Organometallics **2001,** *20,* 4463−4465

Reactivity of Electrophilic Terminal Phosphinidene Complexes: P−P Bond Forming Reactions with Phosphines and Diphosphines

Brian T. Sterenberg, Konstantin A. Udachin, and Arthur J. Carty*

Steacie Institute for Molecular Sciences, National Research Council of Canada,
100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

Received July 18, 2001

*Summary: Reaction of the electrophilic phosphinidene complex [Cp*Mo(CO)$_3${PN^{i}Pr$_2$}][AlCl$_4$] with triethylphosphine results in reversible coordination of the phosphine to the phosphinidene phosphorus atom followed by carbonyl displacement at the metal. Phosphine-coordinated phosphinidene complexes with P−P bonds can be isolated by using diphosphines which coordinate first to the phosphinidene and then chelate to the phosphinidene and metal atoms.*

Transition-metal phosphinidene complexes can be considered analogues of carbene complexes.[1] It has thus been suggested that, like carbenes, they can be divided into nucleophilic and electrophilic classes.[2] While the first nucleophilic terminal phosphinidene complexes were described by Lappert in 1987,[3] the isolation of electrophilic phosphinidene complexes has proven more difficult. We recently described the first structurally characterized examples of base-free electrophilic η^1-phosphinidene complexes.[4] Like Fischer carbenes, the electrophilic phosphinidene ligands have a heteroatom substituent with a lone pair that acts as a π-donor to phosphorus. To demonstrate the electrophilicity of these ligands, the molybdenum phosphinidene complex [Cp*Mo(CO)$_3${PN^{i}Pr$_2$}][AlCl$_4$] (**1**) was reacted with phosphines and diphosphines. Previously, transient electrophilic phosphinidene complexes have been trapped with phosphines to form phosphoranylidenephosphine complexes,[5] while phosphine coordination to the phosphorus atom of phosphenium cations has also been observed.[6]

Reaction of the molybdenum phosphinidene complex [Cp*Mo(CO)$_3${PN^{i}Pr$_2$}][AlCl$_4$] (**1**) with triethylphosphine results in carbonyl substitution at molybdenum to form [Cp*Mo(CO)$_2$(PEt$_3$){PN^{i}Pr$_2$}][AlCl$_4$] (**2**). Compound **2** has been structurally characterized.[7] An ORTEP diagram of the cation is shown in Figure 1. The geometry at the metal is that of a square-based pyramid with two carbonyl groups, the phosphine and the phosphinidene ligands forming the base and the center of the Cp* ligand in the apical position. The phosphine and the phosphinidene ligands are transoid, occupying opposite corners of the square base.

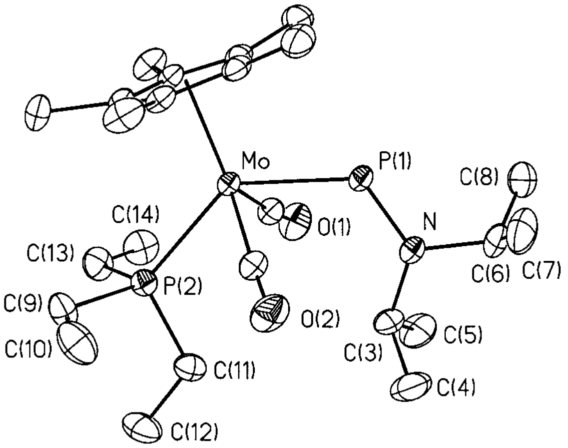


Figure 1. ORTEP diagram of the cation of compound **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been eliminated for clarity. Selected distances (Å) and angles (deg): Mo−P(1) = 2.3816(4) Å, P(1)−N = 1.637(1) Å, Mo−P(2) = 2.5087(4) Å; Mo−P(1)−N = 121.49(5)°.

