Pnicogen Complexes

DOI: 10.1002/anie.201102361

Formation of *cyclo*-E_4^{2-} Units ($E_4 = P_4$, As_4, AsP_3) by a Complex with a Cr–Cr Quintuple Bond**

Christoph Schwarzmaier, Awal Noor, Germund Glatz, Manfred Zabel, Alexey Y. Timoshkin, Brandi M. Cossairt, Christopher C. Cummins, Rhett Kempe, and Manfred Scheer**

In memory of Kurt Dehnicke

Bimetallic species with formal bond orders higher than four have been known as chemical curiosities for decades.[1] Molecules like Cr_2 had been stabilized in inert matrices at low temperature[2] or generated in the gas phase as a short-lived intermediate by pulsed photolysis of chromium hexacarbonyl[3] and by vaporization of the metal.[4] Unfortunately, the stability of the multiply bonded dimer only under extreme conditions restricts its use in chemistry. Recently, Power and co-workers synthesized the first stable molecule with a formal bond order of five based on aryl ligands[5] and the groups of Theopold,[6] Tsai,[7] and Kempe[8] synthesized N-ligand stabilized coordination compounds with such high bond orders and ultra-short metal–metal bonds. Stimulated by these findings immense effort has been directed towards the understanding of very high (formal) bond orders.[9] The new chance is to enable quintuple bond reactivity studies, and thus to illustrate the use of these multiply bonded bimetallic platforms for small-molecule activation, catalysis etc.[10] Until now only very few quintuple bond reactivity studies have appeared.[11]

Activation of white phosphorus by main group elements[12] and transition metals[13] is an active research area in chemistry. However, bimetallic activation by transition metals is very rare. Usually, an addition occurs in a stepwise sequence at one and then afterwards at another vertex of P_4 to give a bimetallic complex with an intact P_4 tetrahedron.[14] Moreover, $[\{Cp^RFe(CO)_2\}_2]$ ($Cp^R = \eta^5$-$C_5H_2tBu_3$, η^5-$C_5H_3tBu_2$) is known to react in a cothermolysis or photolysis with P_4 by opening one P–P bond to result in a butterfly-like P_4^{2-} moiety coordinated by two $\{Cp^RFe(CO)_2\}$ units.[15] In a different approach under reducing conditions Fryzuk et al. showed the formation of a *cyclo*-P_4^{4-} unit with almost equal P–P bond lengths of 2.241(1) Å doubly capped by two Zr complex fragments.[16] Furthermore, a similar structured U complex was reported in the literature.[13a] Similar examples for yellow arsenic As_4 do not exist. These P_4 squares are reminiscent of the dianionic aromatic Zintl phases P_4^{2-},[17] for which also the arsenic species is known.[18] For both types in transition-metal chemistry only monometallic examples of Nb and Ta are known, in which the E_4^{2-} unit reveals a kitelike distortion.[19] Preliminary investigations on the AsP_3 molecule[20a] revealed its similarity to P_4. It can either be coordinated as an intact tetrahedron or become activated by transition-metal and main-group compounds[20] to yield products containing an AsP_3^{2-} butterfly moiety. Complexes with a *cyclo*-AsP_3^{2-} ligand are unknown so far. Here, we report on a novel bimetallic activation of P_4, which could also be applied for the first time to AsP_3 and As_4. The products are bimetallic complexes with *cyclo*-E_4^{2-} ligands as novel terminal *cyclo*-E_4-decks.

