(Aminotroponiminato)yttrium Amides as Catalysts in Alkyne Hydroamination†

Markus R. Bürgstein, Helga Berberich, and Peter W. Roesky*

Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstrasse Geb. 30.45, D-76128 Karlsruhe, Germany

Received December 16, 1997

Summary: The synthesis and characterization of the mono- and bis(N-isopropyl-2-(isopropylamino)troponiminato)yttrium amides [(iPr)$_2$ATI]Y[N(SiMe$_3$)$_2$]$_2$ and [(iPr)$_2$ATI]$_2$Y[N(SiMe$_3$)$_2$], with the corresponding chloro precursors [[(iPr)$_2$ATI]YCl$_2$(THF)$_2$]$_2$ and [(iPr)$_2$ATI]$_2$YCl as starting materials, is reported together with their application as precatalysts for the hydroamination/cyclization of aminoalkynes.

Metallocenes of lanthanides[1] have proven to be highly efficient catalysts[2] for a variety of olefin transformations, including hydrogenation,[3] polymerization,[4] hydroamination,[5,6] hydrosilylation,[7] hydroboration,[8] and reductive or silylative cyclization of α,ω-dienes.[9] Recently, there has been significant research effort to substitute the cyclopentadienyl ligand[10] by anionic nitrogen-based bidentate ligand systems such as benzamidinates or (alkoxysilyl)amides for catalytic applications.[11] Lately, aminotroponiminates ([ATI]$^-$), which are known to stabilize coordinatively unsaturated main-group-metal complexes,[12] have been introduced as cyclopentadienyl alternatives for group 3,[13] group 4,[14] and the lanthanide elements.[13] The neutral ligand system is obtained in high yields in a three-step synthesis starting from tropolone. We report herein the synthesis and characterization of mono- and bis(*N*-isopropyl-2-(isopropylamino)troponiminato)yttrium amides, [(*i*Pr)$_2$-ATI]$_x$Y[N(SiMe$_3$)$_2$]$_y$ ($x = 1$, or 2; $y = 3 - x$), together with their application as catalysts for the hydroamination/cyclization of aminoalkynes, and some initial results regarding the mechanism. To our knowledge these complexes are the first cyclopentadienyl-free catalysts for the hydroamination/cyclization reaction.

The straightforward synthesis of the new catalysts is shown in Scheme 1. Transmetalation of the recently reported yttrium chloro complex [[(*i*Pr)$_2$ATI]YCl$_2$(THF)$_2$]$_2$ (**1**) with an excess of KN(SiMe$_3$)$_2$ in toluene, followed by workup in pentane, afforded the corresponding yttrium bis(amido) complex [(*i*Pr)$_2$ATI]Y[N(SiMe$_3$)$_2$]$_2$ (**2**) as a yellow crystalline solid. The new complex has been characterized by standard analytical/spectroscopic techniques,[15] and the solid-state structure was established by single-crystal X-ray diffraction.[16] The structure (Figure 1) reveals a distorted-tetrahedral arrangement

† Dedicated to Prof. Wolfgang A. Herrmann on the occasion of his 50th birthday.

(1) Review (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283−363. (c) Schumann, H. *Angew. Chem.* **1984**, *96*, 475−493; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474−493.

(2) (a) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247−276. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56.

(3) (a) Roesky, P. W.; Denninger, U.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4486-4492. (b) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765−1784. (c) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254. (d) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266−3268. (e) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118. (f) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401−1403.

(4) (a) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495−2502. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (c) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337−339. (d) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471−6473.

(5) (a) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705−4711. (b) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295−9306. (c) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3370−3372. (d) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707−708. (e) Li, Y.; Fu, P.-F.; Marks, T. J. *Organometallics* **1994**, *13*, 439−440. (f) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294. (g) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716−1718. (h) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108−4109.

(6) Hydroamination with Ac: Haskel, A.; Straub, T.; Eisen, M. E. *Organometallics* **1996**, *15*, 3773−3775.

(7) (a) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am Chem. Soc.* **1995**, *117*, 7157−7168. (b) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347−6351. (c) Sakakura, T.; Lautenschlager, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40−41. (d) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 8564−8566.

