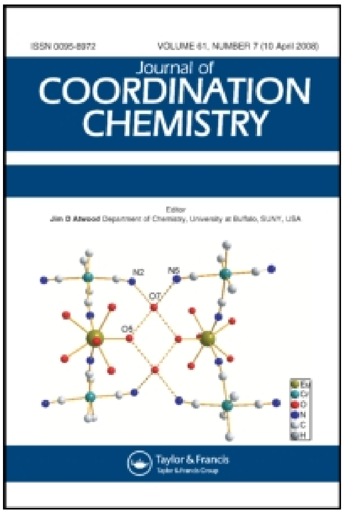

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURE OF A PENTAMETHYLCYCLOPENTADIENYL THULIUMCHLORIDE COMPLEX, $[(C_5ME_5)_2Tm(\mu_3\text{-}CL)_2K(THF)]N$

William J. Evans[a]; Randy N. R. Broomhall-dillard[a]; Samuel E. Foster[a]; Joseph W. Ziller[a]
[a] Department of Chemistry, University of California, Irvine, CA

To cite this Article Evans, William J. , Broomhall-dillard, Randy N. R. , Foster, Samuel E. and Ziller, Joseph W.(1998) 'SYNTHESIS AND STRUCTURE OF A PENTAMETHYLCYCLOPENTADIENYL THULIUMCHLORIDE COMPLEX, $[(C_5ME_5)_2Tm(\mu_3\text{-}CL)_2K(THF)]N$', Journal of Coordination Chemistry, 43: 2, 199 — 206
To link to this Article: DOI: 10.1080/00958979808022668
URL: http://dx.doi.org/10.1080/00958979808022668

J. Coord. Chem., 1998, Vol. 43, pp. 199–206
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STRUCTURE OF A PENTAMETHYLCYCLOPENTADIENYL THULIUMCHLORIDE COMPLEX,$[(C_5ME_5)_2Tm(\mu_3\text{-}CL)_2K(THF)]N$

WILLIAM J. EVANS*, RANDY N.R. BROOMHALL-DILLARD, SAMUEL E. FOSTER and JOSEPH W. ZILLER

Department of Chemistry, University of California, Irvine, Irvine, CA 92697-2025

(Received 16 October 1996; Revised 14 January 1997; in final form 3 March1997)

The first structural data on a pentamethylcyclopentadienyl complex ofthulium,$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**, are reported. $TmCl_3$ reacts with 2 equivalents ofKC_5Me_5 in THF to form **1** in>80% yield. **1** crystallizes from THF/hexanes in thespace group Cc with a = 11.1491(13) Å, b= 28.107(2) Å, c = 8.5921(8) Å, β= 102.485(8)°, V = 2628.8(4) Å^3,and D_{calcd} = 1.570 Mg/m^3 for Z= 4. Least-squares refinement of the model based on 3114reflections ($F^2 > 3.0\sigma(F^2)$)converged to a final R_F = 1.9%. Thepolymeric structure of **1** is generated by triply bridgingchlorides, each of which is connected to one$(C_5Me_5)_2Tm$ bentmetallocene unit and two K(THF) moieties in a T-shaped geometryaround the chloride.

Keywords: thulium, structure, pentamethylcyclopentadienyl, bridging chlorides

INTRODUCTION

Historically, thulium has not been one of the heavily investigatedmetals in the lanthanide series, since other metals of similar size appearto accomplish similar chemistry [1] and are easier to studydue to their lower magnetic moments [2]. Thulium is distinctive in thelanthanide series in that it has a very reactive divalent state: theTm(III)/Tm(II) reduction potential is estimated to be −2.3V*vs* NHE [3].Previously, this highly reducing divalent state was not of chemicalconsequence, since it had only been identified transiently in solution orin the solid state [4].Recently, however, a crystallographically characterizable complex ofTm(II)

---

[*] Author for correspondence.

has been isolated,$TmI_2(MeOCH_2CH_2OMe)_3$ [5], which may be a goodprecursor for new thulium-based chemistry. Future developmentof the chemistry of thulium will require X-ray crystallographicdata on various classes of thulium compounds, but to date very fewthulium structures have been reported. Structural studies onorganometallic thulium complexes and related species are particularlysparse [6-9]. Toour knowledge there are no crystallographic data in the literature onpentamethylcyclopentadienyl thulium complexes. Given the pervasive use ofC_5Me_5 as a co-ligand inorganolanthanide chemistry [1], data onC_5Me_5/Tm complexes should be availablefor comparison. We report here on the structure of$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**.