The Mo−P distance of 2.3816(4) Å is significantly shorter than that observed in the precursor phosphinidene complex [Cp*Mo(CO)$_3${PN^{i}Pr$_2$}][AlCl$_4$] (**1**) of 2.4506(4) Å. Besides the metal, the phosphorus atom is bound to nitrogen with a bond distance of 1.637(1) Å compared with 1.631(1) Å in **1**. These parameters suggest that the presence of the strong donor phosphine ligand significantly increases the amount of π-back-bonding to the phosphinidene ligand, resulting in a shorter Mo−P distance. The increased π-bonding from the metal decreases the amount of π-donation from the nitrogen atom, resulting in a slight lengthening of the P−N distance. The ^{31}P NMR spectrum of **2** shows two resonances at δ 957 and 36 with a common coupling constant of 15 Hz.[8] The extremely low field chemical shift is characteristic of phosphinidene ligands (compare compound **1** at δ 1007).

This reactivity was contrary to our expectation of nucleophilic attack at the phosphinidene ligand; there-

---

(1) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445.

(2) (a) Frison, G.; Mathey, F.; Sevin, A. *J. Organomet. Chem.* **1998**, *570*, 225. (b) Holland, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.

(3) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

(4) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 2657.

(5) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407.

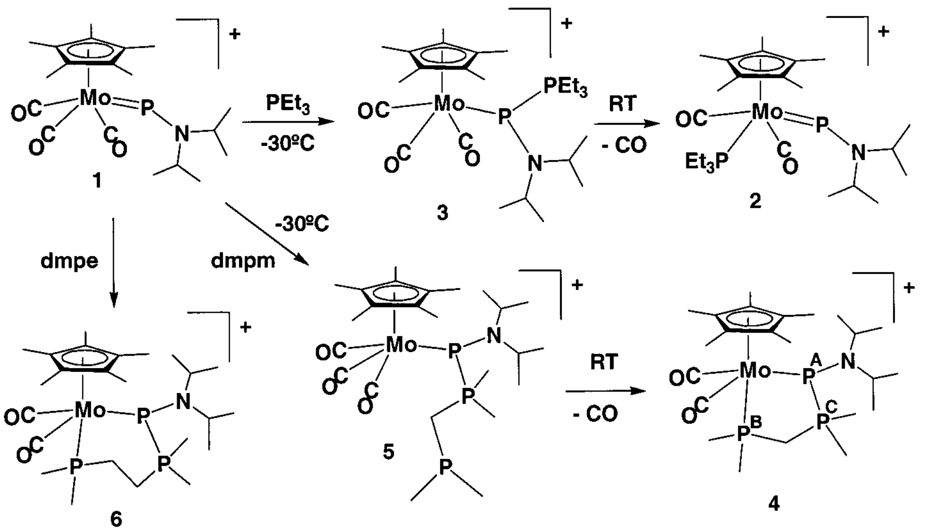
(6) (a) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712. (b) Burford, N.; Losier, P.; Sereda, S. V.; Cameron, T. S.; Wu, G. *J. Am. Chem. Soc.* **1994**, *116*, 6474. (c) David, G.; Niecke, E.; Nieger, M.; Radseck, J. *J. Am. Chem. Soc.* **1994**, *116*, 2191.

(7) Crystallographic data for **2**: monoclinic, $P2_1/c$, $\beta = 94.790(1)°$, $a = 10.1662(5)$ Å, $b = 15.3421(7)$ Å, $c = 21.4861(10)$ Å, $V = 3339.5(3)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.403$ g/cm^3, $T = 173(2)$ K, 8644 independent reflections (R(int) = 0.0278), R1 = 0.0238, wR2 = 0.0591.

