J.; Ehlers, A. W.; Kozhushkov, S. I.; de Meijere, A.; Lutz, M.; Spek, A. L.; Lammertsma, K. *J. Am. Chem. Soc.* **2004**, *126*, 3050−3051.

(11) Doering, W. v. E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162−6165.

(12) Yoshifuji, M.; Toyota, K.; Yoshimura, H.; Hirotsu, K.; Okamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 124−125 and references therein.

(13) Fuchs, E.; Breit, B.; Heydt, H.; Schoeller, W.; Busch, T.; Krüger, C.; Betz, P.; Regitz, M. *Chem. Ber.* **1991**, *124*, 2843−2855.

10.1021/om050530+ CCC: $30.25

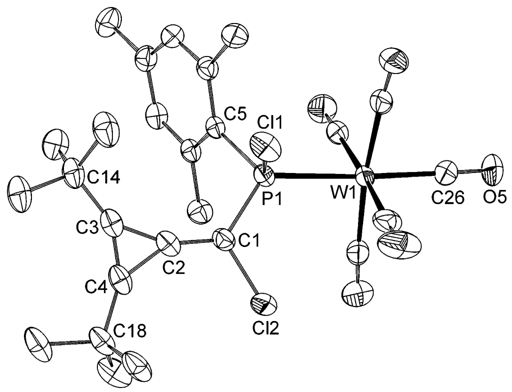
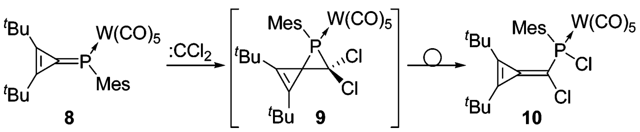
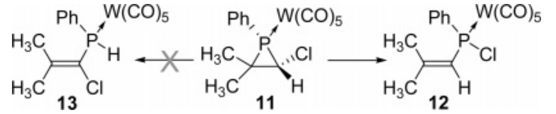


Figure 1. Displacement ellipsoid plot of **10** with ellipsoids drawn at the 50% probability level. Hydrogen atoms and the pentane solvent molecule are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): W1−P1 = 2.4987(7), Cl1−P1 = 2.0920(10), Cl2−C1 = 1.774(3), P1−C1 = 1.782(3), P1−C5 = 1.837(3), C1−C2 = 1.331(4), C2−C3 = 1.433(4), C2−C4 = 1.425(4), C3−C4 = 1.331(4); Cl2−C1−P1 = 115.04(15), C2−C3−C4 = 62.0(2), C3−C2−C4 = 55.49(19), C2−C4−C3 = 62.5(2); C3−C2−C1−P1 = −1.4(8).

Scheme 1. Synthesis of Triafulvene 10



Scheme 2. Rearrangements of Phosphirane 11



at δ(^{1}H, 293 K) 2.54 for the *o*-methyl groups that narrows at higher temperatures. The single-crystal X-ray structure (Figure 1) shows a shortened P−C1 bond (1.782(3) Å) and the cyclopropene ring being nearly coplanar with the Cl2−C1−P1 plane with a C3−C2−C1−P1 torsion angle of −1.4(8)°. Normal C=C bonds (C1−C2 = 1.331(4) Å, C3−C4 = 1.331(4) Å) indicate a diminished π delocalization, which is confirmed by the calculated NICS value of only −21.4, which is considerably less negative than that of cyclopropene (−28.4).

Is phosphaspiropentene **9** an intermediate in the formation of **10**? Such a rearrangement does convert the phosphirane complex **11** into **12** (Scheme 2), but at the much higher temperature of 110 °C.[15] We examine both processes using theoretical methods.