EXPERIMENTAL

All of the chemistry described below was performed under nitrogenwith rigorous exclusion of air and water using standard Schlenk, vacuumline, and glove box techniques. Solvents were dried and distilled [10] and thulium trichloride(Rh^one-Poulenc) was dried [11] as described previously.KC_5Me_5 was prepared from KH andC_5Me_5H (Strem) in THF and dried *invacuo*. Magnetic susceptibility measurements were recorded on aGeneral Electric GN500 following the Evans' method [12]. Infrared spectra wereobtained on a Perkin Elmer 1600 FT-IR spectrometer.

$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,1.

In the glovebox, $TmCl_3$ (79 mg, 0.287 mmol) and THF (5mL) were combined and KC_5Me_5 (100 mg,0.574 mmol) was added to the resulting slurry. The solution immediatelyturned a cloudy, bright yellow and was allowed to stir overnight. Thereaction mixture was centrifuged to remove solids and the THF wasremoved by rotary evaporation, leaving yellow solid **1** (152 mg,86%). IR (KBr): 2966 s, 2905 s, 2719 w, 1484 w, 1436 s, 1376 m, 1261w, 1179 w, 1053 s, 1020 m, 900 m, 867 w, 797 w, 667 wcm^{-1}. Anal. Calcd. for-$[(C_5Me_5)_2TmCl_2K(THF)]_n$:Tm, 27.2. Found: Tm, 28.1. Magnetic susceptibility (293 K) $\chi M = 2.30 \times 10^{-2}$; $\mu_{eff} = 7.3$ μ_B. Crystals suitable for X-ray diffractionwere obtained from slow diffusion of hexanes into a THF solution of**1** at ambient temperature.

X-ray Data Collection, Structure Determination, andRefinement for$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,1

A yellow crystal of approximate dimensions 0.25 × 0.31 ×0.33 mm was mounted on a glass fiber and transferred to the Syntex$P2_1$ diffractometer.

TABLE I Experimental Data for the X-ray Diffraction Study

Formula:$C_{24}H_{38}Cl_2KOTm$
Fw: 621.5
Temperature (K): 183
Crystal System: Monoclinic
Space Group: Cc
a = 11.1491(13) Å
b = 28.107(2) Å
c = 8.5921(8) Å
β = 102.485(8)°
V = 2628.9(4)Å^3
Z = 4
Dcalcd, Mg/m^3 = 1.570
Diffractometer: Syntex $P2_1$ (R3m/VSystem)
Radiation: MoK (λ = 0.710730)
Monochromator: Highly oriented graphite
Data Collected: $+h$, $+k$,$\pm l$
Scan Type: 2ϑ-ϑ
Scan Range: 1.20°
Scan Speed: 3.0 deg min^{-1} (inω)
2ϑ Range: 4.0 to 55.0°
μ(MoK), mm^{-1} = 3.749
Absorption Correction: Semi-empirical(φ-scan method)
Reflections Collected: 3265
Reflections with $F_o > 3.0\sigma(F_o)$: 3114
No. of Variables: 261
RF = 1.9%, RwF = 2.5%
Goodness of Fit: 1.15

Determination of Laue symmetry,crystal class, unit cell parameters and the crystal's orientationmatrix were carried out by previously described techniques similar tothose of Churchill [13].Low temperature (183 K) intensity data were collected *via* a2θ-θ scan technique with MoKa radiation under theconditions given in TableI.

All 3265 data were corrected for absorption [14] and for Lorentz andpolarization effects and placed on an approximately absolute scale. Anyreflection with I(net) < 0 was assigned the value F_o= 0. The systematic extinctions observed were hkl for$h + k = 2n + 1$ and $h0l$ for $1 = 2n + 1$; the diffraction symmetry was 2/m. The twopossible monoclinic space groups are Cc [C_s^4; No. 9] or C2/c[C_{2h}^6; No. 15].The non-centrosymmetric space group was chosen and latershown to be the correct choice.

