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Synthesis and Reactivity of a Phosphite−Boryl Complex of Molybdenum: Formation of (η^5-C_5Me_5)Mo(CO)$_3$(BH$_2$·phosphite) and Its Mo−B, B−P, and B−H Bond Reactions

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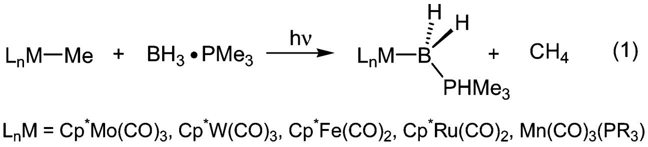
*Summary: The photoreaction of Cp*Mo(CO)$_3$Me in the presence of BH$_3$·P(OMe)(NMeCH$_2$)$_2$ produced the phosphite−boryl Mo complex Cp*Mo(CO)$_3${BH$_2$·P(OMe)(NMeCH$_2$)$_2$}. The complex reacts with MeI and PMe$_3$ with Mo−B and B−P bond cleavage, respectively, and is gradually converted in solution into Cp*Mo(CO)$_2$(H){P(OMe)(NMeCH$_2$)$_2$} with B−H bond cleavage.*

Phosphine−borane (BH$_3$·PR$_3$) is isoelectronic and isostructural with methane. B−H bond activation of phosphine−borane by a transition-metal complex is a subject of current interest, because this reaction can be considered as a model reaction of alkane C−H activation.[1] Many examples of B−H bond activation by transition-metal complexes have been reported for tricoordinate boranes.[2,3] In contrast, little is known of B−H bond activation of tetracoordinate (sp^3-type) boranes such as BH$_3$·PR$_3$. The first example of such B−H bond activation was reported in 1990 by Fehlner and co-workers in the reaction of BH$_3$·THF with Co$_2$(CO)$_8$.[4] The product, Co(CO)$_4$(BH$_2$·THF), is thermally unstable. In the same year, Puddephatt and co-workers prepared a transition-metal complex with a Co−BH$_2$·base unit, [(η^1-dppm)(CO)$_2$Co(μ-dppm)BH$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$),[5] but it is not clear whether B−H bond activation of the BH$_3$·base took place because the complex was prepared in one step by reduction of CoX$_2$ (X = Cl, Br) with NaBH$_4$ in the presence of dppm and CO.

Shimoi and co-workers reported elegant examples of B−H activation of a tetracoordinate borane (eq 1). The photolysis of



Cp*M(CO)$_3$Me (Cp* = η^5-C$_5$Me$_5$, M = Mo, W) in the presence of BH$_3$·PMe$_3$ produced Cp*M(CO)$_3$(BH$_2$·PMe$_3$).[6] They also synthesized Cp*M(CO)$_2$(BH$_2$·PMe$_3$) (M = Fe, Ru)[7] and Mn(CO)$_4$(PR$_3$)(BH$_2$·PMe$_3$) (PR$_3$ = PEt$_3$, PMe$_2$Ph).[8] Shimoi's method, photoreaction of a methyl complex of a transition metal with a phosphine−borane to produce a phosphine−boryl complex, is useful. However, examples shown to date have been limited to trimethylphosphine−borane. Herein we demonstrate that the photoreaction of Cp*Mo(CO)$_3$Me in the presence of a diamino-substituted phosphite−borane, BH$_3$·P(OMe)(NMeCH$_2$)$_2$ (**1a**),[9] produced a phosphite−boryl Mo complex, Cp*Mo(CO)$_3${BH$_2$·P(OMe)(NMeCH$_2$)$_2$} (**1b**). We also report the reactivity of **1b** involving Mo−B bond cleavage by MeI, phosphite substitution by PMe$_3$, and B−H bond activation.

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(1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(2) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.

(3) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.

(4) Basil, J. D.; Aradi, A. A.; Bhattacharyya, N. K.; Rath, N. P.; Eigenbrot, C.; Fehlner, T. P. *Inorg. Chem.* **1990**, *29*, 1260.