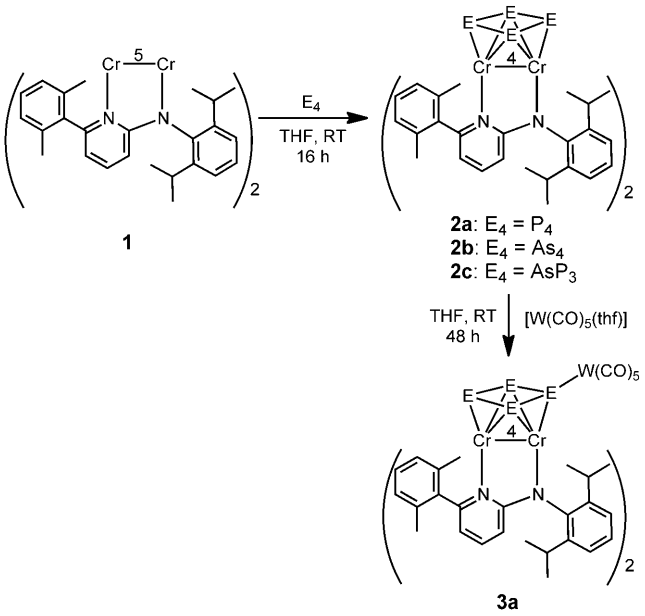
The Cr complex **1**[11a] reacts with white phosphorus, AsP_3, and yellow arsenic, respectively, already at room temperature in THF to afford **2a–c** selectively in high yields within 16 h (**2a**: 97%; **2b**: 68%; **2c**: 69%; Scheme 1). The crystal structure analysis of the isostructural complexes **2a** and **2b** show nearly square-planar geometry for the η^1- and η^2-coordinated P_4 and As_4 units (Figure 1).[23] The P1–P4 (2.176(1) Å), P1–P2 (2.179(2) Å), P2–P3 (2.168(1) Å), and P3–P4 (2.183(2) Å) bonds in **2a** are shorter than that of a P–P single bond.[21] The bond lengths between the bridging P atoms and Cr (av 2.6826 Å and av 2.6820 Å) are larger than the terminal P–Cr bonds (P2–Cr2 2.379(1) Å and P4–Cr1 2.362(1) Å).

Similar structural behavior is observed in **2b** with As1–As2 (2.398(1) Å), As1–As4 (2.405(1) Å), As2–As3 (2.406(1) Å), and As3–As4 (2.388(1) Å) bond lengths, which are shorter than a As–As single bond (2.435 Å determined by electron diffraction[22a] and 2.4372 Å specified by DFT calculations[22b]). Thus, the coordinated P_4 and As_4 units in **2a** and **2b** can be viewed as rarely known *cyclo*-P_4^{2-} and *cyclo*-As_4^{2-} ligands.[17,18] The short Cr–Cr distances of 1.8664(8) and 1.863(2) Å, respectively, in these compounds

[*] Dipl. Chem. C. Schwarzmaier,[+] Dr. M. Zabel, Prof. Dr. M. Scheer
Institute of Inorganic Chemistry, University of Regensburg
93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de
Dr. A. Noor,[+] Dr. G. Glatz, Prof. Dr. R. Kempe
Inorganic Chemistry II, University of Bayreuth
95440 Bayreuth (Germany)
E-mail: kempe@uni-bayreuth.de
Dr. A. Y. Timoshkin
Department of Chemistry, St. Petersburg State University
198504 Old Peterhoff, St. Petersburg (Russia)
Dr. B. M. Cossairt, Prof. C. C. Cummins
Department of Chemistry, MIT
Cambridge, MA 02139 (USA)
[+] These authors contributed equally to this work.

[**] Financial support from the DFG (KE 756/20-1) and the COST action CM0802 PhoSciNet is gratefully acknowledged. C. Schwarzmaier is grateful for a Ph.D. fellowship of the Fonds der Chemischen Industrie. C. C. Cummins thanks the Alexander von Humboldt Foundation for general support. Alexandra Velian is thanked for assistance in the preparation of AsP_3.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102361.



Scheme 1. Synthesis of complexes **2** and **3**. The number above the Cr–Cr bond refers to the bond order.