(8) (a) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121−128. (b) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220−9221.

(9) (a) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416. (b) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123−3125.

(10) Review: Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647−2669; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488.

(11) (a) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics*, **1997**, *16*, 3511−3522. (b) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291−2302.

(12) (a) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100−6105. (b) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123−9126. (c) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546−6551.

(13) Roesky, P. W. *Chem. Ber.* **1997**, *130*, 859−862.

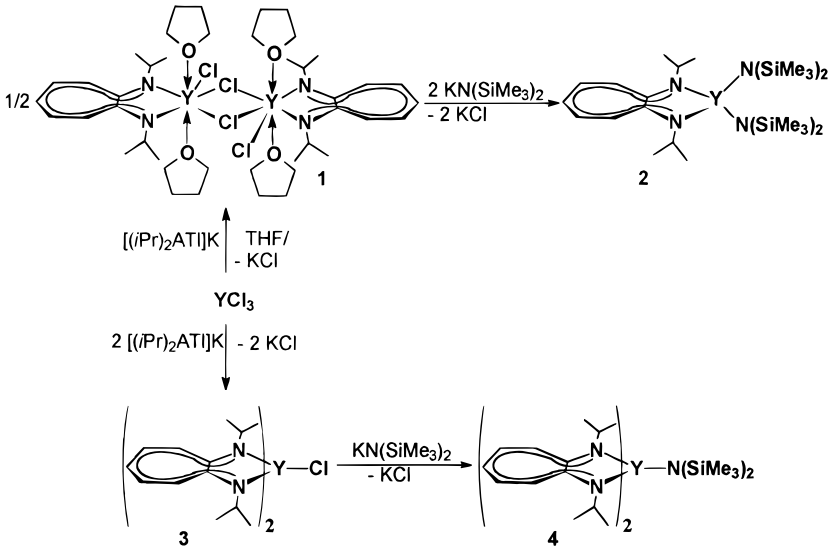
(14) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1996**, *35*, 6074−6079.

(15) **2**: Toluene (20 mL) was condensed at −196 °C onto a mixture of 181 mg (0.20 mmol) of **1** and 200 mg (1.0 mmol) of KN(SiMe$_3$)$_2$. The mixture was stirred for 18 h at room temperature. The solvent was evaporated under vacuum, and 30 mL of pentane was condensed onto the mixture. Then, the solution was filtered and the solvent removed. The remaining solid was recrystallized from pentane. Yield: 74%. ^{1}H NMR (C$_6$D$_6$, 250 MHz, 25 °C): δ 0.32 (s, 18H), 1.43 (d, 12H, J(H,H) = 6.4 Hz), 3.55 (sept, 2H), 6.23−6.31 (m, 3H), 6.78−6.87 (m, 2H). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 25 °C): δ 6.5, 22.3, 48.8, 114.9, 120.1, 136.3, 163.9. ^{29}Si NMR (C$_6$D$_6$, 49.7 MHz, 25 °C): δ −9.3. Anal. Calcd for C$_{25}$H$_{55}$N$_4$Si$_4$Y: C, 48.99; H, 9.04; N, 9.14. Found: C, 48.47; H, 9.01; N, 9.78.

(16) Crystal data for C$_{25}$H$_{55}$N$_4$Si$_4$Y: space group *Pbcn* (No. 60) with a = 18.536(9) Å, b = 13.376(11) Å, c = 13.509(14) Å, at 200 K, Z = 4, V = 3012(5) Å^3; The structure was solved by direct methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-squares techniques using 2097 reflections having $I > 2\sigma(I)$ to $R1$ = 0.034 and $wR2$ = 0.084. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-408286, the name of the author, and the journal citation.