All crystallographic calculations were carried out using the UCImodified version of the UCLA Crystallographic Computing Package [15] and the SHELXTL PLUSprogram set [16]. Theanalytical scattering factors for neutral atoms were used throughoutthe analysis [17a]; boththe real ($\Delta f'$) and imaginary (iΔf″) components ofanomalous dispersion [17b] were included. Thequantity minimized during least-squares analysis was$\Sigma w(F_o - F_c)^2$where $w^{-1} = \sigma^2(F_o) + 0.0003(F_o)^2$.

The structure was solved by direct methods (SHELXTL PLUS); andrefined by full-matrix least-squares techniques. Hydrogenatoms were included using a riding model with d(C-H) =0.96Å and U(iso) = 0.08Å^2. Refinementof positional and thermal parameters led to convergence withR_F = 1.9%, R_{wF} =2.5% and GOF = 1.15 for 261 variables refined against those3114 data with $F_o > 3.0\sigma(F_o)$. Theabsolute structure was determined by refinement of the Rogers' η-parameter [= 1.06(3)] [18]. A finaldifference-Fourier map yielded ρ(max) = 0.41eÅ^{-3}. Atomic coordinates and equivalentisotropic displacement coefficients are given in Table II.

TABLE II Atomic coordinates ($\times 10^5$) and equivalentisotropic displacement coefficients (Å^2 $\times 10^4$)†

	x	*y*	*z*	*U(eq)*
Tm(1)	50000	37115(1)	50000	197(1)
K(1)	37092(13)	51919(4)	45389(12)	302(3)
Cl(1)	47988(14)	43740(4)	28239(13)	297(3)
Cl(2)	36524(13)	42448(4)	64503(13)	280(3)
C(1)	28182(66)	33190(22)	38731(88)	355(19)
C(2)	34234(57)	33083(22)	26023(69)	305(17)
C(3)	44235(52)	30006(19)	30152(69)	372(17)
C(4)	44406(54)	28116(17)	45424(71)	380(17)
C(5)	34590(57)	30223(20)	50907(63)	382(17)
C(6)	16289(60)	35865(30)	38268(100)	581(25)
C(7)	29910(77)	35330(30)	9877(74)	592(24)
C(8)	52657(66)	28710(28)	19049(98)	635(28)
C(9)	51724(97)	23874(21)	52814(138)	739(39)
C(10)	30512(85)	29110(33)	66148(89)	712(31)
C(11)	69324(45)	41954(16)	63996(56)	255(13)
C(12)	73680(44)	38938(18)	53153(59)	270(13)
C(13)	73296(58)	34216(19)	58913(71)	254(15)
C(14)	68719(57)	34283(23)	72749(74)	309(17)
C(15)	66324(45)	39115(19)	76220(56)	280(14)
C(16)	69186(52)	47311(17)	63154(78)	388(17)
C(17)	79013(56)	40428(25)	39305(71)	421(19)
C(18)	79465(59)	30055(21)	52409(82)	466(21)
C(19)	68492(63)	30240(24)	84255(83)	502(21)
C(20)	62755(56)	40839(27)	91144(63)	449(20)
O(1)	13111(45)	53838(18)	39615(60)	539(16)
C(21)	5892(64)	57600(26)	31234(84)	527(23)
C(22)	−1602(63)	59468(29)	42541(96)	603(25)
C(23)	−3138(95)	55165(40)	52206(128)	869(43)
C(24)	6135(104)	51776(46)	49482(177)	1150(59)

†Equivalent isotropic U defined as one thirdof the trace of the orthogonalized Uij tensor