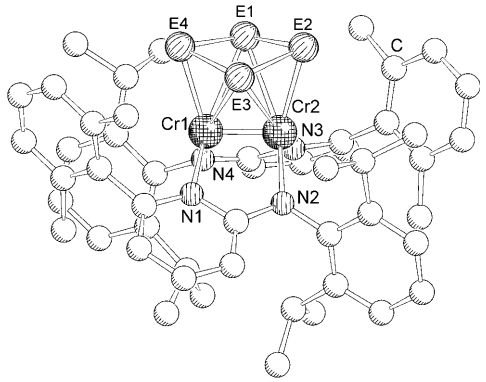


Figure 1. Molecular structure of the isostructural complexes **2a** and **2b**. Hydrogen atoms have been omitted for clarity. **2a** (E = P): Selected bond lengths [Å] and angles [°]: N1–Cr1 2.029(3), N2–Cr2 2.037(3), N3–Cr2 2.029(3), N4–Cr1 2.036(3), P1–P4 2.176(1), P1–P2 2.179(2), P1–Cr1 2.679(1), P1–Cr2 2.687(1), P2–P3 2.168(1), P2–Cr2 2.379(1), P3–P4 2.183(2), P3–Cr2 2.678(1), P3–Cr1 2.682(1), P4–Cr1 2.362(1), Cr1–Cr2 1.8664(8); P4-P1-P2 91.55(5), P3-P2-P1 86.85(5), P2-P3-P4 91.67(5), P1-P4-P3 86.53(5). **2b** (E = As): Selected bond lengths [Å] and angles [°]: N1–Cr1 2.031(6), N2–Cr2 2.049(6), N3–Cr2 2.036(5), N4–Cr1 2.045(5), Cr1–Cr2 1.863(2), Cr1–As4 2.505(1), Cr1–As3 2.769(1), Cr1–As1 2.786(1), Cr2–As2 2.490(1), Cr2–As3 2.769(1), Cr2–As1 2.779(1), As1–As2 2.398(1), As1–As4 2.405(1), As2–As3 2.406(1), As3–As4 2.388(1); As2-As1-As4 92.10(4), As1-As2-As3 85.59(4), As4-As3-As2 92.32(4), As3-As4-As1 85.81(4).

are indicative of quadruple bonds. This essentially means that the Cr–Cr center has been oxidized, which led to a reduction of the P_4 and As_4 units.

The ^{31}P NMR spectrum of **2a** at room temperature displays a complex pattern of two multiplets at $\delta = 243.9$ and 275.6 ppm of an AA′MM′ spin system, for which the coupling constants were simulated.[23] As the two signals are totally symmetrical, an assignment of the chemical shifts to the corresponding P atoms was not possible at this point. To determine the ^{31}P chemical shifts in **2a**, **1** was treated with AsP_3 to yield **2c** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **2c** shows three sharp doublets of an AMN spin system at $\delta =$ 255.6, 260.6, and 291.0 ppm with integral intensities of 1:1:1.[23] The crystal structure analysis of **2c** (Figure 2) reveals that

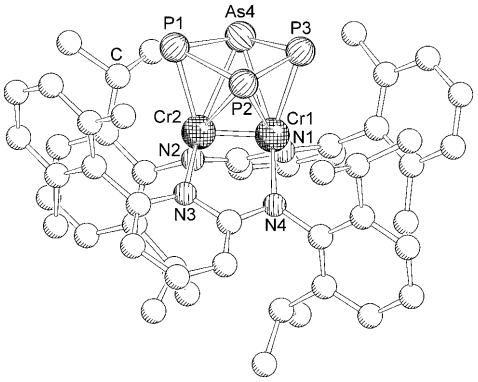


Figure 2. Molecular structure of **2c**. For clarity reasons only one of the two arsenic positions is shown and hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: N1–Cr1 2.031(2), N2–Cr2 2.035(2), N3–Cr2 2.027(2), N4–Cr1 2.035(2), Cr1–Cr2 1.8735(5), Cr2–P4 2.3814(7), Cr2–P3 2.702(4), Cr1–P3 2.561(6), Cr1–P2 2.3926(7), Cr1–As1 2.75(1), Cr2–As1 2.76(1), P4–P3 2.390(1), P3–P2 2.303(2), P2–As1 2.258(9), As1–P4 2.29(1); P4-P3-P2 90.9(2), P3-P2-As1 91.7(3), P2-As1-P4 89.4(4), As1-P4-P3 83.6(3).

arsenic only occupies the bridging positions. Therefore the up-field shifted signals of **2a** and **2c** can be assigned to the terminal phosphorus atoms, the down-field shifted signals to the bridging ones.