(5) Elliot, D. J.; Levy, C. J.; Puddephatt, R. J.; Holah, D. G.; Hughes, A. N.; Magnuson, V. R.; Moser, I. M. *Inorg. Chem.* **1990**, *29*, 5014.

(6) Kawano, Y.; Yasue, T.; Shimoi, M. *J. Am. Chem. Soc.* **1999**, *121*, 11744.

(7) Yasue, T.; Kawano, Y.; Shimoi, M. *Chem. Lett.* **2000**, 58.

(8) Yasue, T.; Kawano, Y.; Shimoi, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1727.

(9) With phosphite−boranes, see: Rana, G.; Vyakaranam, K.; Spielvogel, B. F.; Hosmane, N. S. *Inorg. Chim. Acta* **2003**, *344*, 249.

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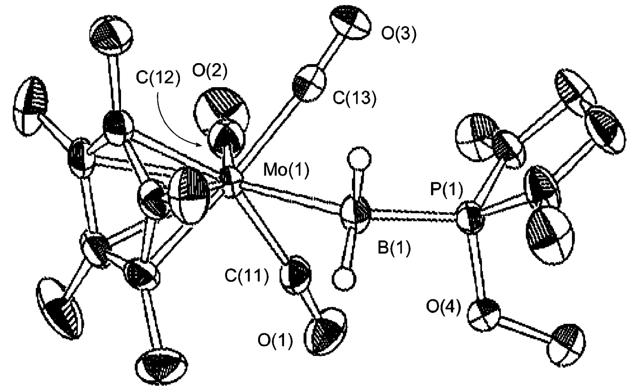
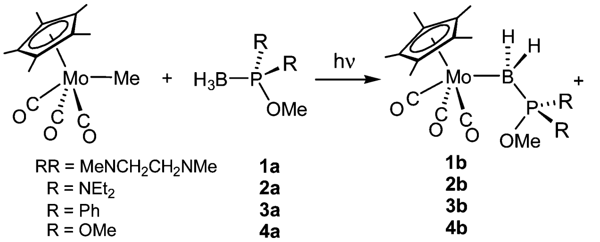


Figure 1. ORTEP drawing of **1b** with ellipsoids given at the 30% probability level. Hydrogen atoms, except for boryl hydrogens, are omitted for simplicity. Selected bond distances (Å): Mo(1)−B(1), 2.472(4); B(1)−P(1), 1.903(4). Selected bond angles (deg): Mo(1)−B(1)−P(1), 123.5(2); B(1)−P(1)−O(4), 105.6(2).

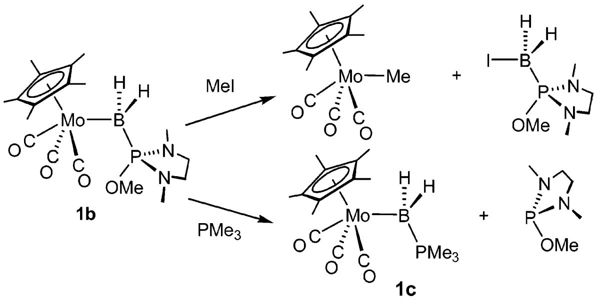
The phosphite−boryl molybdenum complex Cp*Mo(CO)$_3$-{BH$_2$•P(OMe)(NMeCH$_2$)$_2$} (**1b**) was synthesized by the photoreaction of a hexane solution containing BH$_3$•P(OMe)-(NMeCH$_2$)$_2$ (**1a**) and Cp*Mo(CO)$_3$Me (eq 2). **1b** has been characterized by conventional spectroscopic and analytical methods and X-ray crystallography. The molecular structure of **1b** is depicted in Figure 1 with the atomic numbering scheme. The Mo has a four-legged piano-stool geometry bearing an η^5-C$_5$Me$_5$ group, three terminal CO ligands, and a BH$_2$P(OMe)-(NMeCH$_2$)$_2$ ligand with a Mo−B σ-bond. The Mo−B bond distance (2.472(4) Å) and B−P bond distance (1.903(4) Å) are shorter than those in the previously reported trimethylphosphine−boryl complex Cp*Mo(CO)$_3$(BH$_2$•PMe$_3$) (**1c**; Mo−B = 2.495(5) Å and B−P = 1.945(5) Å).[6]



