Phosphorus Chemistry

DOI: 10.1002/anie.200804432

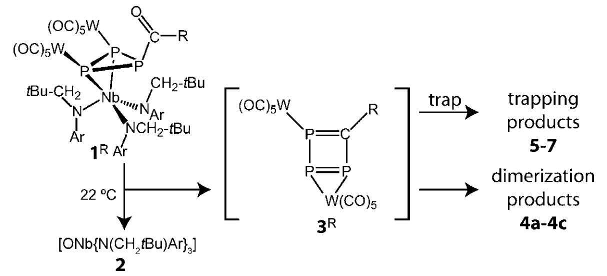
Tetraphosphabenzenes Obtained via a Triphosphacyclobutadiene Intermediate**

*Nicholas A. Piro and Christopher C. Cummins**

The ability to replace "RC" units in organic motifs with isolobal phosphorus atoms has led to phosphorus being dubbed the "carbon copy."[1] Yet while the all-phosphorus analogues of benzene and cyclobutadiene (the epitomes of aromaticity and antiaromaticity) have been considered theoretically,[2–5] they remain elusive. What do exist are a few examples of reduced P_6 and P_4 ligands complexed to one or more metal centers.[6–9] Diphosphacyclobutadiene and valence isomers of triphosphabenzene have been accessed through metal-mediated oligomerization of phosphaalkynes,[10–12] and two related reactions generate triphosphacyclobutadiene ligands π-complexed to reducing metal centers.[13,14] There is also one example of a highly distorted $P_4(CtBu)_2$ ligand complexed between two rhodium centers,[15] and a diradical valence isomer of a tetraphosphabenzene has been reported to contain multiple one-electron bonds.[16] Exploiting the chemistry of P_2-derived *cyclo*-P_3 complexes,[17] we now describe neutral triphosphacyclobutadiene intermediates and isomers of tetraphosphabenzene that are stabilized only by mild {$W(CO)_5$} substituents.[18]

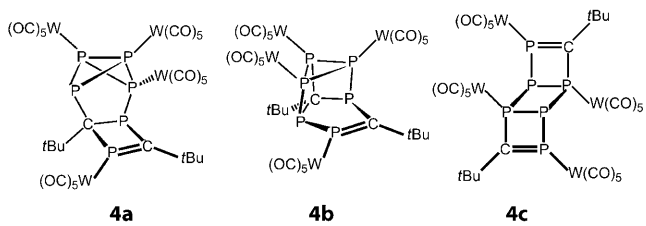
Acylation of the {$W(CO)_5$}-coordinated *cyclo*-P_3 complex $[\{(OC)_5W\}_2P_3Nb\{N(CH_2tBu)Ar\}_3]^-$ with either pivaloyl chloride or 1-adamantanecarbonyl chloride affords the triphosphirene complexes $[\{(OC)_5W\}_2RC(O)P_3Nb\{N(CH_2tBu)Ar\}_3]$, $\mathbf{1}^R$ (Ar = 3,5-$Me_2C_6H_3$, R = 1-adamantyl ($\mathbf{1}^{Ad}$), *tert*-butyl ($\mathbf{1}^{tBu}$)).[17] These complexes are thermally unstable toward deoxygenation of the acyl triphosphirene ligand to form $[ONb\{N(CH_2tBu)Ar\}_3]$ (**2**) and red precipitate of empirical formula $[RCP_3\{W(CO)_5\}_2]$ (Scheme 1). As a monomer, the species $[RCP_3\{W(CO)_5\}_2]$ ($\mathbf{3}^R$) could possess an RCP_3 core with either tetrahedrane or butadiene-like structure; the latter structure would be one RC unit away from the elusive planar P_4.