S0276-7333(97)01107-2 CCC: $15.00
Publication on Web 03/20/1998

Scheme 1



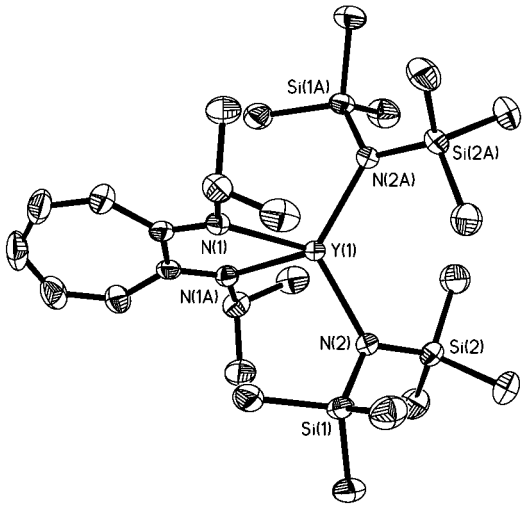


Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Important bond distances (Å) and angles [deg] are as follows: Y(1)−N(1), 2.315(3); Y(1)−N(2), 2.236(3); N(1)−Y(1)−N(1A), 69.00(14); N(2)−Y(1)−N(2A), 121.56(14); N(1A)−Y(1)−N(2), 101.98(10); N(1)−Y(1)−N(2), 126.66(9).

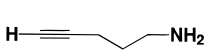
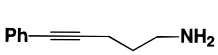
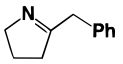
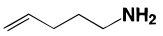
of the ligands around the yttrium atom. The molecule features C_2 symmetry along the Y−C(4) axis. The Y−N(1) distance (2.31(6) Å) is slightly shorter than in [(*i*Pr)$_2$ATI]YCp$_2$* (N−Y = 2.398(2) and 2.390(3) Å)[17] (Cp* = C_5Me_5) and in [(Ph)N=C(Ph)C(Ph)=N(Ph)]-YCp$_2$* (2.408(4) Å).[18] The Y−N(2) distance (2.236(3) Å) is in agreement with other Y−N(SiMe$_3$)$_2$ compounds, like the homoleptic amide Y[N(SiMe$_3$)]$_3$[19] (2.211(9) Å) and [*t*Bu(Ar)$_2$SiO]Y[N(SiMe$_3$)$_2$]$_2$ (Ar = 2-C$_6$H$_4$(CH$_2$-NMe$_2$)) (2.237(9) Å).[20] In comparison to these two compounds the N(2)−Y−N(2A) angle (121.56(14)°) is about 8° larger, thus showing a smaller steric demand of the rigid and planar [(*i*Pr)$_2$ATI]$^-$ ligand (N(1)−Y−N(1A) = 69.00(14)°).

Transmetalation of [(*i*Pr)$_2$ATI]K with anhydrous yttrium trichloride in THF in a 2:1 molar ratio does not lead selectively to a product of composition [(*i*Pr)$_2$ATI]$_2$-YCl (**3**). Usually traces of [(*i*Pr)$_2$ATI]$_3$Y and **1** are also formed during the course of the reaction. Recrystallization of the crude product does not yield pure **3** but instead increases the ratio of **1**. In contrast, when the reaction is run with a 10% excess of [(*i*Pr)$_2$ATI]K, only **3** and homoleptic [(*i*Pr)$_2$ATI]$_3$Y are formed. In this case, **3** can be obtained after recrystallization as analytically pure product. Subsequent reaction of **3** with KN(SiMe$_3$)$_2$ in toluene yields [(*i*Pr)$_2$ATI]$_2$Y[N(SiMe$_3$)$_2$] (**4**) as a yellow crystalline powder (Scheme 1). Both complexes **3** and **4** have been characterized by standard analytical/spectroscopic techniques.[21,22] Complex **4** exhibits a dynamic behavior in solution, which is caused by a rearrangement between a pseudo-square-pyramidal[23] and a pseudo-trigonal-bipyramidal[24] coordination

(17) Roesky, P. W. *Eur. J. Inorg. Chem*., in press.
(18) Scholz, A.; Thiele, K.-H.; Scholz, J.; Weimann, R. *J. Organomet. Chem*. **1995**, *501*, 195−200.
(19) Westerhausen, M.; Hartmann, M.; Pfitzner, A. Schwarz, W. *Z. Anorg. Allg. Chem*. **1995**, *621*, 837−850.
(20) Shao, P.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem*. **1994**, *33*, 6334−6339.