(2)

In the proton-coupled ^{11}B NMR spectrum, **1b** exhibits a triplet of doublets coupled with two protons and a phosphorus atom (J_{BH} = 120.4 Hz, J_{BP} = 130.0 Hz), showing the existence of a BH$_2$−P fragment. The ^{31}P NMR spectrum shows a quartet at 103.6 ppm (J_{PB} = 127.6 Hz). The starting phosphite−borane **1a** shows a quartet of doublets at −42.2 ppm (J_{BH} = 96.3 Hz, J_{BP} = 96.3 Hz) in the ^{11}B NMR spectrum and a quartet at 113.3 ppm (J_{PB} = 102.1 Hz) in the ^{31}P NMR spectrum. As one goes from **1a** to **1b**, the ^{11}B NMR chemical shift moves ca. 13 ppm to lower field and the ^{31}P NMR chemical shift moves ca. 10 ppm to higher field, which corresponds to the relation between BH$_3$•PMe$_3$ and **1c** (12 ppm lower field shift in the ^{11}B NMR and 3 ppm higher field shift in the ^{31}P NMR). The ^{1}H and ^{13}C NMR spectra of **1b** support the structure shown by X-ray analysis.

Scheme 1

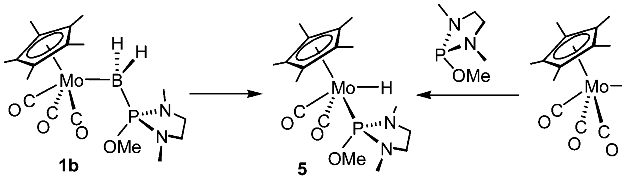


The photoreactions of other phosphite−boranes BH$_3$•P(OMe)-R$_2$ (R = NEt$_2$, Ph, OMe) were examined. In all cases, the ^{11}B and ^{31}P NMR spectra of the respective reaction mixtures suggested the formation of the corresponding phosphite−boryl complex. However, these compounds were thermally unstable, so that attempted isolation was not successful. BH$_3$•P(OPh)$_3$ did not react under the reaction conditions.

The ν(CO) IR bands of **1b** (1966 and 1880 cm^{-1}) are 42−49 cm^{-1} lower than those of Cp*Mo(CO)$_3$Me (2005 and 1929 cm^{-1}) but 24−37 cm^{-1} higher than those of the corresponding trimethylphosphine−boryl complex **1c** (1942 and 1843 cm^{-1}). Since strong M$^{\delta-}$−B$^{\delta+}$ polarization has been suggested for **1c**,[6] similar polarization is expected for **1b**, but the extent is not as great as that of **1c**.

The reaction of **1b** with MeI yielded Cp*Mo(CO)$_3$Me and BH$_2$I•P(OMe)(NMeCH$_2$)$_2$ (Scheme 1). The reactivity is similar to that shown by **1c** and is explained by M$^{\delta-}$−B$^{\delta+}$ polarization. The reaction of the phosphine−borane complex **1c** with HCl, Me$_3$SiCl, and PMe$_3$ has been reported to cause Mo−B bond cleavage. However, B−P bond cleavage has not been reported. Complex **1b** showed such reactivity in the reaction with an equimolar amount of PMe$_3$. The products were **1c** and free P(OMe)(NMeCH$_2$)$_2$. This phosphite−phosphine displacement reaction is quantitative, according to ^{31}P NMR measurements. In contrast, **1c** reacted with PMe$_3$ to give [Cp*Mo(CO)$_3$]$^-$ [H$_2$B(PMe$_3$)$_2$]$^+$, where the Mo−B bond is cleaved (Scheme 1).[6]

Complex **1b** is stable in the solid state unless it is exposed to air. However, it was found to be converted gradually into Cp*Mo(CO)$_2$(H){P(OMe)(NMeCH$_2$)$_2$} (**5**) in solution (eq 3).