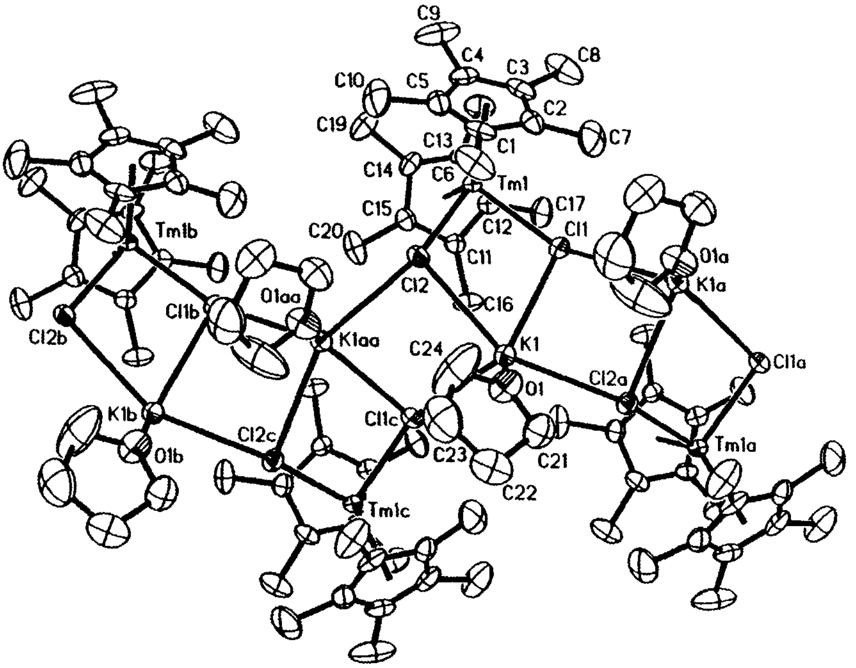

FIGURE 1 Thermal ellipsoid plot of$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**, drawn at the 50% probability level.

RESULTS AND DISCUSSION

$TmCl_3$ reacts with KC_5Me_5in THF to form a polymeric KCl adduct,$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**, in >80% yield. **1** was characterized byX-ray crystallography, Figure 1, and found to be isostructural andisomorphous with the cerium analog,$[(C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)]_n$,**2** [19]. In bothcompounds, the lanthanide metal is formally eight coordinate and adoptsthe geometry typical for trivalent$(C_5Me_5)_2Ln$ complexes,namely a bent metallocene unit with two monodentate ligands attached.Complexes **1** and **2** are polymeric *via* thecoordination sphere of the potassium ion. With only one molecule ofsolvation, the potassium attaches to four triply-bridgingchlorides to generate the polymeric structure shown in Figure 1. The chloride ions have adistorted T-shaped geometry with two M-Cl-Mangles in the 90-100° range and one M-Cl-Mangle of 142-154° (M = K or Tm).

The bond distances and angles in **1** (Table III) are as expectedcompared to **2** when the difference in the radii of the metals isconsidered. For example, theLn-$C(C_5Me_5)$ average distances are2.64(2) Å and 2.79(2) Å for **1** and **2**,respectively,

TABLE III Bond distances (Å) and Angles (°) for$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**