A large barrier of 71.3 kcal mol^{-1} (B3LYP/6-31G**) has been reported for converting the parent **11′** into **12′** (H for Me, Ph; no W(CO)$_5$) by P−C bond cleavage with a concurrent Cl shift from C to P,[16] which, of course, does not comply with the experimental observations,[15] nor does the calculated favored H shift that would give **13**. Clearly, the transition-metal group has a major influence, which we substantiate using BP86/6-31G**-(LANL2DZ) calculations.[17]

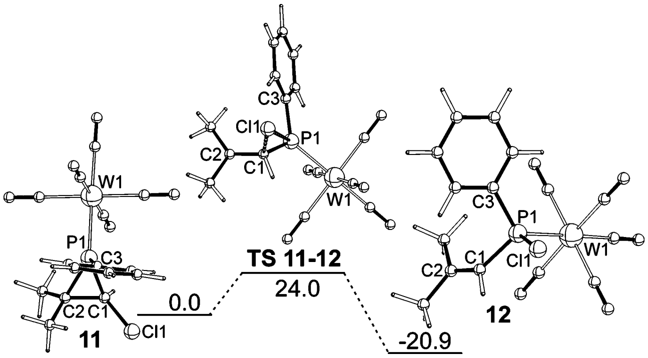


Figure 2. Relative BP86/6-31G** (LANL2DZ for W) energies (ZPE corrected, in kcal mol^{-1}) for the conversion of **11** into **12**. Selected bond lengths (Å) of **11**: W1−P1 = 2.539, P1−C1 = 1.877, P1−C2 = 1.909, P1−C3 = 1.834, C1−Cl1 = 1.785, C1−C2 = 1.539. Selected bond lengths (Å) of **TS***anti*Cl-shift (**TS11** → **12**): W1−P1 = 2.475, P1−Cl1 = 3.508, P1−C1 = 1.782, P1−C2 = 2.751, P1−C3 = 1.806, C1−Cl1 = 2.313, C1−C2 = 1.418. Selected bond lengths (Å) of **12**: W1−P1 = 2.527, P1−Cl1 = 2.133, P1−C1 = 1.832, P1−C3 = 1.846, C1−C2 = 1.356.

Adding the singlet phosphinidene PhP=W(CO)$_5$ to 1-chloro-2-methylpropene gives **11**, likely by a barrier-free non-least-motion trajectory,[18] with less exothermicity (23.0 kcal mol^{-1}) than for the parent ethylene (35.9 kcal mol^{-1}),[19] due to the reduced nucleophilicity of 1-chloro-2-methylpropene. Converting structure **11** in a single step to the 20.9 kcal mol^{-1} more stable vinylchlorophosphine **12**, in which the chloride anti to the P−W(CO)$_5$ group migrates to phosphorus, requires a 24.0 kcal mol^{-1} barrier to be overcome (Figure 2). Converting phosphirane **11** into vinylphosphine **13**, by migrating H instead of Cl, has only a marginal exothermicity (3.2 kcal mol^{-1}) and a higher barrier ($\Delta E^{\ddagger} = 39.1$ kcal mol^{-1}), suggesting this to be a less likely process, which concurs with the experimental observations. The barrier for rearranging **11** into **12** is comparable to the dissociation energy to regenerate PhP=W(CO)$_5$ and 1-chloro-2-methylpropene (23.0 kcal mol^{-1}), which clarifies the modest isolated yields for **11** (11%) and **12** (39%).[15]

In contrast, the analogous phosphirane **14** does not rearrange thermally and a Pd(PPh$_3$)$_4$-catalyzed reaction is needed (85 °C) to afford vinylchlorophosphine **15** (Scheme 3).[15] BP86/6-31G**(LANL2DZ) calculations reveal that converting structure **14** to the 18.6 kcal mol^{-1} more stable vinylchlorophosphine **15**, in which the

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[14] Schubert, H. H.; Stang, P. J. *J. Org. Chem.* **1984**, *49*, 5087−5090.

[15] Tran Huy, N. H.; Mathey, F. *J. Org. Chem.* **2000**, *65*, 652−654.

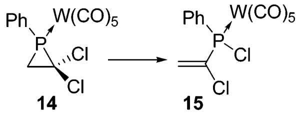
[16] Mátrai, J.; Dransfield, A.; Veszprémi, T.; Nguyen, M. T. *J. Org. Chem.* **2001**, *66*, 5671−5678.

[17] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 1998. See the Supporting Information.