(8) Data for [Cp*Mo(CO)$_2$(PEt$_3$)(PN^{i}Pr$_2$)][AlCl$_4$] (**2**): IR(ν(CO)) 1976, 1902 cm^{-1}; ^{31}P{^{1}H} NMR δ 957 (b, ^2J(PP) = 15 Hz, Mo*P*N^{i}Pr$_2$), 36.0 (d, ^2J(PP) = 15 Hz, Mo*P*Et$_3$); ^{1}H NMR δ 5.00 (septet, 1H, ^3J(HH) = 6.7 Hz), C*H*(CH$_3$)$_2$), 4.60 (bm, C*H*(CH$_3$)$_2$), 2.03 (dq, 6H, ^3J(HH) = 7.7, ^2J(HP) = 7.7 Hz, PCH_2CH$_3$), 1.97 (s, 15H, C$_5$(CH_3)$_5$), 1.56 (d, 6H, ^3J(HH) = 6.6 Hz, CH(CH_3)$_2$), 1.43 (d, 6H, 3*J*(HH) = 6.7 Hz, CH(CH_3)$_2$), 1.21 (dt, 9H, ^3J(HH) = 7.7, ^3J(PH) = 8.2 Hz, PCH$_2$CH_3). Anal. Calcd for C$_{24}$H$_{44}$NO$_2$P$_2$AlCl$_4$Mo: C, 40.87; H, 6.29; N, 1.99. Found: C, 40.83; H, 6.66; N, 2.00.

10.1021/om010640q CCC: $20.00
Publication on Web 09/29/2001

Scheme 1



fore, the reaction was studied at low temperature. Addition of the phosphine to dark red solutions of **1** at −80 °C resulted in a yellow solution which upon warming to room temperature evolved gas and changed back to dark red. The ^{31}P NMR spectrum of the yellow product recorded at −30 °C showed two resonances at δ 78.9 and 32.3 with a coupling constant of 512 Hz. The large coupling constant is indicative of direct P−P bonding and compares with values of 455 and 340 Hz observed in phosphine-coordinated phosphenium ions[6] and the 361−444 Hz coupling constants observed in phosphoranylidene complexes formed via the trapping of transient phosphinidene complexes with phosphines.[5] The IR spectrum shows three ν(CO) bands at 2013, 1947, and 1917 cm^{-1}, indicating that the three carbonyls of the starting material are retained. The initial site of attack by the phosphine is therefore at the phosphinidene phosphorus as expected, forming $[Cp^*Mo(CO)_3\{P(PEt_3)N^iPr_2\}][AlCl_4]$ (**3**).[9] Upon warming, a carbonyl is lost and the phosphine ligand migrates from the phosphinidene ligand to the metal. The coordination of the phosphine to the phosphinidene is thus reversible.

A comparison of the ν(CO) frequencies of **3** (2013, 1947, and 1917 cm^{-1}) with those of the starting phosphinidene complex **1** (2041, 1986, 1959 cm^{-1})[4] shows a significant shift to lower frequency upon coordination of the phosphine to the phosphinidene. This is consistent with a reduction in the π back-bonding to the phosphinidene and an increase in π back-bonding to the carbonyl ligands but does not explain why the carbonyl ligand in **3** is labile, while those in the parent phosphinidene complex **1** are not. The lability of the carbonyl in **3** is attributed to a stabilization of the 16-electron intermediate formed upon carbonyl loss by the lone pair of the phosphine-coordinated phosphinidene ligand. The lone pair of the base-free phosphinidene ligand, given its electrophilic nature, is too low in energy to provide the same stabilization and facilitate carbonyl loss from **1**.

Although the triethylphosphine-coordinated phosphinidene complex has been spectroscopically characterized, a crystallographically characterized example would be of interest. Compound **1** was therefore reacted with bis(dimethylphosphino)methane (dmpm), leading to $[Cp^*Mo(CO)_2\{\eta^2\text{-}P(N^iPr_2)P(CH_3)_2CH_2P(CH_3)_2\}][AlCl_4]$ (**4**), in which the two ends of the dmpm ligand coordinate to the phosphinidene phosphorus and the metal, respectively. The ^{31}P NMR spectrum of **4** shows three resonances at δ 109.3 (P^A), 41.2 (P^B), and 10.8 (P^C) (see Scheme 1 for atom assignments).[10] A very large one-bond coupling of 532 Hz is observed between P^A and P^C, while P^C and P^B share a ^2J(PP) value of 98 Hz across the methylene group of dmpm. A ^2J(PP) value of 13 Hz is also observed between the two metal-bound phosphorus atoms.