Tm(1)-K(1)	4.393(1)	Tm(1)-C(11)	2.611(5)
Tm(1)-Cl(1)	2.614(1)	Tm(1)-C(12)	2.645(5)
Tm(1)-Cl(2)	2.620(1)	Tm(1)-C(13)	2.671(6)
Tm(1)-C(1)	2.656(7)	Tm(1)-C(14)	2.654(6)
Tm(1)-C(2)	2.656(6)	Tm(1)-C(15)	2.633(4)
Tm(1)-C(3)	2.615(6)	Tm(1)-Cnt(1)	2.341
Tm(1)-C(4)	2.614(5)	Tm(1)-Cnt(2)	2.353
Tm(1)-C(5)	2.602(6)		
K(1)-Cl(1)	3.115(2)	K(1)-K(1A)	4.429(1)
K(1)-Cl(2)	3.136(2)	K(1)-Cl(1A)	3.074(2)
K(1)-O(1)	2.667(5)	K(1)-Cl(2A)	3.079(2)
Cl(1)-Tm(1)-Cl(2)	87.9(1)	Cl(2)-K(1)-Cl(1A)	84.5(1)
K(1)-Tm(1)-C(1)	96.0(1)	O(1)-K(1)-Cl(1A)	105.8(1)
Cnt(1)-Tm(1)-Cl(1)	105.7	Cl(1)-K(1)-Cl(2A)	84.8(1)
Cnt(1)-Tm(1)-Cl(2)	105.6	Cl(2)-K(1)-Cl(2A)	152.7(1)
Cnt(2)-Tm(1)-Cl(1)	105.4	Cl(1A)-K(1)-Cl(2A)	121.2(1)
Cnt(2)-Tm(1)-Cl(2)	106.3	Tm(1)-Cl(1)-K(1)	99.7(1)
Cnt(1)-Tm(1)-Cnt(2)	135.6	Tm(1)-Cl(1)-K(1B)	153.6(1)
Cl(1)-K(1)-Cl(2)	71.1(1)	K(1)-Cl(1)-K(1B)	91.4(1)
Cl(1)-K(1)-O(1)	122.6(1)	Tm(1)-Cl(2)-K(1)	99.1(1)
Cl(2)-K(1)-O(1)	97.8(1)	Tm(1)-Cl(2)-K(1A)	142.8(1)
Cl(1)-K(1)-Cl(1A)	127.6(1)	K(1)-Cl(2)-K(1A)	90.9(1)

and the difference in their eight coordinate radii is 0.149Å [20]. Similarly,the Ln-Cl average distances are 2.617(3) Å and 2.777(1)Å for **1** and **2**, respectively.

The formation of alkali metal halide adducts in lanthanide chemistry isnot unusual and many pentamethylcyclopentadienyl complexes of thegeneral formula$(C_5Me_5)_2LnX_2M(solvent)_n$are known where M = alkali metal, X = halides or*pseudo*halides, solvent = ethers and other coordinatingsolvents [21-25].In most cases, the alkali metal is solvated by two donor ligands, as inthe crystallographically characterized complexes$(C_5Me_5)_2Yb(\mu\text{-}I)_2Li(OEt_2)_2$ [23],$(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ [23],$(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ [21],$(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(OEt_2)_2$ [24], and$(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(MeOCH_2CH_2OMe)_2$ [25]. However, it was previouslyshown that the$CeCl_3/2KC_5Me_5$combination crystallizes from THF as a monosolvate,$[(C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)]_n$,**2**, which fills the remaining space in the coordination sphere ofpotassium by oligomerization [19]. Identification of theisostructural thulium analog, **1**, shows that this oligomericstructure does not necessarily require a large lanthanide, like cerium,and can result with smaller metals at the end of the series as well.Hence, the data obtained to date suggest that the formation ofmonomeric disolvates versus polymeric monosolvates is more dependent onthe alkali metal than on the lanthanide.

CONCLUSION

$[(C_5Me_5)_2Tm(\mu_3\text{-}Cl)_2K(THF)]_n$,**1**, has been prepared in good yields from the $TmCl_3$and KC_5Me_5 and is isostructural with acerium analog. This bis(pentamethylcyclopentadienyl) thulium complexrepresents the first structurally characterizedpentamethylcyclopentadienyl complex of thulium.

SUPPLEMENTARY MATERIAL

X-ray diffraction and structure factor tables available fromWJE.

Acknowledgements

For support of this research, we thank the Division of ChemicalSciences of the Office of Basic Energy Sciences of the Department ofEnergy.

References

[1] H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.* **95**, 865 (1995). M. N. Bochkarev, L. N. Zakharov and G. S. Kalinina,"Organoderivatives of Rare Earth Elements" in *Topics inf-Element Chemistry Vol. 3*, S. P. Sinha Ed. (Kluwer, Boston,1994); C. J. Schaverien, *Adv. Organomet. Chem.* **36**, 283 (1994); F. T. Edelman in *ComprehensiveOrganometallic Chemistry II*, M. F. Lappert, Ed. (Elsevier, Oxford,1995) p. 11; T. J. Marks and R. D. Ernst in *ComprehensiveOrganometallic Chemistry* G. Wilkinson, F. G. A. Stone, and E. W. Abel,Eds. (Pergamon Press, Oxford, 1982) Chapt 21.