The poor solubility of the precipitate generated during the formation of **2** from $\mathbf{1}^{Ad}$ proved a hindrance to identifying the phosphorus-containing products. However, the *tert*-butyl



Scheme 1. Oxygen-atom transfer from an acyl triphosphirene ligand to the niobium center liberates the putative triphosphacyclobutadiene intermediate $\mathbf{3}^R$. One of several possible linkage isomers of $\mathbf{3}^R$ is drawn.

variant $\mathbf{1}^{tBu}$ produces a coproduct with increased solubility in various solvents, allowing for a more thorough characterization. ^{31}P NMR spectroscopic data acquired on the crude reaction mixture formed by stirring $\mathbf{1}^{tBu}$ for several hours at 22 °C indicated that a mixture of phosphorus-containing products had formed, though one major product was present. Single-crystal X-ray diffraction analyses performed on several small, red-orange crystals that were grown from CH_2Cl_2 solutions of the product mixture revealed three structurally distinct isomers, **4a–c** (Scheme 2).[19] All of these compounds



Scheme 2. Structures of identified dimerization products **4a–c**.

were dimers of the $[tBuCP_3\{W(CO)_5\}_2]$ unit, and their structures can be compared to those known for phosphaalkyne tetramers.[20,21] One fraction was isolated in approximately 30 % yield as a red powder that was insoluble in Et_2O and showed sparing solubility in CH_2Cl_2, and this red powder was subjected to an X-ray powder diffraction study. Powder diffraction patterns for **4a–c** were simulated on the basis of the single-crystal data, and these patterns were compared to the experimental patterns for the isolated compound. While two of the simulations showed a poor match to experiment, the simulated pattern for **4a** was in very good agreement with the diffraction pattern of the isolated powder (Figure 1; see Figure S2 in the Supporting Information for simulated

[*] N. A. Piro, Prof. Dr. C. C. Cummins
Department of Chemistry, Massachusetts Institute of Technology
77 Massachusetts Avenue, Room 6-435
Cambridge, MA 02139-4307 (USA)
Fax: (+1) 617-258-5700
E-mail: ccummins@mit.edu
Homepage: http://web.mit.edu/ccclab/

[**] We gratefully acknowledge the U.S. National Science Foundation for support through grant CHE-719157 and a predoctoral fellowship to N.A.P. We also thank Thermphos International for a donation of funds and supplies and Prof. David B. Collum (Cornell) for bringing spiro[2.4]-hepta-4,6-diene to our attention.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804432.

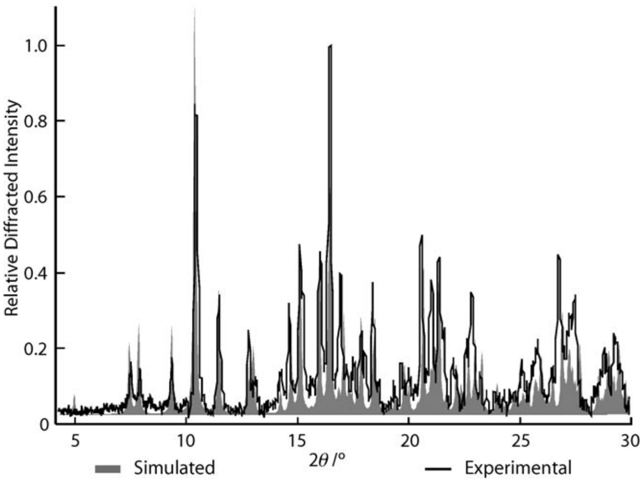


Figure 1. X-ray powder diffraction of **4a** confirmed its structural identity by comparison of simulated and experimental data.

patterns of **4b** and **4c**). Comparing the ^{31}P NMR spectrum of the crude reaction mixture to that of isolated **4a** further confirmed this species as the major product. Furthermore, the complex splitting pattern in the ^{31}P NMR spectrum was successfully simulated using the connectivity determined by X-ray diffraction (Figure S4, Supporting Information).[22] While the structural identity of the product originating from the fragmentation of $\mathbf{1}^{Ad}$ could not be definitively confirmed, on the basis of the data available from $\mathbf{1}^{tBu}$ it is assigned as one or more isomers of the dimer $[(AdCP_3\{W(CO)_5\}_2)_2]$.