As in the triethylphosphine reaction, the initial site of attack is at the phosphinidene phosphorus. The phosphine adduct $[Cp^*Mo(CO)_3\{\eta^1\text{-}P(N^iPr_2)P(CH_3)_2CH_2P(CH_3)_2\}][AlCl_4]$ (**5**) was observed at low temperature as the initial product in the reaction. The ^{31}P NMR spectrum of **5** shows three resonances.[11] The phosphinidene resonance appears at δ 97.2 with a ^1J(PP) value of 506 Hz. There is no coupling to the other phosphorus center. The peak for the coordinated phosphine occurs at δ 17.1 as a doublet of doublets with a large ^1J(PP) value as well as a 34 Hz coupling to the other end of the dmpm ligand. The free phosphine appears at δ −49.6, close to the peak for free dmpm. The IR spectrum of **5** contains three carbonyl stretching bands at 2004, 1935, and 1919 cm^{-1}, very similar to those of compound **3**. Upon warming to room temperature, vigorous evolution of gas is observed and the color changes from yellow to orange with the formation of **4**.

Compound **4** has been characterized by X-ray crystallography, and although the solution was sufficient to

---

(9) Data for $[Cp^*Mo(CO)_3\{P(PEt_3)N^iPr_2\}][AlCl_4]$ (**3**): IR(ν(CO), −80 °C) 2013, 1947, 1917 cm^{-1}; ^{31}P{^{1}H} NMR (−30 °C) δ 78.9 (d, Mo*P*P), 32.3 (d, MoP*P*), ^1J(PP) = 512 Hz; ^{1}H NMR δ 3.3 (b, 2H, C*H*(CH$_3$)$_2$), 2.0 (b, 6H, PC*H*$_2$CH$_3$), 1.95 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.3 (bm, 12 H, CH(C*H*$_3$)$_2$), 1.14 (b, 9H, PCH$_2$C*H*$_3$).

(10) Data for $[Cp^*Mo(CO)_2\{\eta^2\text{-}P(N^iPr_2)P(Me_2)CH_2P(Me_2)\}][AlCl_4]$ (**4**): IR (ν(CO)): 1959, 1890 cm^{-1}; ^{31}P{^{1}H} NMR δ 109.3 (dd, ^1J(PP) = 532 Hz, ^2J(PP) = 13 Hz, Mo*P*P), 41.2 (dd, ^2J(PP) = 98 Hz, ^2J(PP) = 13 Hz, Mo*P*CH$_2$P), 10.8 (dd, ^1J(PP) = 532 Hz, ^2J(PP) = 98 Hz, MoP*P*). ^{1}H NMR: δ 3.38 (b, 2H), 2.52 (b, 2H), 1.95 (15 H), 1.86 (b, 6H), 1.74 (b, 6H), 1.20 (b, 12H). Anal. Calcd for $C_{23}H_{43}O_2P_3NAlCl_4Mo$: C, 38.20; H, 5.99; N, 1.94. Found: C, 37.82; H, 6.14; N, 2.08.

(11) Data for $[Cp^*Mo(CO)_3\{P(N^iPr_2)P(Me_2)CH_2P(Me_2)\}][AlCl_4]$ (**5**): IR (ν(CO), −80 °C): 2004, 1935, 1919 cm^{-1}; ^{31}P{^{1}H} NMR (−30 °C) δ 97.2 (d, ^1J(PP) = 506 Hz), 17.1 (dd, ^1J(PP) = 506 Hz, ^2J(PP) = 34 Hz), −49.6 (d, ^2J(PP) = 34 Hz); ^{1}H NMR δ 3.27 (b, 2H, NC*H*(CH$_3$)$_2$), 1.96 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.87 (bm, 2H, PC*H*$_2$P), 1.44 (d, ^1J(HH) = 6 Hz, NCH(C*H*$_3$)$_2$), 1.3 (b, 12H, P(C*H*$_3$)$_2$), 1.2 (b, 2H, NCH(C*H*$_3$)$_2$).