[18] (a) Bulo, R. E.; Ehlers, A. W.; de Kanter, F. J. J.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K.; Wang, B. *Chem. Eur. J.* **2004**, *10*, 2732−2738. (b) Wit, J. B. M. Ph.D. Thesis, Vrije Universiteit, Amsterdam, The Netherlands, 2001, Chapter 7.

[19] 66 kcal mol^{-1} at B3LYP/6-31G*: Keating, A. E.; Merrigan, S. R.; Singleton, D. A.; Houk, K. N.; *J. Am. Chem. Soc.* **1999**, *121*, 3933−3938.

Scheme 3. Rearrangement of Phosphirane 14



chloride anti to the $\mathrm{P{-}W(CO)_5}$ group migrates to phosphorus,[20] is more demanding than the rearrangement of **11** and requires a 31.5 kcal mol^{-1} barrier to be overcome. This barrier is much higher than the dissociation energy needed to regenerate $\mathrm{Ph\text{-}P{=}W(CO)_5}$ and 1,1-dichloroethene (23.2 kcal mol^{-1}), explaining why this reaction does not proceed thermally.

Extending the calculations to the addition of $\mathrm{CCl_2}$ to phosphatriafulvene **8**″ (H for *t*Bu, Ph for mesityl; labeled ″) indicates a large exothermicity (52.3 kcal mol^{-1}) for the formation of phosphaspiropentene **9**″. We note that the addition of $\mathrm{PhP{=}W(CO)_5}$ to 3,3-dichlorotriafulvene, which would also give **9**″, is less exothermic (22.9 kcal mol^{-1}), because metal complexation reduces the reactivity of phosphinidenes.[21] Without the $\mathrm{W(CO)_5}$ group, $^1\mathrm{PPh}$ (A_1) adds to 3,3-dichlorotriafulvene with a reaction energy of −71.7 kcal mol^{-1}.

The single-step conversion of the $\mathrm{W(CO)_5}$-complexed phosphaspiropentene **9**″ into chlorophosphine **10**″ occurs more easily ($\Delta E^{\ddagger} = 18.6$ kcal mol^{-1}, $\Delta E = -24.7$ kcal mol^{-1}; Figure 3)[22] than the analogous **14** → **15** rearrangement ($\Delta E^{\ddagger} = 31.5$ kcal mol^{-1}), and is favored by 4.6 kcal mol^{-1} over the dissociation into $\mathrm{PhP{=}W(CO)_5}$ and 3,3-dichlorotriafulvene. The higher reactivity of **9**″ compared to that of **11** can be rationalized by the destabilization of the phospirene ring upon spiro fusion. Both the phosphorus[23] and the electron-withdrawing chloro substituents activate phosphirene **14** (NICS = −34.8) compared to the parent cyclopropene[24] (NICS = −42.8); additional spiro fusion in **9**″ further reduces the σ aromaticity (NICS = −26.9). This effect is also reflected by the elongated distal and proximal P−C bonds[9] (P1−C1 = 1.927 Å, P1−C2 = 1.866 Å) as compared to the corresponding bond lengths of **14** (P1−C1 = 1.897 Å, P1−C2 = 1.847 Å) and phosphaspiropentane **7**[8] (experimental: P1−C1 = 1.855 Å, P1−C2 = 1.794 Å).

Conclusions

Phosphaspiropentene **9** is the plausible kinetic product that results from addition of dichlorocarbene to phosphatriafulvene **8**. The calculated barrier of 18.6 kcal mol^{-1} for rearrangement to the more stable P-substituted triafulvene **10** is consistent with the temperature of −40 °C at which the reaction proceeds. Currently, we are testing other carbenes to obtain the, as yet, elusive phosphaspiropentenes.