The structures of **4a–c** suggest the intermediacy of the triphosphacyclobutadiene molecule $\mathbf{3}^{R}$, which is depicted as one of several possible linkage isomers in Scheme 1. To probe the chemistry of such an intermediate, we attempted to trap the reactive species $\mathbf{3}^{Ad}$ with suitable substrates. The platinum complex $[(Ph_3P)_2Pt(C_2H_4)]$ has been used successfully to trap units of P=P unsaturation with simple displacement of the ethylene molecule, but such reactivity was not found with intermediate $\mathbf{3}^{Ad}$.[23–27] Instead, a product incorporating the ethylene unit into the CP_3 framework, $[(Ph_3P)(OC)Pt\{P_3C(C_2H_4)Ad\}\{W(CO)_5\}_2]$ (**5**), was isolated in low yield and characterized by NMR spectroscopy and X-ray crystal structure determination.[28]

Seeking to trap the putative triphosphacyclobutadiene intermediate in a simple one-to-one reaction, we employed organic dienes that are known to react by [4+2]-cycloadditions with diphosphenes.[29–31] When $\mathbf{1}^{Ad}$ was allowed to fragment in the presence of either 1,3-cyclohexadiene or 2,3-dimethylbutadiene, mixtures of products were observed by ^{31}P NMR spectroscopy. Spiro[2.4]hepta-4,6-diene is known to be a particularly active Diels–Alder reagent,[32] and when **1** was allowed to fragment in the presence of this diene, one major product was observed by ^{31}P NMR spectroscopy. This product, $[C_7H_8(P_3CAd)\{W(CO)_5\}_2]$ (**6**), has resonances consistent with the desired trapping of the diphosphene functional group, while the phosphaalkene moiety (^{31}P NMR $\delta =$ 295 ppm) remains intact. Extraction of coproduct **2** with *n*-pentane and recrystallization of the remaining fraction from toluene affords compound **6**.[33] A single-crystal X-ray diffraction study revealed the stereochemistry of the product to be consistent with the prediction arrived at through consideration of steric and secondary orbital interactions: the π bonds of the diene/alkene interact with the four-membered ring, while the sterically protruding spiro group aligns opposite the ring (Figure 2).[18] This product demonstrates clean diphosphene-like reactivity for the triphosphacyclobutadiene intermediate.

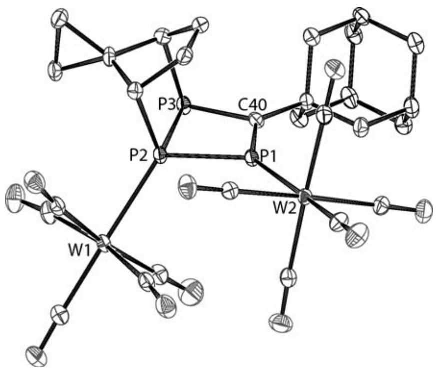


Figure 2. X-ray crystal structure of complex **6**. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C40 1.690(3), P1–P2 2.1969(11), P2–P3 2.2173(11), P3–C40 1.843(3), P1–W2 2.4515(8), P2–W1 2.5044(8); C40-P1-P2 89.02(11), P1-P2-P3 79.82(4), C40-P3-P2 84.66(11), P1-C40-P3 106.48(17).

The dimerization reactions of triphosphacyclobutadiene $\mathbf{3}^{R}$ that are observed when no trap is present in solution suggest that this intermediate can participate as both a dieneophile and as a diene partner in [4+2]-cycloaddition reactions, much as does cyclobutadiene itself.[18,34,35] If this is the case then it should be possible to trap $\mathbf{3}^{R}$ with a molecule containing a reactive π bond. 1-Adamantylphosphaalkyne was employed in this role because of its potential to yield the Dewar isomer of tetraphosphabenzene as a trapping product.[12,36] Gentle thermolysis of $\mathbf{1}^{Ad}$ and AdCP for 4 h at 35 °C in benzene affords one major product, as assayed by ^{31}P NMR spectroscopy. This product exhibits two coupled resonances in the ^{31}P NMR spectrum at $\delta = 248$ and -13 ppm. These data are consistent with the C_2-symmetric tetraphosphadewarbenzene $[(AdC)_2P_4\{W(CO)_5\}_2]$ (**7**, Figure 3a). This structure was confirmed by a single crystal X-ray diffraction study on an orange crystal of **7** grown from benzene solution (Figure 3b).