The structure of **2c** reveals a mixed 1:1 occupancy of phosphorus and arsenic only at the positions E1 and E3.[23] In both cases the molecule shows a nearly square-planar arrangement of the AsP_3^{2-} unit. The E–E bond lengths of 2.258(9) to 2.390(1) Å are consistent with a distortion of the *cyclo*-E_4 unit due to the size difference between phosphorus and arsenic. The Cr1–Cr2 distance of 1.8735(5) Å is a little bit longer than the ones observed in **2a** and **2b**.

In an effort to use the lone pairs of the P_4^{2-} moiety, **2a** was allowed to react with an excess of $[W(CO)_5(thf)]$ to give exclusively the monosubstituted derivative **3a** (Scheme 1). The crystal structure of **3a** (Figure 3) reveals P–P distances comparable to those in the uncoordinated **2a**, however, an elongation for the Cr–Cr bond length to 1.9038(6) is observed. The coordination of any further tungsten pentacarbonyl fragment might be restricted by the steric crowding of the molecule.

At room temperature the ^{31}P NMR spectrum of **3a** shows a broad pseudo triplet at $\delta = 250$ ppm for the uncoordinated P atoms, and a very broad signal between $\delta = 210$ and 230 ppm for the P atoms coordinated to the tungsten fragment,[23] indicating a scrambling of the tungsten carbonyl unit. Compared to the ^{31}P NMR spectrum of **2a**, the chemical shift of $\delta = 250$ ppm indicates that in solution the bridging atoms P2/P4 coordinate to the $\{W(CO)_5\}$ fragment, which differs from the result of the crystal structure analysis

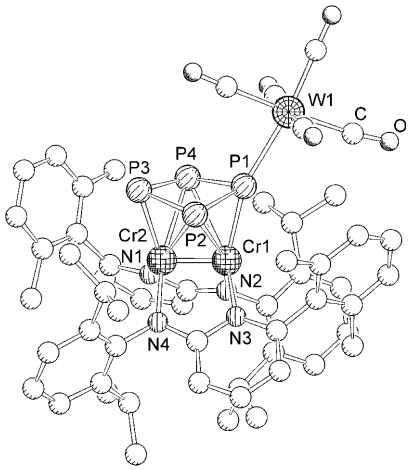


Figure 3. Molecular structure of **3a**. Hydrogen atoms and one CH_2Cl_2 molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–P1 2.5646(6), Cr1–Cr2 1.9038(6), Cr1–P1 2.3741(7), Cr1–P2 2.7365(9), Cr1–P4 2.7630(9), Cr1–N2 2.023(2), Cr1–N3 2.011(2), Cr2–P2 2.6944(8), Cr2–P3 2.3382(9), Cr2–P4 2.6411(8), Cr2–N1 2.011(2), Cr2–N4 1.998(2), P1–P2 2.1804(11), P1–P4 2.1869(11), P2–P3 2.1797(11), P3–P4 2.1708(11); W1-P1-Cr1 159.37(4), W1-P1-P2 124.67(4), W1-P1-P4 112.28(3), Cr1-P1-P2 73.72(3), P2-P1-P4 88.27(4), P1-P2-P3 89.97(4), P2-P3-P4 88.70(4), P1-P4-P3 90.03(4).

