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First Chemical Transformations of Lanthanide Borohydride Compounds: Synthesis and Crystal Structures of $[(\eta\text{-}C_8H_8)Nd(BH_4)(THF)]_2$ and $[(\eta\text{-}C_8H_8)Nd(THF)_4][BPh_4]$

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*Summary: Reaction of $Nd(BH_4)_3(THF)_3$ with K_2COT ($COT = \eta\text{-}C_8H_8$) in tetrahydrofuran (THF) gave the first (cyclooctatetraene)lanthanide borohydride, (COT)Nd-$(BH_4)(THF)_2$ (**1**). By treatment with $NHEt_3BPh_4$, **1** was transformed into $[(COT)Nd(THF)_4][BPh_4]$ (**3**), a unique example of a (cyclooctatetraene)lanthanide cation; both **1** and **3** gave (COT)Nd(Cp*)(THF) ($Cp^* = \eta\text{-}C_5Me_5$) upon reaction with KCp*.*

Although they have been known for a long time, the lanthanide borohydrides $Ln(BH_4)_3(THF)_x$ (Ln = lanthanide metal, THF = tetrahydrofuran) have received scant attention and their chemical reactivity has not been evaluated.[1,2] With the exception of $(THF)(BH_4)_2$-$Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(THF)_2$, which was isolated from the reaction of $Nd(BH_4)_3(THF)_2$ with KC_7H_9,[3] the rare trivalent organolanthanide borohydrides are limited to bis(cyclopentadienyl) complexes;[4−7] these were prepared by treatment of the corresponding halides with $LiBH_4$ or $NaBH_4$. The scarcity of lanthanide borohydrides appears most peculiar in comparison to the wealth of inorganic and organometallic compounds that have been synthesized from $U(BH_4)_4$ and $U(BH_4)_3$-$(THF)_4$.[8,9] These complexes, which in some cases were more stable than their chloride analogues and which could be conveniently converted into new derivatives by further reaction of the BH_4 groups with anionic reagents or proton acidic substrates, revealed the utility of the borohydride ligand in f-element chemistry. Taking this background into account, we decided to investigate the reactivity of the lanthanide borohydrides. With the synthesis of $(COT)Nd(BH_4)(THF)_2$ (**1**), $[(COT)Nd(THF)_4]$-$[BPh_4]$ (**3**), and (COT)Nd(Cp*)(THF) (**4**) ($COT = \eta\text{-}C_8H_8$, $Cp^* = \eta\text{-}C_5Me_5$), we present herein new chemical transformations of Ln-BH_4 compounds and demonstrate that the complex $Ln(BH_4)_3(THF)_x$ can be a valuable precursor of organometallic derivatives, in particular of cationic species. We also describe the crystal structures of $[(COT)Nd(BH_4)(THF)]_2$ (**2**), which, like that of $[(C_5H_3\text{-}Bu^t{}_2)_2Ce(BH_4)]_2$,[6] exhibits the $(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2$ coordination mode of the BH_4 ligand, and of **3**, which is a unique example of a (cyclooctatetraene)lanthanide cation.

Reaction of $Nd(BH_4)_3(THF)_3$[2] (1507 mg, 3.72 mmol) with $K_2C_8H_8$ (678 mg, 3.72 mmol) in THF (30 mL) gave the mono(cyclooctatetraene) compound $(COT)Nd(BH_4)$-$(THF)_2$ (**1**) (Scheme 1). After 24 h at 20 °C, the off-white precipitate of KBH_4 was filtered off and the green solution was evaporated, leaving the green powder of **1**, which was crystallized from THF−pentane (1358 mg, 3.24 mmol, 87%). The NMR spectrum of **1** (pyridine-d_5, 20 °C)[10] exhibits a singlet at −10.27 ppm and a broad resonance at 44 ppm corresponding respectively to the

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(1) (a) Klejnot, O. Dissertation, University of Munich, 1955. (b) Zange, E. *Chem. Ber.* **1960**, *93*, 652. (c) Mirsaidov, U.; Kurbonbekov, A.; Rotenberg, T. G.; Dzhuraev, K. *Inorg. Mater.* (*Transl. of Neorg. Mater.*) **1978**, *14*, 1340. (d) Mirsaidov, U.; Rakhimova, A.; Dymova, T. N. *Inorg. Mater.* (*Transl. of Neorg. Mater.*) **1979**, *15*, 1248. (e) Mirsaidov, U.; Shaimuradov, I. B.; Khikmatov, M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1986**, *31*, 753. See also: *Gmelin Handbook of Inorganic and Organometallic Chemistry*; Springer-Verlag: Berlin, 1991; RE Main Vol. C 11b, p 472.