Upon prolonged light-exposure of solutions of **7**, isomerization takes place to provide **8**, which at 20 °C displays two broad resonances in the ^{31}P NMR spectrum at $\delta = +19$ and -108 ppm. This conversion can be accelerated by photolysis of **7** in THF with high-intensity broadband light to afford complete conversion to **8** in less than 20 min. An X-ray diffraction study performed on crystals grown from mixtures of **7** that had been exposed to ambient light revealed a benzvalene structure with a diphosphene moiety η^2-coordinated to one $\{W(CO)_5\}$ unit and η^1-coordinated to the second $\{W(CO)_5\}$ (Figure 3c). The two broad signals in the ^{31}P NMR spectrum of **8** can be attributed to a dynamic process in which the exchange of $\{W(CO)_5\}$ units between faces and termini of

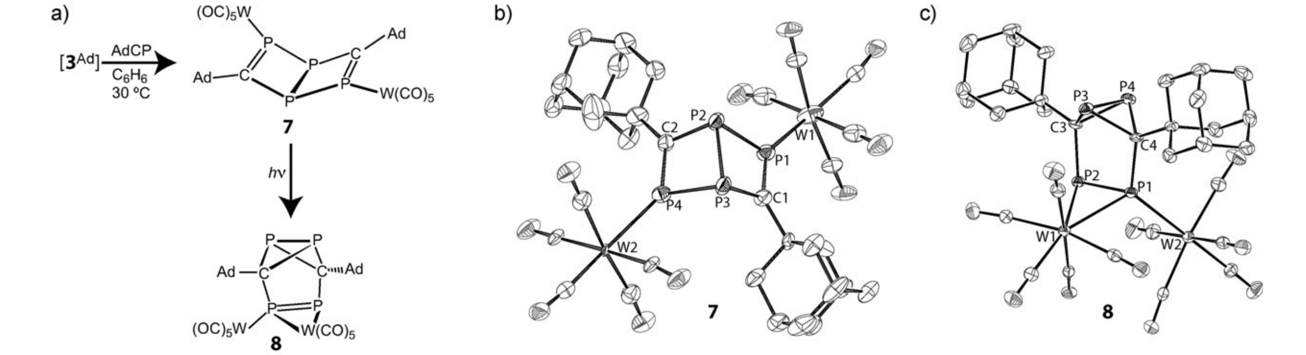
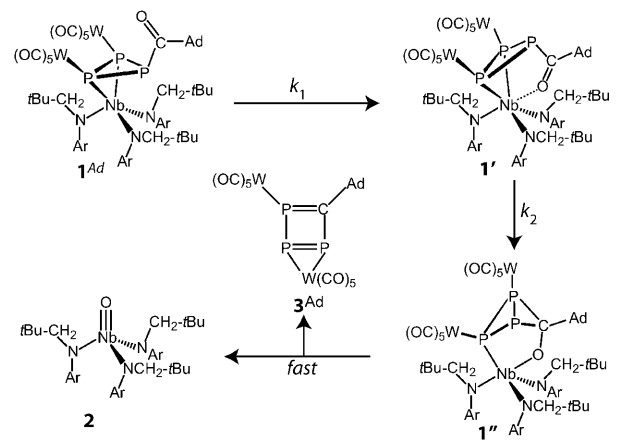


Figure 3. a) Synthesis of two valence isomers of tetraphosphabenzene supported by 2 equiv $\{W(CO)_5\}$. b), c) X-ray crystal structures of **7** and **8**. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **7**: P1–C1 1.71(1), P1–P2 2.197(5), P2–P3 2.220(5), P3–C1 1.83(1); P4-P3-C1 101.4(5), P1-C1-P3 104.8(6), P2-P1-C1 90.0(5). **8**: P1–P2 2.1047(15), P3–P4 2.1559(17), W(1)–P(1) 2.6269(11), W(1)–P(2) 2.6704(10), P1–W2 2.5807(11); C3-P3-C4 82.27(19), P3-C4-P4 70.15(15), C4-P1-P2 96.93(14), C3-P2-P1 95.16(14).

