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V *. THE CRYSTAL AND MOLECULAR STRUCTURE OF DI-η^5-CYCLOPENTADIENYL-1,2-DIMETHOXYETHANEYTTERBIUM(II)

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Summary

Crystals of di-η^5-cyclopentadienyl-1,2-dimethoxyethaneytterbium(II) are monoclinic, space group *Cc*, with *a* 9.25(2), *b* 23.49(5), *c* 8.23(2) Å, β 123.59(4)° and $Z = 4$. The ytterbium ion is pseudo-tetrahedrally coordinated by two cyclopentadienyl groups and a bidentate 1,2-dimethoxyethane ligand, and there is no intermolecular association. The sites of the cyclopentadienyl ligands are disordered.

Introduction

Recently, structures of complexes of substituted di-η^5-cyclopentadienyl-ytterbium(II) derivatives, viz. $(\eta^5\text{-}Me_5C_5)_2Yb(thf)\cdot 0.5(PhMe)$ [2] (thf = tetrahydrofuran), $(\eta^5\text{-}MeC_5H_4)_2Yb(thf)$ [3], $(\eta^5\text{-}Me_3SiC_5H_4)_2Yb(thf)_2$ [4] and $(\eta^5\text{-}Me_5C_5)_2Yb(pyridine)_2$ [5] have been reported. A few complexes with possible bidentate ligands have been prepared viz. $(\eta^5\text{-}Me_5C_5)_2YbL$; L = $MeOCH_2CH_2OMe$ [6], $Me_2PCH_2PMe_2$ [7], or $Me_2PCH_2CH_2PMe_2$ [7]. For $(\eta^5\text{-}Me_5C_5)_2Yb(Me_2PCH_2CH_2PMe_2)$, a polymeric structure with bridging bidentate ligands was proposed [7], whilst in solutions of $(\eta^5\text{-}Me_5C_5)_2Yb(Me_2PCH_2PMe_2)$ the phosphine is either unidentate and exchanging rapidly or chelating. However, there have been no crystal structures of complexes of di(organo)ytterbium(II) derivatives with potential bidentate ligands, and a similar situation obtains for di(organo)-europium(II) and -samarium(II) derivatives. We now report the crystal structure of $(\eta^5\text{-}C_5H_5)_2Yb(MeOCH_2CH_2OMe)$. This appears to be the first structure of an unsubstituted di-η^5-cyclopentadienylytterbium(II) derivative.

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Experimental

Crystals of $Cp_2Yb(dme)$ (Cp = η^5-cyclopentadienyl, dme = 1,2-dimethoxyethane) were obtained on cooling the product of the reaction of thallous cyclopentadienide with ytterbium metal in dme [8] to 0°C. The crystals were transferred to a nitrogen filled drybox [9], covered with dry, degassed mineral oil and sealed in glass Lindemann capillaries. A suitable single crystal with approximate dimensions of $0.6 \times 0.2 \times 0.4$ mm was used for data collection.

Data collection

Data were collected on an automatic four-circle diffractometer equipped with a Si(Li) detector and an energy discriminator with Ag-K_α radiation (λ 0.5608 Å). The intensities of 2275 reflections with $2 \leq 2\theta \leq 36°$ were measured using an ω–2θ scan mode. A standard reflection was measured every 25 reflections and had decreased to ca. 20% of its original intensity during data collection. The intensities were corrected by normalization to the preceding standard. Lorentz, polarization and absorption correction and averaging [10] gave 946 unique reflections.

Crystal data

Di-η^5-cyclopentadienyl-1,2-dimethoxyethaneytterbium(II), $C_{14}H_{20}O_2Yb$, M = 393.33. Monoclinic, space group Cc, a 9.25(2), b 23.49(5), c 8.23(2) Å, β 123.59(4)° U 1489.4 Å^3, $Z = 4$, D_c 1.754 g cm^{-3}, $F(000) = 760$, Ag-K_α radiation, λ 0.5608 Å, μ(Ag-K_α) 33.70 cm^{-1}.

Structure solution and refinement

Trial coordinates for the ytterbium atom were obtained from a Patterson synthesis and were refined by least-square methods to give a discrepancy index of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.17$ with an isotropic temperature factor. A difference Fourier calculation with the data from 421 reflections with $F_o > 6\sigma(F_o)$ using SHELX-76 [11] revealed the non-hydrogen atoms of the 1,2-dimethoxyethane ligand. However, the carbon atoms of the cyclopentadienyl ligands were weak and showed areas of additional electron density in their neighbouring regions indicating disorder. This disorder was refined by describing each cyclopentadienyl ring as two rigid pentagons, approximately staggered, with carbon–carbon bond lengths constrained to 1.378 Å. Site occupancy factors were refined for each cyclopentadienyl ligand but restrained so that the occupancy factor of each pentagonal ring pair summed to one.