(Figure 3). At 183 K the dynamic behavior is slowed down and the broad signals are well resolved to reveal four sets of signals at $\delta = 269$, 254, 251, and 133 ppm. The high-field shifted signal at $\delta = 133$ ppm indicates the coordination to the W atom.[24] Unfortunately, even at low temperatures no ^{183}W-satellites are detected due to the limited solubility and the line broadening. The signals for the noncoordinating P atoms show roughly the same chemical shifts as the corresponding atoms of **2a**. Simulation of the experimental data proved the suggested AMNX spin system with chemically but not magnetically equivalent P1/P3 atoms and afforded the associated coupling constants.[23]

To shed more light onto the interaction of the Cr–Cr quintuple bond with P_4, theoretical calculations were performed.[23] The reaction of **1** with P_4 to give **2a** in the gas phase is predicted to be exothermic by 24 kJ mol^{-1}. Taking into account that planarization of tetrahedral P_4 requires 335 kJ mol^{-1}, the interaction of the planar P_4 with **1** fully compensates these unfavorable energy changes. The interaction is accompanied by the expected elongation of the Cr–Cr bond by 0.098 Å (the experimental increase in the Cr–Cr bond length from **1** to **2a** is 0.117 Å) and the decrease of the Wiberg bond index for the Cr–Cr bond from 4.39 in **1** to 2.91 in **2a**, which is consistent with the oxidation of the Cr–Cr center by P_4.

The subsequent reaction of **2a** with $\{W(CO)_5\}$, which leads to **3a**, is exothermic by 93 kJ mol^{-1}. This interaction only marginally influences the Cr–Cr bond: the Cr–Cr bond length is elongated by only 0.008 Å (the experimental bond length increase from **2a** to **3a** is 0.037 Å). Correspondingly, the Wiberg bond index of 2.86 for **3a** is only slightly lower than that for **2a**.

To further investigate the discrepancy between the solid-state and solution structure of **3a**, four isomers were located on the potential energy surface, two with the $\{W(CO)_5\}$ fragment coordinated either to the bridging P2/P4 or the terminal P1/P3 atoms and the other two isomers featuring a butterfly-type P_4 unit with a direct P2–P4 bond and coordination of $\{W(CO)_5\}$ to a terminal or bridging P atom (Figure 4).

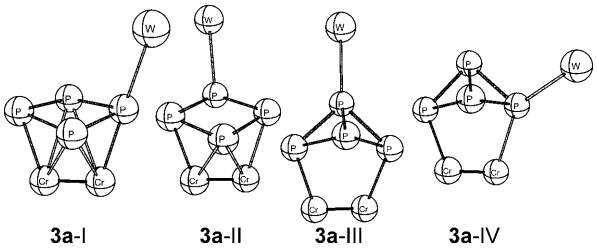


Figure 4. Theoretically considered isomers of **3a**. Carbonyl groups and organic ligands have been omitted for clarity.

Isomers **3a**-II, **3a**-III, and **3a**-IV are 12, 53, and 82 kJ mol^{-1} higher in energy than **3a**-I at the B3LYP[25]/def2-TZVPP[26] level of theory, but with the smaller def2-SVP basis set the **3a**-II isomer is predicted to be by 2 kJ mol^{-1} lower in energy than **3a**-I. Since the energy difference between isomers **3a**-I and **3a**-II is small, both isomers are expected to co-exist in solution.

In conclusion, quintuply bonded systems have been used for the activation of white phosphorus, yellow arsenic, and AsP_3 at room temperature to give novel complexes containing *cyclo*-P_4^{2-}, *cyclo*-As_4^{2-}, and *cyclo*-AsP_3^{2-} units. For the first time these molecules have been activated in a one-step bimetallic fashion and the resulting products show a novel coordination mode as terminal E_4-decks over two metal centers. Moreover, the subsequent reaction of the *cyclo*-P_4 species with an excess of $[W(CO)_5(thf)]$ leads to the coordination of a single $\{W(CO)_5\}$ moiety.