the diphosphene can equate pairs of P atoms. Upon cooling to −100 °C these two resonances resolve into four ($\delta = 37$ (d), 10 (br), −21 (d), −232 ppm (br)) with a doublet pair displaying strong coupling ($^1J_{PP} = 450$ Hz) that is consistent with P–P multiple bonding. This product can be seen as arising from intramolecular [2+2]-cycloaddition of the phosphaalkene moieties of **7** and subsequent radical rearrangements, and it is consistent with the "rule of five."[37] Such rearrangements have also been observed for monophosphadewarbenzenes.[38] The *Z*-diphosphene of **8** shows a short P–P distance of 2.1047(15) Å and angles of 96.93(14) and 95.16(14)°. It is remarkable that such a species is stabilized by only one π complexation and one σ complexation from the relatively mild $\{W(CO)_5\}$ unit.[39,40]

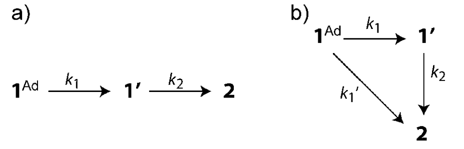
To investigate the mechanism by which **2** and $\mathbf{3}^{Ad}$ are generated from $\mathbf{1}^{Ad}$, the kinetics of this reaction were monitored by both ^{1}H and ^{31}P NMR spectroscopy. The decay of starting material **1** was found to follow clean first-order kinetics, but the growth of an intermediate was found to accompany production of **2**. This intermediate (**1′**) displays three ^{31}P environments and two *t*Bu environments of the anilide ligands in its NMR spectra. The ^{31}P resonances are a triplet ($J_{PP} = 175$ Hz) at $\delta = -4$ ppm and two broad resonances at $\delta = -28$ and −37 ppm. By introducing a ^{13}C label at the acyl carbon atom (C1) it was determined that in **1′**, C1 is attached only to the one phosphorus atom with a chemical shift of $\delta = -4$ ppm ($J_{CP} = 108$ Hz). Furthermore, the ^{13}C chemical shift for C1 in **1′** was found to shift downfield by 46 ppm relative to the starting material (from 213 to 259 ppm), consistent with Lewis acid activation of the carbonyl group,[41] leading to the proposed structure for **1′** that is shown in Scheme 3.

From **1′** we can envision attack by one of the niobium-bound phosphorus atoms on the Lewis acid activated carbonyl group to give **1″** with a structure that is poised to eliminate the triphosphacyclobutadiene $\mathbf{3}^{Ad}$ upon formation of **2** through a six-electron rearrangement with formation of the strong niobium oxo bond. Importantly, the same intermediate **1′** was observed in the presence of either AdCP or spiro[2.4]hepta-4,6-diene.



Scheme 3. Proposed mechanism for formation of transient triphosphacyclobutadiene $\mathbf{3}^{Ad}$ proceeding via the observed intermediate **1′**.

The decay of starting material $\mathbf{1}^{Ad}$ follows first-order exponential behavior, but the ratios of species $\mathbf{1}^{Ad}$, **1′**, and **2** did not fit the simple kinetic model shown in Scheme 4a. Rather, the data were better suited by a model in which there is a competitive process that proceeds without an observable intermediate with a rate constant $k_1' \approx k_1$, Scheme 4b (see the Supporting Information for details). It is possible that the coordination sites of the two $\{W(CO)_5\}$ units coupled to subtle conformational differences lead to two rates of rearrangement from structures analogous to **1′**.



Scheme 4. Kinetic scheme (b) provides a better fit to the time-dependent concentrations of $\mathbf{1}^{Ad}$, **1′**, and **2** than does the simpler model (a).