(2) (a) Mirsaidov, U.; Rotenberg, T. G.; Dymova, T. N. *Dokl. Akad. Nauk. Tadzh. SSR* **1976**, *19*, 30; *Chem. Abstr.* **1976**, *85*, 136374. (b) $Nd(BH_4)_3(THF)_3$ was conveniently prepared in 79% yield by a slight modification of the described procedure. A round-bottom flask was charged with $NdCl_3$ (3.253 g, 12.98 mmol) and $NaBH_4$ (1.628 g, 43.02 mmol; 10% excess instead of 50−100%), and THF (150 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 60 °C for 48 h (instead of 12 h at 20 °C). The solvent was evaporated off and the residue dried under dynamic vacuum for 16 h. The solid was thoroughly extracted with THF (50 mL) and the solution was filtered and evaporated, leaving the product as a pale violet pinkish powder (4.152 g, 10.25 mmol). ^1H NMR (200 MHz): in pyridine-d_5, δ 79 ($w_{1/2} = 1350$ Hz, 12 H, BH_4), 3.48 and 1.45 (s, 12 H + 12 H, THF); in THF-d_8, δ 92 ($w_{1/2} = 470$ Hz, BH_4).

(3) Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2501.

(4) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1983**, 206.

(5) Deng, D.; Zheng, X.; Qian, C.; Sun, J.; Zhang, L. *J. Organomet. Chem.* **1994**, *466*, 95.

(6) Lobkovsky, E. B.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L.; Antipin, M. Y. *J. Organomet. Chem.* **1991**, *406*, 343.

(7) (a) Marks, T. J.; Grynkewich, G. W. *Inorg. Chem.* **1976**, *15*, 1302. (b) Schumann, H.; Genthe, W. *J. Organomet. Chem.* **1981**, *213*, C7. (c) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194. (d) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, M.; Sayer, B. G.; Thompson, J. I. A.; McGlinchey, J. *Inorg. Chem.* **1984**, *23*, 1072. (e) Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289. (f) Laske, D. A.; Duchateau, R.; Teuben, J. H.; Spek, A. L. *J. Organomet. Chem.* **1993**, *462*, 149.

(8) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (b) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

(9) (a) Ephritikhine, M. *New J. Chem.* **1992**, *16*, 451. (b) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.

(10) ^1H NMR spectra (200 MHz, 20 °C) and elemental analyses of the complexes are as follows. For **1** in pyridine-d_5: δ 44 (br, $w_{1/2} = 360$ Hz, 4H, BH_4), 3.49 and 1.45 (s, 8 H + 8 H, THF), −10.27 (s, 8 H, COT). Anal. Calcd for $C_{16}H_{28}BO_2Nd$: C, 47.16; H, 6.93; B, 2.65. Found: C, 46.88; H, 6.78; B, 2.74. For **3** in pyridine-d_5: δ 7.89 (br t, 8 H, *o*-Ph), 7.10 (t, $J = 8.5$ Hz, 8 H, *m*-Ph), 6.93 (t, $J = 7.0$ Hz, 4 H, *p*-Ph), 3.49 and 1.45 (s, 16 H + 16 H, THF), −10.88 (s, 8 H, COT). Anal. Calcd for $C_{48}H_{60}BO_4Nd$: C, 67.34; H, 7.06; B, 1.26. Found: C, 66.52; H, 6.59; B, 1.32. For **4** in benzene-d_6: δ 4.41 (br, $w_{1/2} = 90$ Hz, 15 H, Cp*), 3.84 (s, $w_{1/2} = 25$ Hz, 4 H, THF), −3.61 (br s, $w_{1/2} = 85$ Hz, 4 H, THF), −16.2 (br s, $w_{1/2} = 140$ Hz, 8 H, COT). Anal. Calcd for $C_{22}H_{31}ONd$: C, 57.98; H, 6.86; O, 3.51. Found: C, 57.72; H, 6.76; O, 3.33.