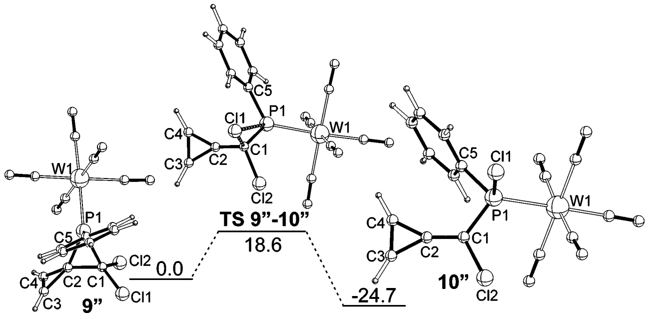


Figure 3. Relative BP86/6-31G** (LANL2DZ for W) energies (ZPE corrected, in kcal mol^{-1}) for the conversion of **9**″ into **10**″. Selected bond lengths (Å) of **9**″: W1−P1 = 2.520, P1−C1 = 1.927, P1−C2 = 1.866, P1−C5 = 1.834, C1−Cl1 = 1.789, C1−Cl2 = 1.791, C1−C2 = 1.498, C2−C3 = 1.489, C2−C4 = 1.491, C3−C4 = 1.312. Selected bond lengths (Å) of **TS9**″**-10**″: W1−P1 = 2.497, P1−Cl1 = 3.525, P1−C1 = 1.810, P1−C2 = 2.536, P1−C5 = 1.826, C1−Cl1 = 2.239, C1−Cl2 = 1.783, C1−C2 = 1.416, C2−C3 = 1.426, C2−C4 = 1.420, C3−C4 = 1.344. Selected bond lengths (Å) of **10**″: W1−P1 = 2.517, P1−Cl1 = 2.141, P1−C1 = 1.814, P1−C5 = 1.854, C1−Cl2 = 1.771, C1−C2 = 1.350, C2−C3 = 1.442, C2−C4 = 1.438, C3−C4 = 1.335.

Experimental Section

Computations. All density functional theory calculations (BP86) were performed with the Gaussian98 suite of programs,[17] using the LANL2DZ basis and pseudopotentials for tungsten and the 6-31G** basis for all other atoms. The natures of all transition structures were confirmed with frequency calculations. Intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between reactant and product. The nucleus independent chemical shift[25] (NICS) values were calculated at the B3LYP/6-311G+(2p,d) level, leaving out the substituents.

General Considerations. NMR spectra were recorded on Bruker Advance 250 (^{31}P; 85% $\mathrm{H_3PO_4}$) and MSL 400 instruments (^{1}H, ^{13}C) and referenced internally to residual solvent resonances (^{1}H, δ 7.25 ppm ($\mathrm{CDCl_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$, 77.0 ppm ($\mathrm{CDCl_3}$)). The IR spectrum was recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and the high-resolution mass spectrum (HR-MS) was performed on a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV. The melting point of **10** was measured on a sample in an unsealed capillary and is uncorrected.

Synthesis of 10. $\mathrm{CHCl_3}$ (56 μL, 0.7 mmol) was added under nitrogen at 0 °C to a solution of **8**[13] (87 mg, 0.14 mmol) and *t*-BuOK (79 mg, 0.7 mmol) in dry pentane (3 mL). After additional stirring for 30 min at 0 °C and another 30 min at room temperature, the reaction mixture was filtered and concentrated and **10** could be obtained as colorless crystals in 95% yield (104 mg; =**10**·(pentane)) after crystallization at −20 °C. Characterization data for **10**: mp 100 °C dec; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (101.3 MHz, $\mathrm{CDCl_3}$, 293 K) δ 110.0 (^1J(P,W) = 282.7 Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{CDCl_3}$, 328 K) δ 20.5 (s; *p*-$C\mathrm{H_3}$-ArP), 24.5 (d, ^3J(C,P) = 5.4 Hz; *o*-$C\mathrm{H_3}$-ArP), 28.4 (s; $\mathrm{C(}C\mathrm{H_3)_3}$), 29.6 (s; $\mathrm{C(}C\mathrm{H_3)_3}$), 32.3 (s; $C\mathrm{(CH_3)_3}$), 32.4 (d, ^4J(C,P) = 0.8 Hz; $C\mathrm{(CH_3)_3}$), 86.6 (d, ^1J(C,P) = 52.5 Hz; =CCl), 131.4 (d, ^3J(C,P) = 7.3 Hz; *m*-ArP), 135.2 (d, ^2J(C,P) = 9 Hz; *o*-ArP), 135.2 (d, ^2J(C,P) = 9 Hz; C=CCl), 135.7 (d, ^1J(C,P) = 26.8 Hz; *ipso*-ArP), 139.9 (d, ^4J(C,P) = 1.5 Hz; *p*-ArP), 146.0 (s; =$C\mathrm{C(CH_3)_3}$), 147.4 (d, ^3J(C,P) = 6.4 Hz; =$C\mathrm{C(CH_3)_3}$), 196.8 (d, ^2J(C,P) = 7.3 Hz, ^1J(C,W) = 127.2 Hz; *cis*-CO), 200.3 (d, ^2J(C,P) = 31.1 Hz, ^1J(C,W) = 141.6 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $\mathrm{CDCl_3}$, 328 K) δ 0.86 (s, 9H; $\mathrm{C(C}H_3)_3$), 1.40 (s, 9H; $\mathrm{C(C}H_3)_3$),