Herein we have described the first reactivity of a triphosphacyclobutadiene intermediate. The reactions observed suggest that this species can dimerize or serve as either a reactive *Z*-diphosphene or as a four-π-electron cycloaddition partner, depending on the reagents present. Such reactivity has led to the synthesis of the most phosphorus-rich congeners of benzene isomers reported, the Dewar and benzvalene isomers of tetraphosphabenzene. This chemistry was accessed by exploiting the thermodynamic driving force of strong niobium oxo bond formation to offset the energetic costs of high-energy small-molecule transient generation.[30,42,43]

Experimental Section

All manipulations were carried out under anhydrous and oxygen-free conditions. Full synthetic protocols and spectroscopic data for all compounds and kinetics experiments are presented in the Supporting Information. Details of the X-ray structure determinations are presented in the Supporting Information, Table 1S. CCDC 700883, 700884, 700885, 700886, and 700887 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6: Solid red $\mathbf{1}^{Ad}$ (195 mg, 0.125 mmol, 1 equiv) was dissolved in a THF solution (14 wt %, 2 g) of spiro[2.4]hepta-4,6-diene (280 mg, 24 equiv) and the solution was then diluted with THF to a total volume of 5 mL. The solution was stirred at 22 °C for 5 h, after which time the solution was bright yellow in color. The mixture was filtered through celite, and the filtrate was concentrated to dryness under dynamic vacuum. The resulting residue was suspended in pentane (4 mL) and cooled to −35 °C for 24 h to precipitate the product as a bright yellow powder, which was collected atop a sintered glass frit and washed with cold pentane (65 mg, 53 % yield). ^{31}P NMR (C_6D_6, 20 °C, 121.5 MHz): $\delta = 295.4$ (dd, $^1J_{PP} = 125$ Hz, $^2J_{PP} = 28$ Hz, $J_{PW} = 240$ Hz, C=P), 3.0 (dd, $^1J_{PP} = 156$ Hz, $^2J_{PP} = 28$ Hz, C=P-P-*P*), −24.9 ppm (dd, $^1J_{PP} = 156$ Hz, $^1J_{PP} = 125$ Hz, $J_{PW} = 210$ Hz, C=P-*P*-P).

7: Solid red $\mathbf{1}^{Ad}$ (360 mg, 0.230 mmol, 1 equiv) and solid colorless AdCP (83 mg, 0.46 mmol, 2 equiv) were mixed and then dissolved in benzene (10 mL) to give a deep red solution. The solution was heated to 35 °C for 3.5 h, after which time the orange mixture was filtered through celite and evaporated to dryness. Niobium oxo **2** was extracted from the orange residue with pentane (ca. 10 mL) and the remaining solid was collected on a frit and then washed with pentane (3 mL) and dried in vacuo to yield **7** as an orange powder (130 mg, 53 % yield). ^{31}P NMR (C_6D_6, 20 °C, 202.5 MHz): $\delta = 248.3$ (m, C=*P*, 2 P), −13.3 ppm (m, *P-P*, 2 P).

Received: September 8, 2008
Published online: December 19, 2008

Keywords: niobium · phosphabenzenes · phosphacyclobutadienes · phosphorus · triphosphirenes