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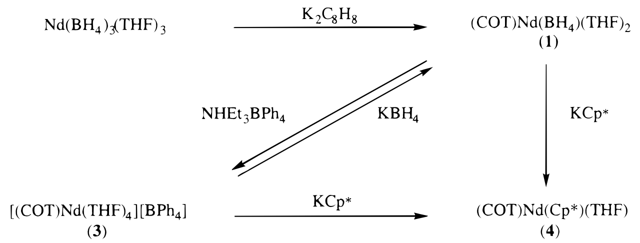
Scheme 1. Synthesis of the Compounds



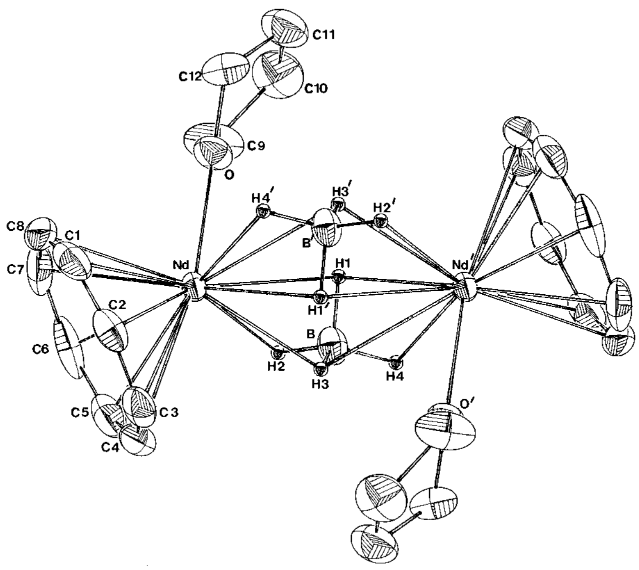


Figure 1. ORTEP drawing of [(COT)Nd(BH$_4$)(THF)]$_2$ with probability ellipsoids drawn at the 30% level. Atoms labeled with primes are related to unlabeled atoms by the center of symmetry.

C_8H_8 and BH_4 ligands. In the IR (Nujol) spectrum, the sharp singlet at 2424 cm^{-1} and the broad band centered at 2000 cm^{-1} are characteristic of tridentate BH_4 groups,[8] indicating that **1** would adopt a monomeric structure, like the other two organoneodymium borohydrides $(C_5H_3\{SiMe_3\}_2)_2Nd(BH_4)(THF)$[4] and $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$,[5] and in contrast to the dimeric chloride analogue $[(COT)NdCl(THF)_2]_2$.[11] Crystallization of **1** from benzene led to the dissociation of a THF molecule, with formation of green crystals of $[(COT)Nd(BH_4)(THF)]_2$ (**2**). The IR spectrum of **2** shows, in the 2000−2500 cm^{-1} region, a single broad and strong absorption centered at 2255 cm^{-1}, which is diagnostic of bridging borohydride ligands.[6,8] The dimeric structure of **2** was determined by X-ray crystallography (Figure 1).[12] The centrosymmetric complex is built up of two monomeric units which are bridged by two BH_4 groups. Each Nd atom is in a three-legged piano-stool environment, defined by the boron and oxygen atoms and the C_8H_8 ligand; the angles B−Nd−B′, B−Nd−O, and B′-Nd−O are respectively 82.9(2), 84.3(2), and 85.0(2)° and the angles COT−Nd−B, COT−Nd−B′, and COT−Nd−O (COT is the centroid of the C_8H_8 ligand) are 129.6(1), 132.9(1), and 125.49(9)°. Coordination of the eight-membered planar ring (within ±0.02 Å) is quite similar to that found in other mono(cyclooctatetraene)neodymium compounds,[13] with Nd−C bond lengths ranging from 2.626(6) to 2.644(6) Å (average 2.63(1) Å) and the Nd−COT(centroid) distance equal to 1.906(6) Å. The Nd−O bond distance of 2.481(5) Å is also unexceptional. Most interesting is the ligation mode of the BH_4 ligand; the boron atom is linked to each metal center via a μ_2-hydrogen (H(2) and H(4)), and the other two H atoms (H(1) and H(3)) bridge the B and both Nd atoms in a μ_3 fashion. This coordination type of the borohydride ligand was encountered only once in the cerium compound $[(C_5H_3Bu^t_2)_2Ce(BH_4)]_2$.[6] The Nd···B distances (2.875(6) and 2.941(6) Å), which may be compared with the Ce···B distances (2.93(2) Å), are longer than that of 2.664(25) Å determined in $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$,[5] the sole neodymium borohydride to have been previously crystallographically characterized. There is apparently no significant difference in the bond distances Nd−μ_2-H and Nd−μ_3-H, or B−μ_2-H and B−μ_3-H, which vary respectively from 2.52 to 2.93 Å and 1.12 to 1.14 Å; the average values of 2.72 and 1.13 Å for the metal−hydrogen and boron−hydrogen distances in **2** are similar to those of 2.69 and 1.19 Å in the cerium complex. The H−B−H angles in **2** range from 99.1(5) to 115.5(5)°, and the tetrahedral BH_4 group seems much less distorted than in the cerium complex, where these angles vary from 87.7(1) to 139.4(1)°. In considering the few bridging borohydride compounds of the f-elements which have been characterized by their crystal structure, it is interesting to note that the $(\mu_3\text{-H})_2B(\mu_2\text{-H})_2$ ligation was observed in the dimeric lanthanide complexes **2** and $[(C_5H_3Bu^t_2)_2Ce(BH_4)]_2$ while the $(\mu_2\text{-H})_2B(\mu_2\text{-H})_2$ coordination mode was