Received: April 5, 2011
Published online: June 22, 2011

Keywords: arsenic · chromium · phosphorus · quintuple bonds

[1] M. Morse, *Chem. Rev.* **1986**, *86*, 1049 – 1109.
[2] a) E. P. Kündig, M. Moskovits, G. A. Ozin, *Nature* **1975**, *254*, 503 – 504; b) W. Klotzbücher, G. A. Ozin, *Inorg. Chem.* **1977**, *16*, 984 – 987.
[3] Yu. M. Efremov, A. N. Samoilova, L. V. Gurvich, *Opt. Spektrosk.* **1974**, *36*, 654 – 657.
[4] V. E. Bondybey, J. H. English, *Chem. Phys. Lett.* **1983**, *94*, 443 – 447.
[5] a) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844 – 847; b) R. Wolf, C. Ni, T. Nguyen, M. Brynda, G. J. Long, A. D. Sutton, R. C. Fischer, J. C. Fettinger, M. Hellman, L. Pu, P. P. Power, *Inorg. Chem.* **2007**, *46*, 11277 – 11290; c) E. Rivard, P. P. Power, *Inorg. Chem.* **2007**, *46*, 10047 – 10064.
[6] K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162 – 14163.

[7] a) Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem.* **2008**, *120*, 7360 – 7363; *Angew. Chem. Int. Ed.* **2008**, *47*, 7250 – 7253; b) C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem.* **2008**, *120*, 10081 – 10084; *Angew. Chem. Int. Ed.* **2008**, *47*, 9933 – 9936; c) Y.-C. Tsai, H.-Z. Chen, C.-C. Chang, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *J. Am. Chem. Soc.* **2009**, *131*, 12534 – 12535.

[8] a) A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, *120*, 7356 – 7359; *Angew. Chem. Int. Ed.* **2008**, *47*, 7246 – 7249; b) A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1149 – 1152.

[9] a) L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848 – 851; b) G. Frenking, R. Tonner, *Nature* **2007**, *446*, 276 – 277; c) G. Merino, K. J. Donald, J. S. D'Acchioli, R. Hoffmann, *J. Am. Chem. Soc.* **2007**, *129*, 15295 – 15302; d) U. Radius, F. Breher, *Angew. Chem.* **2006**, *118*, 3072 – 3077; *Angew. Chem. Int. Ed.* **2006**, *45*, 3006 – 3010; e) G. Frenking, *Science* **2005**, *310*, 796 – 397; f) M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power, B. O. Roos, *Angew. Chem.* **2006**, *118*, 3888 – 3891; *Angew. Chem. Int. Ed.* **2006**, *45*, 3804 – 3807; g) G. La Macchia, M. Brynda, L. Gagliardi, *Angew. Chem.* **2006**, *118*, 6356 – 6359; *Angew. Chem. Int. Ed.* **2006**, *45*, 6210 – 6213; h) J. Huang, Q. Li, H. Ren, H. Su, J. Yang, *J. Chem. Phys.* **2006**, *125*, 184713; i) B. O. Roos, P. A. Malmqvist, L. Gagliardi, *J. Am. Chem. Soc.* **2006**, *128*, 17000 – 17006; j) F. Weinhold, C. R. Landis, *Science* **2007**, *316*, 61 – 63; k) G. La Macchia, L. Gagliardi, P. P. Power, M. Brynda, *J. Am. Chem. Soc.* **2008**, *130*, 5104 – 5114; l) G. La Macchia, F. Aquilante, V. Veryazov, B. O. Ross, L. Gagliardi, *Inorg. Chem.* **2008**, *47*, 11455 – 11457; m) B. Xu, Q.-S. Li. Y. Xie, H. F. Shaefer III, *J. Chem. Theory Comput.* **2010**, *6*, 735 – 746; n) M. Brynda, L. Gagliardi, B. O. Roos, *Chem. Phys. Lett.* **2009**, *471*, 1 – 10; o) R. Ponec, F. Feixas, *J. Chem. Phys. A* **2009**, *113*, 8394 – 8400; p) D. B. Donald, *J. Phys. Chem. A* **2009**, *113*, 1559 – 1563; q) G. La Macchia, G. Li Manni, T. K. Todorova, F. Aquilante, B. O. Roos, L. Gagliardi, *Inorg. Chem.* **2010**, *49*, 5216 – 5222.

[10] F. Wagner, A. Noor, R. Kempe, *Nat. Chem.* **2009**, *1*, 529 – 536.