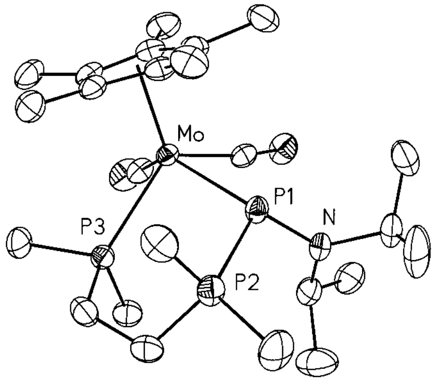


Figure 2. ORTEP diagram of the cation of compound **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been eliminated for clarity. Selected distances (Å) and angles (deg): Mo−P(1) = 2.5835(6) Å, P(1)−N = 1.688(2), P(1)−P(2) = 2.2149(9), Mo−P(3) = 2.5167(7); Mo−P(1)−N = 118.41(8), Mo−P(1)−P(2) = 111.21(3), N−P(1)−P(2) = 106.09(9), P(1)−Mo−P(3) = 88.41(8).

confirm the proposed structure, the quality was poor because of problems with twinning. The bis(dimethylphosphino)ethane (dmpe) analogue **6**[12] was thus prepared and structurally characterized. The ORTEP diagram of the cation is shown in Figure 2.[13] The geometry at the metal is again that of a square-based pyramid, with the phosphine and the coordinated phosphinidene in a cisoid arrangement. The molybdenum, the three phosphorus atoms, and two methylene carbons form a six-membered ring with a roughly chair-shaped conformation. The P(1)−P(2) distance of 2.2149(9) Å is within the range observed for P−P single bonds in diphosphines (2.205(1)−2.260(1) Å)[14] but is substantially longer than the P−P distance of 2.156(2) Å observed in the phosphoranylidenephosphine complex [$Et_3P{=}P(CO_2Et)W(CO)_5$].[5]

The Mo−P(1) distance of 2.5835(6) Å has lengthened considerably compared to the Mo−P distance of 2.4506(4) Å in the phosphinidene complex **1**. Coordination of the phosphine fills the empty p_z orbital on P(1), eliminating the possibility of π-back-donation from the metal to this low-lying orbital. The Mo−P(1) distance is in fact longer than the molybdenum−phosphine distance of 2.5167(7) Å. In addition to P(2) and Mo, P(1) is bound to nitrogen with a P−N bond distance of 1.688(2) Å, substantially longer than the P−N distance of 1.631(1) Å in the starting phosphinidene complex **1** and consistent with a P−N single bond.[15] This lengthening results from the elimination of the nitrogen to phosphorus donation upon coordination of the basic phosphine to the phosphorus. The geometry at P(1) is pyramidal.

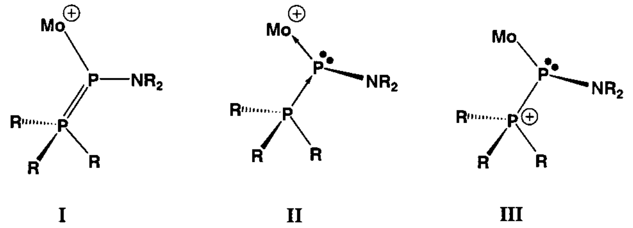


Figure 3.

Compounds **3** and **4**−**6**, in which the phosphine coordinates to the phosphinidene, could be formulated as phosphoranylidenephosphine complexes, as shown in structure **I** (Figure 3). However, the structural parameters indicate that the P−P bond is best considered to be single and the geometry at P(1) is pyramidal. The complexes are therefore best described as base-coordinated phosphinidenes (structure **II**) or phosphonium-substituted terminal phosphido complexes (structure **III**) which are equivalent. The spectroscopic and structural parameters of **3** and **4**−**6** are in fact reminiscent of those of the related phosphido complex [Cp*Mo(CO)$_3$-{P(Cl)N^{i}Pr$_2$}], the precursor to phosphinidene complex **1**.[16] The very large P−P coupling constants suggest that there is a substantial donor interaction; however, factors influencing ^1J(PP) coupling constants are not well understood, and large P−P coupling constants have been observed in weakly coordinated systems.[17] The ready transformation from **3** to **2** shows that the coordinated phosphine is labile.