(3)

The C$_6$D$_6$ solution of **1b** was monitored by NMR spectroscopy. In the ^{31}P NMR spectrum, the quartet at 103.6 ppm due to **1b** decreased in intensity and finally disappeared. Instead, a singlet at 183.6 ppm (a doublet with J_{PH} = 62.7 Hz in the proton-coupled measurement) appeared. In the ^{1}H NMR spectrum, a distinctive doublet attributable to a hydride ligand appeared at −5.81 ppm (J_{PH} = 62.7 Hz). The conversion was complete within 24 h at room temperature and was quantitative according to the ^{31}P NMR monitoring. In the ^{11}B NMR spectrum, no new signals were observed; thus, the fate of boron was not clear. It was also found that **5** can be prepared by reaction of Cp*Mo-(CO)$_3$H with P(OMe)(NMeCH$_2$)$_2$[10,11] and characterized by X-ray structure analysis.

The reaction pathway from **1b** to **5** is not clear at present, but it is possible that Cp*Mo(CO)$_3$ abstracts a H from the B to give CpMo(CO)$_3$H, which then reacts with the P(OMe)-

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[10] (a) Asdar, A.; Lapinte, C.; Toupet, L. *Organometallics* **1989**, *8*, 2708. (b) Tudoret, M.-J.; Robo, M.-L.; Lapinte, C. *Organometallics* **1992**, *11*, 1419.

[11] Nakazawa, H.; Kubo, K.; Kai, C.; Miyoshi, K. *J. Organomet. Chem.* **1992**, *439*, C42.

[12] Ramirez, F.; Patwardham, A. V.; Kugler, H. J.; Smith, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 6276.

$(NMeCH_2)_2$ formed in solution to give **5**. Such a reaction has not been reported for the corresponding trimethylphosphine−boryl complex (**1c**).

Experimental Section. General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Hexane and pentane were distilled from sodium metal and were stored under a nitrogen atmosphere. $P(OMe)(NMeCH_2)_2$,[12] $P(OMe)(NEt_2)_2$,[13] and $P(OMe)Ph_2$,[14] were prepared according to the literature methods. $Cp^*Mo(CO)_3Me$[15] and $Cp^*Mo(CO)_3H$[16] were prepared by the published procedures.

Photoirradiation was performed with a 400 W medium-pressure mercury arc lamp at 0 °C. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. A JEOL LA-300 multinuclear spectrometer and JEOL JNM-AL400 spectrometer were used to obtain ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra. ^1H and ^{13}C NMR data were referenced to Me_4Si. ^{11}B and ^{31}P NMR data were referenced to $BF_3{\cdot}OEt_2$ and 85% H_3PO_4, respectively.