[11] a) A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Nat. Chem.* **2009**, *1*, 322 – 325; b) C. Ni, B. D. Ellis, G. J. Long, P. P. Power, *Chem. Commun.* **2009**, 2332 – 2334; c) A. Noor, E. S. Tamne, S. Qayyum, T. Bauer, R. Kempe, *Chem. Eur. J.* **2011**, *17*, 6900 – 6903.

[12] M. Scheer, G. Balàzs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236 – 4256.

[13] a) B. M. Crossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4161 – 4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178 – 4235; c) M. Peruzzini, L. Gonsalvi, A. Romerosa, *Chem. Soc. Rev.* **2005**, *34*, 1038 – 1047.

[14] a) M. Peruzzini, M. Marvelli, A. Romerosa, R. Rossi, F. Vizza, F. Zanobini, *Eur. J. Inorg. Chem.* **1999**, 931 – 933; b) M. Di Vaira, P. Frediani, S. Seniori Costantini, M. Peruzzini, P. Stoppioni, *Acta Crystallogr. Sect. A* **2005**, *61*, c298; c) P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, *Chem. Eur. J.* **2007**, *13*, 6682 – 6690; d) M. Caporali, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, F. Zanobini, *Eur. J. Inorg. Chem.* **2010**, 152 – 158; e) D. Yakhvarov, P. Barbaro, L. Gonsalvi, S. M. Carpio, S. Midollini, A. Orlandini, M. Peruzzini, O. Sinyashin, F. Zanobini, *Angew. Chem.* **2006**, *118*, 4288 – 4291; *Angew. Chem. Int. Ed.* **2006**, *45*, 4182 – 4185.

[15] a) O. J. Scherer, G. Schwarz, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1996**, *622*, 951 – 957; b) O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* **1998**, *17*, 4110 – 4112.

[16] W. W. Seidel, O. T. Summerscales, B. U. Patrick, M. D. Fryzuk, *Angew. Chem.* **2009**, *121*, 121 – 123; *Angew. Chem. Int. Ed.* **2009**, *48*, 115 – 117.

[17] a) F. Kraus, J. C. Aschenbrenner, N. Korber, *Angew. Chem.* **2003**, *115*, 4162 – 4165; *Angew. Chem. Int. Ed.* **2003**, *42*, 4030 – 4033; b) F. Kraus, N. Korber, *Chem. Eur. J.* **2005**, *11*, 5945 – 5959.

[18] a) N. Korber, M. Reil, *Chem. Commun.* **2002**, 84 – 85; b) F. Kraus, T. Hanauer, N. Korber, *Inorg. Chem.* **2006**, *45*, 1117 – 1123.

[19] a) O. J. Scherer, J. Vondung, G. Wolmershäuser, *Angew. Chem.* **1989**, *101*, 1395 – 1397; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355 – 1357; b) O. J. Scherer, J. Vondung, G. Wolmershäuser, *J. Organomet. Chem.* **1989**, *376*, C35 – C38; c) O. J. Scherer, R. Winter, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1993**, *619*, 827 – 835.

[20] a) B. M. Cossairt, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 15501 – 15511; b) B. M. Cossairt, C. C. Cummins, *Chem. Eur. J.* **2010**, *16*, 12603 – 12608.

[21] L. R. Maxwell, S. B. Hendrichs, V. M. Mosley, *J. Chem. Phys.* **1995**, *103*, 699; see also reference [12].

[22] a) Y. Morino, T. Ukaji, T. Ito, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 64 – 71; b) H. A. Spinney, N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 16233 – 16243.

[23] See the Supporting Information for details for the X-ray structure analyses and the DFT calculations. CCDC-816510 (**2a**), CCDC-816511 (**2b**), CCDC-816512 (**2c**), and CCDC-816513 (**3a**) 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.

[24] Compare the high-field shift of a terminal P_1 ligand complex after addition of $[W(CO)_5thf]$: M. Scheer, J. Müller, M. Häser, *Angew. Chem.* **1996**, *108*, 2637 – 2641; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2492 – 2496.

[25] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[26] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; b) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.