These results confirm that terminal, isolable phosphinidene complexes such as **1** bearing electron-donating substituents on phosphorus are indeed, like Fischer carbenes, electrophilic in character. In contrast, nucleophilic terminal phosphinidene complexes react with phosphines via attack at the metal center.[18] An extensive derivative chemistry based on P−X (X = nucleophile) bond formation can be confidently predicted for electrophilic phosphinidenes of the type described herein.

Acknowledgment. This work was supported by the National Research Council of Canada and the Natural Sciences and Engineering Research Council of Canada (to A.J.C.) and an NRC-NSERC Canadian Government Laboratories Visiting Fellowship (to B.T.S.).

Supporting Information Available: Text and tables giving synthetic procedures and analytical, spectroscopic, and crystallographic data for compounds **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010640Q

---

[12] Data for [Cp*Mo(CO)$_2${η^2-P(N^{i}Pr$_2$)P(Me$_2$)CH$_2$CH$_2$P(Me$_2$)}][AlCl$_4$] (**6**): IR(ν(CO)) 1973, 1905 cm^{-1}; ^{31}P{^{1}H} NMR δ 56.8 (d, ^1J(PP) = 614 Hz, Mo*P*P), 2.3 (d, ^2J(PP) = 39 Hz, Mo*P*CH$_2$CH$_2$P), −2.7 (dd, ^1J(PP) = 614 Hz, ^2J(PP) = 39 Hz, MoP*P*); ^{1}H NMR δ 3.40 (bm, 2H, NC*H*CH$_3$), 2.42 (bm, 2H, PC*H*$_2$CH$_2$P), 2.08 (bm, 2H, PCH$_2$C*H*$_2$P), 1.94 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.69 (d, 6H, ^3J(HH) = 8 Hz, NCHC*H*$_3$), 1.65 (d, 6H, ^3J(HH) = 8 Hz, NCHC*H*$_3$), 1.19−1.16 (b, 12H, P(C*H*$_3$)$_2$P). Anal. Calcd for $C_{24}H_{45}O_2P_3NAlCl_4Mo$: C, 39.10; H, 6.15; N, 1.90. Found: C, 38.57; H, 6.68; N, 1.83.

[13] Crystallographic data for **6**: triclinic, $P\bar{1}$, $\alpha = 97.141(1)°$, $\beta = 94.790(1)°$, $\gamma = 94.520(1)°$, $a = 8.7257(4)$ Å, $b = 12.0445(5)$ Å, $c = 16.6316(8)$ Å, $V = 1708.9(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.433$ g/cm^3, $T = 173(2)$ K, 8783 independent reflections (R(int) = 0.0261), R1 = 0.0367, wR2 = 0.0918.

[14] (a) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; MacDonald, C. L. B.; Wiacek, R. J.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *Chem. Commun.* **2000**, 2045. (b) Vohs, J. K.; Wei, P.; Su, J.; Beck, B. C.; Goodwin, S. D.; Robinson, G. H. *Chem. Commun.* **2000**, 1037. (c) Becker, G.; Golla, W.; Grobe, J.; Klinkhammer, K. W.; Van, D. L.; Maulitz, A. H.; Mundt, O.; Oberhammer, H.; Sachs, M. *Inorg. Chem.* **1999**, *38*, 1099. (d) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch., B* **1988**, *43*, 952. (e) Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 1699. (f) Becker, V. G.; Mundt, O.; Rössler, M. *Z. Anorg. Allg. Chem.* **1980**, *468*, 55. (g) Richter, V. R.; Kaiser, J.; Sieler, J.; Hartung, U. H.; Peter, C. *Acta Crystallogr., Sect. B* **1977**, *33*, 1887.

[15] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[16] Sterenberg, B. T.; Carty, A. J. *J. Organomet. Chem.* **2001**, *617–618*, 696.

[17] Eichele, K.; Wasylishen, R. E.; Schurko, R. W.; Burford, N.; Whitla, W. A. *Can. J. Chem.* **1996**, *74*, 2372.

[18] Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914.