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[11] (a) Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitweiser, A. *J. Am. Chem. Soc.* **1973**, *95*, 8650. (b) Shen, Q.; Chen, W.; Jin, Y.; Shan, C. *Pure Appl. Chem.* **1988**, *60*, 1251. (c) Edelmann, F. T. *New J. Chem.* **1995**, *19*, 535.

[12] Crystal data for **2**: formula $C_{24}H_{40}B_2O_2Nd_2$, monoclinic, space group $P2_1/c$, a = 9.801(5) Å, b = 11.430(4) Å, c = 12.576(4) Å, β = 110.11(3)°, V = 1323(1) Å^3, Z = 2, d_{calcd} = 1.684 g cm^{-3}. X-ray diffraction data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Reflections (1736) with 2° < 2θ < 50° were collected by the ω/2θ-scan technique. Three standard reflections were measured after each 1 h; a decay was observed (2% in 49 h) and linearly corrected. The data were corrected for Lorentz−polarization effects and absorption (ψ scan). The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. H atoms of the BH_4 ligand were found in the last Fourier diffraction map and introduced in the refinement at fixed positions. The COT and THF H atoms were introduced at calculated positions (C−H = 0.95 Å, B = 6 Å^2) and constrained to ride on their C atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MolEN system. The final R factor was 0.020 (R_w = 0.032) for 1736 reflections with $|F_o| > 3\sigma(F_o)$. Crystal data for **3**: formula $C_{48}H_{60}BO_4Nd$, monoclinic, space group $P2_1/n$, a = 11.275(7) Å, b = 26.972(7) Å, c = 13.936(2) Å, β = 91.33(3)°, V = 4237(4) Å^3, Z = 4, d_{calcd} = 1.342 g cm^{-3}. X-ray diffraction data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Reflections (3550) with 2° < 2θ < 44° were collected by the ω/2θ-scan technique. Three standard reflections were measured after each 1 h; a decay was observed (8% in 55 h) and linearly corrected. The data were corrected for Lorentz−polarization effects and absorption (ψ scan). The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. H atoms were introduced at calculated positions (C−H = 0.95 Å, B = 6 Å^2) and constrained to ride on their C atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MolEN system. The final R factor was 0.035 (R_w = 0.039) for 3550 reflections with $|F_o| > 3\sigma(F_o)$.

[13] (a) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625. (b) Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C10. (c) Zhang, S.; Jin, J.; Wei, G.; Chen, W.; Liu, J. *J. Organomet. Chem.* **1994**, *483*, 57. (d) Schumann, H.; Winterfeld, J.; Hemling, H.; Hahn, E.; Reich, P.; Brzezinka, K. W.; Edelmann, F. T.; Kilimann, U.; Schäfer, M.; Herbst-Irmer, R. *Chem. Ber.* **1995**, *128*, 395. (e) Jin, J.; Zhuang, X.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1995**, *490*, C8. (f) Xia, J.; Zhuang, X.; Jin, Z.; Chen, W. *Polyhedron* **1996**, *19*, 3399.

found in the polymeric uranium compounds $U(BH_4)_4$[14] and $U(BH_4)_4(OR_2)$ (R = Me, Et).[15]