(21) **3**: THF (20 mL) was condensed at −196 °C onto a mixture of 260 mg (1.1 mmol) of [(*i*Pr)$_2$ATI]K and 97 mg (0.5 mmol) of YCl$_3$. The mixture was stirred for 18 h at room temperature. The solvent was evaporated under vacuum, and 30 mL of toluene were condensed onto the mixture. Then, the solution was filtered and the solvent removed. This procedure was repeated twice. The remaining solid was recrystallized twice from THF/pentane (1:2). Yield: 85%. ^{1}H NMR (d_8-THF, 250 MHz, 25 °C): δ 1.37 (d, 24H, J(H,H) = 6.8 Hz), 4.18 (sept, 4H, J(H,H) = 6.8 Hz), 6.12 (t, 2H, J(H,H) = 8.9 Hz), 6.49 (d, 4H, J(H,H) = 11.5 Hz), 6.82−6.90 (m, 4H, H$_{4,6}$). ^{13}C{^{1}H} NMR (d_8-THF, 62.9 MHz, 25 °C): δ 21.9, 50.3, 113.6, 116.8, 134.0, 164.8. Anal. Calcd for C$_{26}$H$_{38}$-ClN$_4$Y: C, 58.81; H, 7.21; N, 10.55. Found: C, 58.20; H, 7.01; N, 10.03.
(22) **4**: Toluene (20 mL) was condensed at −196 °C onto a mixture of 150 mg (0.28 mmol) of **2** and 56 mg (0.28 mmol) of KN(SiMe$_3$)$_2$. The mixture was stirred for 18 h at room temperature. The solvent was evaporated under vacuum, and 30 mL of pentane was condensed onto the mixture. Then, the solution was filtered and the solvent removed. The remaining solid was recrystallized from pentane. Yield 71%. ^{1}H NMR (C$_6$D$_6$, 250 MHz, 25 °C): δ 0.27 (s, 18H), 1.37 (br, 24H), 4.27 (m, 4H, (CH$_3$)$_2$C*H*), 6.25 (t, 2H, J(H,H) = 8.9 Hz), 6.56 (d, 4H, J(H,H) = 11.4 Hz), 6.80−6.88 (m, 4H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 25 °C): δ 5.2, 22.4, 49.4, 115.3, 118.2, 134.7, 165.1. ^{29}Si NMR (C$_6$D$_6$, 49.7 Hz, 25 °C): δ −10.1. Anal. Calcd for C$_{32}$H$_{56}$N$_5$Si$_2$Y: C, 58.60; H, 8.61; N, 10.68. Found: C, 58.50; H, 8.90; N, 11.26.
(23) (a) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem*. **1994**, *33*, 3487−3497. (b) Deacon, G. B.; Feng, T.; Skelton, B. W.; White, A. H. *Aust. J. Chem*. **1995**, *48*, 741−756.
(24) (a) Deacon, G. B.; Nickel, S.; MacKinnon, P.; Tiekink, E. R. T. *Aust. J. Chem*. **1990**, *43*, 1245−1257. (b) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem*. **1989**, *28*, 4308−4309.

Table 1. Catalytic Hydroamination/Cyclization Results[a]

Entry	Substrate	Product	Precatalyst	$N_t[h^{-1}]$
1			**5**	3.3
			4	0.6
			2	0.4
2			**5**	8.6
			4	1.5[b]
			2	0.5
3			**5**	0.5
			4	-
			2	-