[1] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**.
[2] M. Hofmann, P. von R. Schleyer, M. Regitz, *Eur. J. Org. Chem.* **1999**, 3291 – 3303.
[3] K. Kobayashi, H. Miura, S. Nagase, *THEOCHEM* **1994**, *311*, 69 – 77.
[4] G. Ohanessian, P. C. Hiberty, J. M. Lefour, J. P. Flament, S. S. Shaik, *Inorg. Chem.* **1988**, *27*, 2219 – 2224.
[5] S. Nagase, K. Ito, *Chem. Phys. Lett.* **1986**, *126*, 43 – 47.
[6] O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *Angew. Chem.* **1985**, *97*, 358 – 359; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 351 – 353.
[7] O. J. Scherer, J. Vondung, G. Wolmershäuser, *Angew. Chem.* **1989**, *101*, 1395 – 1397; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355 – 1357.
[8] O. J. Scherer, R. Winter, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1993**, *619*, 827 – 835.
[9] M. E. Barr, S. K. Smith, B. Spencer, L. F. Dahl, *Organometallics* **1991**, *10*, 3983 – 3991.
[10] P. Binger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, S. Leininger, *Angew. Chem.* **1995**, *107*, 2411 – 2414; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227 – 2230.
[11] R. Gleiter, H. Lange, P. Binger, J. Stannek, C. Krüger, J. Bruckmann, U. Zenneck, S. Kummer, *Eur. J. Inorg. Chem.* **1998**, 1619 – 1621.
[12] A. Mack, S. Danner, U. Bergsträßer, H. Heydt, M. Regitz, *J. Organomet. Chem.* **2002**, *643–644*, 409 – 415.
[13] P. Binger, S. Leininger, K. Günther, U. Bergsträßer, *Chem. Ber.* **1997**, *130*, 1491 – 1494.
[14] M. Scheer, J. Krug, *Z. Anorg. Allg. Chem.* **1998**, *624*, 399 – 405.
[15] P. Binger, B. Biedenbach, R. Mynott, R. Benn, A. Rufińska, P. Betz, C. Krüger, *J. Chem. Soc. Dalton Trans.* **1990**, 1771 – 1777.
[16] Y. Canac, D. Bourissou, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Science* **1998**, *279*, 2080 – 2082.
[17] N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9524 – 9535.
[18] It is noteworthy, however, that Lewis acids have been reported to affect the reaction mechanisms and product distributions of reactive diphosphacyclobutadiene intermediates, and the two {$W(CO)_5$} moieties may have similar effects: C. Fish, M. Green, R. J. Kilby, J. E. McGrady, D. A. Pantazis, C. A. Russell, *Dalton Trans.* **2008**, 3753 – 3758.
[19] Unit cell parameters and connectivity could be determined from all structures, but on two of the three full refinement was not possible owing to very high residual electron density or low-resolution data.
[20] T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter, M. Regitz, *Angew. Chem.* **1989**, *101*, 1035 – 1037; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1013 – 1014.
[21] B. Geißler, S. Barth, U. Bergsträßer, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. v. R. Schleyer, M. Regitz, *Angew. Chem.* **1995**, *107*, 485 – 488; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484 – 487.
[22] P. H. M. Budzelaar, *gNMR*, v. 5.1.
[23] R. Pietschnig, E. Niecke, *Organometallics* **1996**, *15*, 891 – 893.
[24] P. Jutzi, U. Meyer, S. Opiela, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1992**, *439*, 279 – 301.
[25] I. G. Phillips, R. G. Ball, R. G. Cavell, *Inorg. Chem.* **1992**, *31*, 1633 – 1641.
[26] J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, J. F. Nixon, *J. Chem. Soc. Chem. Commun.* **1981**, 1141 – 1143.
[27] N. A. Piro, C. C. Cummins, *Inorg. Chem.* **2007**, *46*, 7387 – 7393.
[28] See the Supporting Information for a structure and details on compound **5**.
[29] L. Weber, *Chem. Rev.* **1992**, *92*, 1839 – 1906.
[30] N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, *313*, 1276 – 1279.
[31] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182 – 7185; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052 – 7055.
[32] L. G. Menchikov, O. M. Nefedov, *Russ. Chem. Rev.* **1994**, *63*, 449 – 469.
[33] Compound **6** could not be completely separated from a second minor product believed to be an isomer of **6**.
[34] L. Watts, J. D. Fitzpatrick, R. Pettit, *J. Am. Chem. Soc.* **1965**, *87*, 3253 – 3254.

[35] L. Watts, J. D. Fitzpatrick, R. Pettit, *J. Am. Chem. Soc.* **1966**, *88*, 623–624.
[36] J. Fink, W. Rösch, U.-J. Vogelbacher, M. Regitz, *Angew. Chem.* **1986**, *98*, 265–266; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 280–282.
[37] N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito, CA, **1991**, p. 429.
[38] K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink, M. Regitz, *Angew. Chem.* **1987**, *99*, 67–68; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 85–86.
[39] M. Yoshifuji, N. Shinohara, K. Toyota, *Tetrahedron Lett.* **1996**, *37*, 7815–7818.
[40] G. Huttner, J. Borm, L. Zsolnai, *J. Organomet. Chem.* **1986**, *304*, 309–321.
[41] D. H. Barich, J. B. Nicholas, T. Xu, J. F. Haw, *J. Am. Chem. Soc.* **1998**, *120*, 12342–12350.
[42] J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2004**, *126*, 13916–13917.
[43] B. M. Cossairt, C. C. Cummins, *Angew. Chem.* **2008**, *120*, 8995–8998; *Angew. Chem. Int. Ed.* **2008**, *47*, 8863–8866.