Preparation of $Cp^*Mo(CO)_3\{BH_2{\cdot}P(OMe)(NMeCH_2)_2\}$ (1b). $BH_3{\cdot}P(OMe)(NMeCH_2)_2$ (**1a**; 178 mg, 1.10 mmol) was added to a solution of $Cp^*Mo(CO)_3Me$ (495 mg, 1.50 mmol) at 0 °C. After photoirradiation of the solution for 3 h,[6] volatile materials were removed under reduced pressure. The orange powder thus formed was washed with hexane and dried in vacuo to give 500 mg (1.05 mmol) of $Cp^*Mo(CO)_3\{BH_2{\cdot}P(OMe)(NMeCH_2)_2\}$ (**1b**; 70% yield based on $Cp^*Mo(CO)_3Me$ and 95% yield based on **1a**). The reaction of $Cp^*Mo(CO)_3Me$ with **1a** in a 1:1 molar ratio gave a low isolated yield of **1b** (43%). Use of a slight excess of $Cp^*Mo(CO)_3Me$ is important to obtain a sufficient isolated yield of **1b**. Anal. Calcd for $C_{18}H_{30}BN_2O_4PMo$: C, 45.40; H, 6.35; N, 5.88. Found: C, 45.17; H, 6.19; N, 5.56. ^1H NMR (300 MHz, C_6D_6, 25 °C; δ, ppm): 1.93 (s, 15H, C_5Me_5), 2.41−2.69 (m, 4H, NCH_2CH_2N), 2.56 (d, $J_{PH} = 9.3$ Hz, 6H, NMe), 2.93 (d, $J_{PH} = 11.2$ Hz, 3H, OMe). ^{11}B NMR (96.3 MHz, C_6D_6, 25 °C; δ, ppm): −29.6 (dt, $J_{PB} = 130.0$ Hz, $J_{HB} = 120.4$ Hz). $^{13}C\{^1H\}$ NMR (75.3 MHz, C_6D_6, 25 °C; δ, ppm): 10.7 (s, C_5Me_5), 32.5 (d, $J_{PC} = 1.5$ Hz, NMe), 32.6 (d, $J_{PC} = 1.5$ Hz, NMe), 49.7 (s, OMe), 50.1 (d, $J_{PC} = 1.5$ Hz, NCH_2), 50.3 (d, $J_{PC} = 2.3$ Hz, NCH_2), 102.6 (s, C_5Me_5), 235.1 (br, CO), 236.0 (s, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 25 °C; δ, ppm): 103.6 (q, $J_{BP} = 127.6$ Hz). IR (hexane; cm^{-1}): ν(CO) 1966 (s), 1880 (s).

^{11}B and ^{31}P NMR Spectra of 2a,b, 3a,b, and 4a,b. ^{11}B NMR (96.3 MHz, hexane, 25 °C; δ, ppm): **2a**, −40.9 (d, $J_{PB} = 95.3$ Hz); **2b**, −31.3 (d, $J_{PB} = 116.5$ Hz); **3a**, −40.1 (d, $J_{PB} = 59.7$ Hz); **3b**, −29.9 (d, $J_{PB} = 73.2$ Hz); **4a**, −45.7 (d, $J_{PB} = 94.2$ Hz); **4b**, −35.6 (d, $J_{PB} = 128.5$ Hz). ^{31}P NMR (121.5 MHz, hexane, 25 °C; δ, ppm): **2a**, 121.2 (q, $J_{BP} = 93.6$ Hz); **2b**, 112.5 (q, $J_{BP} = 113.0$ Hz); **3a**, 109.8 (q, $J_{BP} = 59.5$ Hz); **3b**, 106.0 (q, $J_{BP} = 74.1$ Hz); **4a**, 121.1 (q, $J_{BP} = 95.6$ Hz); **4b**, 108.9 (q, $J_{BP} = 125.0$ Hz).

Preparation of $Cp^*Mo(CO)_2(H)\{P(OMe)(NMeCH_2)_2\}$ (5). To a solution of $Cp^*Mo(H)(CO)_3$ (3.09 g, 9.77 mmol) in hexane (30 mL) was added $P(OMe)(NMeCH_2)_2$ (**1a**; 1.6 mL, 10.0 mmol) at room temperature. After 1 h, volatile materials were removed under reduced pressure. The resulting orange-brown materials were dissolved in 2 mL of hexane. After it was cooled to −78 °C, the reaction mixture led to the formation of an orange solid, which was washed with 2 mL of hexane at −78 °C, collected by filtration, and dried in vacuo to give an orange powder of $[Cp^*Mo(H)(CO)_2\{P(OMe)(NMeCH_2)_2\}]$ (**5**; 3.62 g, 8.30 mmol, 85%). Anal. Calcd for $C_{17}H_{29}N_2O_3PMo$: C, 46.79; H, 6.70; N, 6.42. Found: C, 46.62; H, 6.71; N, 6.21. ^1H NMR (400 MHz, C_6D_6, 25 °C; δ, ppm): −5.81 (d, $J_{HP} = 62.7$ Hz, 1H, MoH), 1.89 (s, 15H, Cp*), 2.62 (d, $J_{HP} = 11.6$ Hz, 6H, NMe), 2.71 (m, 2H, CH_2), 2.90 (m, 2H, CH_2), 3.04 (d, $J_{HP} = 11.6$ Hz, 3H, OMe). $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 25 °C; δ, ppm): 11.3 (s, $C_5(CH_3)_5$), 33.5 (d, $J_{CP} = 10.6$ Hz, NMe), 51.2 (d, $J_{CP} = 5.3$ Hz, OMe), 52.2 (d, $J_{CP} = 6.8$ Hz, CH_2), 103.0 (s, C_5Me_5), 241.5 (br, CO). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 25 °C; δ, ppm): 183.58 (s). IR (C_6D_6; cm^{-1}): ν(CO) 1930 (s), 1851 (s).