[2] W. J. Evans and M. A. Hozbor, *J. Organomet. Chem.* **326**, 299 (1987).

[3] L. R. Morss, *Chem. Rev.* **76**, 827 (1976); A. N. Kamenskaya, *Russ. J. Inorg. Chem.* **29**, 251 (1984).

[4] A. N. Kamenskaya, N. B. Mikheev and N. P. Kholmorgorova, *Russ. J. Inorg. Chem.* **28**, 1420 (1983); R. A. Sallach and J. D. Corbett, *Inorg. Chem.* **7**, 993 (1964). F. A. Hart in*Comprehensive Coordination Chemistry*; G. Wilkinson, R. D. Gillard,J. A. McCleverty, Eds. (Pergamon Press, Oxford, 1987) Chapt. 39; G. H. Dieke, *Spectra and EnergyLevels of Rare Earth Ions in Crystals*; H. M. Crosswhite andH. Crosswhite, Eds. (Wiley, New York, 1968).

[5] M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard and W. J. Evans, *Angew. Chem., Int. Ed. Engl.* in press.

[6] S. H. Eggers, W. Hinrichs, J. Kopf, W. Jahn and R. D. Fischer, *J. Organomet. Chem.* **311**, 313 (1986).

[7] H. Schumann, J. Winterfeld, H. Hemling, F. E. Hahn, P. Reich, K. -W. Brzezinka, F. T. Edelmann, U. Kilimann, M. Schafer and R. Herbst-Irmer, *Chem. Ber.* **128**, 395 (1995).

[8] G. W. Rabe, J. Riede and A. Schier, *J. Chem. Soc., Chem. Commun.*, 577 (1995).

[9] W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber and G. R. J. Artus, *Z. Naturforsch.,Teil B* **49**, 1789 (1994).

[10] W. J. Evans, L. R. Chamberlain, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.* **110**, 6423 (1988).

[11] M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.* **24**, 387 (1962).

[12] D. F. Evans, *J. Chem. Soc.*, 2003 (1959). J. K. Becconsall, *Mol. Phys.* **15**, 129 (1968).

[13] M. R. Churchill, R. A. Lashewycz and F. Rotella, *J. Inorg. Chem.* **16**, 265 (1977).

[14] G. M. Sheldrick, XEMPProgram, Siemens Analytical X-Ray Instruments, Inc., Madison, WI1990.

[15] UCLA Crystallographic ComputingPackage, University of California Los Angeles, 1981, C. Strouse; personalcommunication.

[16] G. M. Sheldrick, SiemensAnalytical X-Ray Instruments, Inc., Madison, WI 1990.

[17] *International Tables forX-Ray Crystallography* (Kynoch Press, Birmingham, England,1974) (a) pp 99-101; (b) pp 149-150.

[18] D. Rogers, *Acta. Cryst.* **A37**, 734 (1981).

[19] W. J. Evans, J. M. Olofson, H. Zhang and J. L. Atwood, *Organometallics*7, 629 (1988).

[20] R. D. Shannon, *ActaCryst.* **A32**, 751 (1976).

[21] W. J. Evans, T. J. Boyle and J. W. Ziller, *Inorg. Chem.* **31**, 1120 (1992) and references therein.

[22] W. J. Evans and S. E. Foster, *J. Organomet. Chem.* **433**, 79 (1992) and references therein.

[23] P. L. Watson, J. F. Whitney and R. L. Harlow, *Inorg. Chem.* **20**, 3271 (1981).

[24] M. D. Rausch, K. J. Moriarty, J. L. Atwood, J. A. Weeks, W. E. Hunter and H. G. Brittain,*Organometallics* **5**, 1281 (1986); P. N. Hazin, J. C. Huffman and J. W. Bruno, *Organometallics*6, 23 (1987).

[25] I. Albrecht, E. Hahn, J. Pickardt and H. Schumann, *Inorg. Chim. Acta* **110**, 145 (1985); H. Schumann, I. Albrecht, J. Loebel, E. Hahn, M. B. Hossain and D. van der Helm, *Organometallics* **5**, 1296 (1986) (1986).