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[20] The syn Cl shift is less favorable: $\Delta E^{\ddagger} = 41.1$ kcal mol^{-1}.

[21] Ehlers, A. W.; Baerends, E. J.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2831−2838.

[22] There are numerous examples of DFT overestimating activation barriers, e.g.: Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K.; Würthwein, E.-U.; Grimme, S. *Chem., Eur. J.* **2004**, *10*, 6468−6475.

[23] Li, Z.-H.; Moran, D.; Fan, K.-N.; Schleyer, P. v. R. *J. Phys. Chem. A* **2005**, *109*, 3711−3716.

[24] (a) Dewar, M. J. S. *Bull Soc. Chim. Belg.* **1979**, *88*, 957−967. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669−682. (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800−3810. (d) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467−7477.

[25] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

2.25 (s, 3H; *p*-CH_3-ArP), 2.54 (br s, 6H; *o*-CH_3-ArP), 6.84 (d, ^4J(H,P) = 4.2 Hz, 2H; *m*-ArP); IR (KBr) ν 1939 (s/br, CO_{eq}), 2074 cm^{-1} (w, CO_{ax}); MS (EI, 70 eV) *m/z* (%) 706 (0.5) $[M]^+$, 671 (0.5) $[M - Cl]^+$, 566 (10) $[M - 5CO]^+$; HR-MS *m/z* calcd for $[M - 5CO]^+$ 566.0893, found 566.0900.

Crystal Structure Determination of Compound 10. Crystal data: $C_{26}H_{29}Cl_2O_5PW\cdot0.5C_5H_{12}$, fw 743.28, colorless needle, 0.42 × 0.24 × 0.06 mm^3; monoclinic crystal system, space group *C*2/*c* (No. 15); cell parameters $a = 19.0406(2)$ Å, $b = 18.9032(2)$ Å, $c = 19.5695(2)$ Å, $\beta = 117.0955(5)°$, $V = 6270.57(11)$ Å^3. $Z = 8$, $\rho = 1.575$ g/cm^3. A total of 71 511 reflections were measured up to $((\sin \theta)/\lambda) = 0.65$ Å^{-1} on a Nonius KappaCCD instrument with rotating anode (graphite monochromator, Mo Kα, $\lambda = 0.710\ 73$ Å) at a temperature of 150 K. An analytical absorption correction was applied ($\mu = 3.94$ mm^{-1}, 0.27−0.72 correction range). There were 7212 unique reflections ($R_{int} = 0.049$). The structure was solved with automated Patterson methods with the program DIRDIF99[26] and refined with the program SHELXL97[27] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and were refined as rigid groups. The pentane solvent molecule is located on a 2-fold axis in the unit cell. There were 348 refined parameters, with 20 restraints. R ($I > 2\sigma(I)$): R1 = 0.0237, wR2 = 0.0545. R (all reflections): R1 = 0.0321, wR2 = 0.0586. GOF = 1.065. The residual electron density was between −1.52 and 0.94 e/Å^3. The drawings, geometry calculations, and checks for higher symmetry were performed with the program PLATON.[28]

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Supporting Information Available: Tables giving Cartesian coordinates (Å) and energies (au) of all stationary points and a CIF file giving crystallographic data for compound **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] 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, Nijmegen, The Netherlands, 1999.

[27] Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997.

[28] Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.