X-ray Crystallography. Crystals of **1b** and **5** suitable for X-ray diffraction studies were mounted in glass capillaries. Data for **1b** were collected at −73 °C on Rigaku RAXIS-IV imaging plate diffractometer equipped with monochromated Mo Kα radiation. Calculations for **1b** were performed with the teXsan crystallographic software package of Molecular Structure Corp. Data for **5** were collected at −70 °C on a Rigaku AFC-7/Mercury CCD area-detector diffractometer equipped with monochromated Mo Kα radiation. Calculations for **5** were performed with the CrystalClear software package of Molecular Structure Corp. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms, except for the MoH hydrogen of **5**, were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters.

X-ray Crystal Structure Determination of 1b. Orange crystals of **1b** suitable for an X-ray diffraction study were obtained by cooling a hexane solution to −20 °C for a few days. Crystal data: $C_{18}H_{30}N_2BO_4PMo$, $M_r = 476.17$, orange plate, $0.50 \times 0.35 \times 0.05$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.2680(2)$ Å, $b = 14.5460(4)$ Å, $c = 17.1080(5)$ Å, $\beta = 105.371(1)°$, $V = 2223.9(1)$ Å^3, $Z = 4$, μ(Mo Kα) = 68.4 mm^{-1}, $D_{calcd} = 1.422$ g/cm^3, 5534 reflections collected, 4600 ($I > 3\sigma(I)$) unique reflections used in all calculations, 245 variables, $R = 0.042$, $R_w = 0.085$, goodness of fit 1.48.

X-ray Crystal Structure Determination of 5. Yellow crystals of **5** suitable for an X-ray diffraction study were obtained by cooling a pentane solution to −20 °C for a few days. Crystal data: $C_{17}H_{29}N_2O_3PMo$, $M_r = 436.34$, yellow prisms, $0.30 \times 0.08 \times 0.17$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.829(4)$ Å, $b = 8.886(4)$ Å, $c = 13.847(5)$ Å, $\alpha = 90.660(4)°$, $\beta = 101.191(7)°$, $\gamma = 111.629(9)°$, $V = 986.6(6)$ Å^3, $Z = 2$, μ(Mo Kα) = 76.2 mm^{-1}, $D_{calcd} = 1.469$ g/cm^{-3}, 4349 reflections collected, 4211 ($I > 2\sigma I$) unique reflections used in all calculations, 238 variables, $R = 0.048$, $R_w = 0.121$, goodness of fit 1.17.

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Supporting Information Available: Tables giving crystal data and figures giving structural views of **1b** and **5**; X-ray crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Nakazawa, H.; Kadoi, Y.; Miyoshi, K. *Organometallics* **1989**, *8*, 2851.

[14] Arbuzov, B. A.; Grechkin, N. P. *Zh. Obshch. Khim.* **1950**, *20*, 107; *Chem. Abstr.* **1950**, *44*, 5832.

[15] Roger, C.; Tudoret, M. J.; Guerchais V.; Lapinte, C. *J. Organomet. Chem.* **1989**, *365*, 347.

[16] (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357. (b) Asdar, A.; Tudoret, M. J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353.