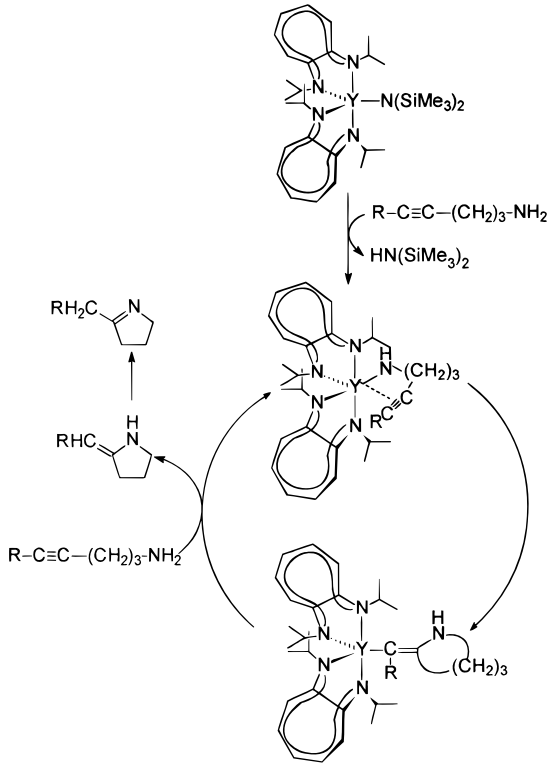
[a] Conditions: temperature, 21 °C; reaction in benzene; quantitative conversion. [b] Isolated yield 73%.

sphere around the yttrium atom. At low temperatures (223 K) both isomers are observed in about a 1:1 ratio. In the pseudo-trigonal-bypyramidal-coordinated isomer each bidentate ligand occupies an axial and an equatorial site,[12c] thus showing two different signals for the isopropyl groups in the ^{1}H NMR spectra. Additionally, a third signal for the isopropyl groups of the pseudo-square-pyramidal-coordinated isomer is observed. These signals start to coalesce with rising temperature and have a coalescence temperature of about $T_c = 263$ K. At even higher temperatures (up from 313 K) the signals due to the isopropyl groups appear as one doublet, indicating a rapid pseudorotation.

The catalytic hydroamination/cyclization of aminoolefins and aminoalkynes has been pioneered by Marks et al. with a variety of lanthanocene catalysts.[5] For this reaction the catalytic activity of the new cyclopentadienyl-free complexes was investigated and a comparison made between **2**, **4**, and Cp_2*YCH(SiMe$_3$)$_2$ (**5**).[25] The rigorously anaerobic reaction of the catalysts with dry, degassed aminoolefin and aminoalkynes (catalyst:substrate ≫ 1:50) proceeds regiospecifically (>95%) to completion in benzene, as shown in Table 1. Catalytic rate measurements and product characterization procedures were as described previously.[5]

The catalytic activity of **4** for the catalytic hydroamination/cyclization of aminoalkynes is about a factor of 5−7 slower than for the established analogous Cp_2* system (entries 1 and 2). Since the rate of the catalysis mostly depends on the steric demands of the ligand,[5] a further tuning of **4** may result in a more competitive system. To our surprise even **2** shows a significant catalytic activity in the hydroamination/cyclization reaction. To our knowledge none of the few established Cp*LnR$_2$ (Ln = La, Ce, Lu; R = alkyl, amide)[26] compounds were ever used as precatalysts in this reaction. Under the same reaction conditions the chloro compounds **1** and **3** were also used as catalysts, but the catalytic activities as well as the product yields are significantly lower than the one observed for **2** and **4**. Kinetic studies of both **2** and **4** indicate zero-order behavior in substrate over a 10-fold concentration range, and so we suggest a mechanism for **4** close to the established one of Cp_2*LnCH(SiMe$_3$)$_2$.[5b,e] Thus, the turnover limiting step is intramolecular alkyne insertion into the Y−N bond followed by rapid protonolysis of the resulting Y−C bond (Scheme 2). Since the hydroamination of aminoalkynes is >35 kcal/mol more exothermic and thus faster than for aminoolefins,[5] it might be expected that no conversion is observed at room temperature for aminoolefins with **2** and **4** as catalysts (entry 3).

Scheme 2



Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Liebig fellowship, P.W.R.). Additionally, generous support from Prof. Dr. D. Fenske is gratefully acknowledged.

Supporting Information Available: Text describing synthetic, spectroscopic, and analytical data for compounds **2**−**4**, figures giving kinetic plots, and X-ray experimental details, including tables of positional and anisotropic displacement parameters and bond lengths and angles (12 pages). Ordering information is given on any current masthead page.

OM9711077

(25) den Hahn, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726−1741.

(26) (a) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637−2646. (b) van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 1459−1467. (c) van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255−258.