Cationic complexes of the early transition metals and f-elements deserve special attention, since their participation in some catalytic processes has been recognized. With the exception of $[(Cp^*)La(CH\{SiMe_3\}_2)(THF)_3][BPh_4]$,[16] all the cationic organolanthanide complexes reported so far are bis(cyclopentadienyl) derivatives; these were most generally prepared by oxidation of the corresponding divalent compounds,[17] heterolytic cleavage of a metal-halide bond,[18] or protonolysis of a metal–carbon[16,17d,19] or metal–nitrogen[20] bond. We found that borohydride complexes could also be convenient precursors of cationic species, by protonation with acidic ammonium salts.[21] Treatment of **1** (545 mg, 1.30 mmol) with $NHEt_3BPh_4$ (548 mg, 1.30 mmol) in THF (40 mL) led, after 3 h at room temperature, to the formation of a pale green powder of $[(COT)Nd(THF)_4][BPh_4]$ (**3**), which was deposited from the light green solution; after filtering and drying under vacuum, **3** was isolated in 35% yield (390 mg, 0.46 mmol). Not surprisingly, **3** reacted with KBH_4 to give back the neutral complex **1** (quantitative yield by NMR). The NMR spectrum of **3** in pyridine-d_5 shows the COT signal at −10.88 ppm.[10] The crystals of **3** are composed of discrete cation–anion pairs.[12] The BPh_4 anion displays the expected geometry; an ORTEP drawing of the cation is represented in Figure 2. The Nd atom is in a slightly distorted square pyramidal environment; the COT–Nd–O and O–Nd–O angles average respectively 123(5) and 72.5(5)°. Coordination of the COT and THF ligands is unexceptional, with average Nd–C and Nd–O bond distances of 2.64(2) and 2.53(2) Å.

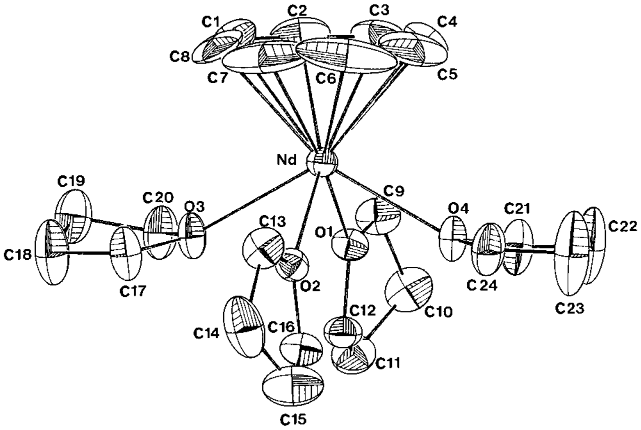

Figure 2. ORTEP drawing of $[(COT)Nd(THF)_4]^+$ with probability ellipsoids drawn at the 30% level.

Complexes **2** and **3** are valuable precursors for the synthesis of (COT)NdX derivatives, by reaction with anionic ligands (Scheme 1). For example, the mixed-ring compound (COT)Nd(Cp*)(THF) (**4**) was readily obtained in ca. 75% yield by treatment with 1 equiv of KCp* in THF and was isolated as a green powder after the usual workup. Ring opening of THF did not occur, in contrast to that observed in similar reactions of $[(Cp^*)_2Ln(THF)_x]^+$,[17b,22] suggesting that a COT ligand on a cation makes it less electrophilic than two Cp* ligands. Complex **4** is a new member of the family of compounds $(COT)Ln(Cp^*)(THF)_x$ ($x = 0, 1$); as expected from previous studies, the THF ligand in **4** is firmly attached to the metal center.[23] Further studies of the synthesis, structure, and reactivity of organolanthanide borohydride complexes are continuing.

Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **2** and **3** (20 pages). Ordering information is given on any current masthead page.

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[14] (a) Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; La Placa, S. J.; Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009. (b) Charpin, P.; Nierlich, M.; Vigner, D.; Lance, M.; Baudry, D. *Acta Crystallogr.* **1987**, *C43*, 1465.

[15] Rietz, R. R.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1978**, *17*, 653.

[16] Schaverien, C. J. *Organometallics* **1992**, *11*, 3476.

[17] (a) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620. (b) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D. *Organometallics* **1990**, *9*, 2124. (c) Deng, D.; Zheng, X.; Qian, C.; Sun, J.; Dormond, A.; Baudry, D.; Visseaux, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1665. (d) Schumann, H.; Winterfeld, J.; Keitsch, M. R.; Hermann, K.; Demtschuk, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1457. (e) Yuan, F.; Shen, Q.; Sun, J. *J. Organomet. Chem.* **1997**, *538*, 241.

[18] Hazin, P. N.; Bruno, J. W.; Schulte, G. K. *Organometallics* **1990**, *9*, 416.

[19] Heeres, H. J.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1991**, *414*, 351.

[20] Evans, W. J.; Kociok-Köhn, G.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1081.

[21] Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1994**, 847 and unpublished results.

[22] Schumann, H.; Glanz, M.; Hemling, H.; Görlitz, F. H. *J. Organomet. Chem.* **1993**, *462*, 155.

[23] (a) Bruin, P.; Booij, M.; Teuben, J. H.; Oskam, A. *J. Organomet. Chem.* **1988**, *350*, 17. (b) Schumann, H.; Köhn, R. D.; Reier, F. W.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388.