Hydrogen atoms were not observed but were placed in calculated positions 1.08 Å [11] from the carbon atoms to which they are bonded with a common estimated isotropic temperature factor. They were included in least-squares refinement but not refined. Neutral scattering factors were employed for all atoms and corrected for anomalous dispersion [12]. Final full-matrix least-squares refinement with weighting according to $w = 0.263\ [\sigma(F)]^{-2}$ and with anisotropic thermal parameters for ytterbium and isotropic thermal parameters for all other atoms gave discrepancy indices of $R_w = 0.035$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ for 421 reflections with $F_o > 6\sigma(F_o)$. For the data from all 946 unique reflections $R = 0.053$. A difference Fourier calculation after the final cycle of least-squares refinement had a maximum electron density of ca. 2e/Å^3 approximately 1.2 Å from ytterbium.

Results and discussion

The molecular structure of di-η^5-cyclopentadienyl-1,2-dimethoxyethaneytterbium(II) consists of discrete monomeric units. A perspective drawing of the complex is shown in Fig. 1. Atomic coordinates and thermal parameters are given in Table 1. The stereochemistry around the ytterbium ion is approximately tetrahedral with the centroids of the cyclopentadienyl rings and the oxygens of a bidentate dme forming the apices of the tetrahedron. Pseudo-tetrahedral stereochemistry has been reported for many divalent and trivalent cyclopentadienylytterbium derivatives [5,13,14]. Although 1,2-dimethoxyethane is chelated to ytterbium, the complex $Cp_2Yb(dme)$ is decomposed by benzene yielding unsolvated Cp_2Yb. Thus, facile ligand displacement cannot be interpreted as indicating unidentate dme and, in this case, may be due to the low solubility of Cp_2Yb. Similarly, deductions about phosphine coordination

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^3$, $\times 10^4$ FOR Yb), THERMAL PARAMETERS $Å^2 \times 10^3$) AND SITE OCCUPANCY FACTORS [a]

Atom	x	y	z	Site occupancy factor	U_{iso}
Yb [b]	$\frac{1}{2}$	3750(1)	$\frac{1}{2}$		
C(1)	701(4)	454(2)	764(4)		92(9)
C(2)	679(4)	410(2)	859(4)		74(9)
C(3)	771(4)	364(2)	860(4)	0.684(9)	72(9)
C(4)	851(4)	379(2)	766(4)		91(9)
C(5)	807(4)	435(2)	707(4)		181(10)
C(1′)	729(5)	453(2)	715(6)		90(10)
C(2′)	657(5)	440(2)	819(6)		9(9)
C(3′)	715(5)	387(2)	899(6)	0.316(9)	3(9)
C(4′)	828(5)	367(2)	844(6)		32(9)
C(5′)	831(5)	408(2)	731(6)		10(9)
C(6)	200(5)	469(2)	283(5)		100(8)
C(7)	100(5)	389(2)	410(6)		101(8)
C(8)	191(5)	354(2)	554(6)		116(9)
C(9)	394(5)	272(2)	718(5)		111(9)
C(10)	323(5)	312(2)	159(5)		44(9)
C(11)	483(5)	287(2)	242(5)		55(9)
C(12)	596(5)	327(2)	248(5)	0.404(10)	86(9)
C(13)	505(5)	377(2)	169(5)		146(10)
C(14)	337(5)	368(2)	114(5)		30(9)
C(10′)	310(4)	340(2)	114(4)		81(9)
C(11′)	409(4)	294(2)	226(4)		76(9)
C(12′)	581(4)	307(2)	305(4)	0.596(10)	56(9)
C(13′)	589(4)	360(2)	240(4)		46(8)
C(14′)	421(4)	381(2)	122(4)		96(9)
O(1)	233(3)	429(1)	412(4)		94(7)
O(2)	312(4)	322(1)	569(4)		87(6)

[a] Hydrogen atoms were placed in calculated positions. Isotropic thermal parameters of 0.95 $Å^2 \times 10^3$ were assumed. [b] The ytterbium atom was refined anisotropically. The anisotropic thermal factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ where $U_{11} = 0.0482(8)$, $U_{22} = 0.0763(10)$, $U_{33} = 0.0358(7)$, $U_{23} = 0.0023(20)$, $U_{13} = 0.00246(6)$ and $U_{12} = -0.0072(31)$.

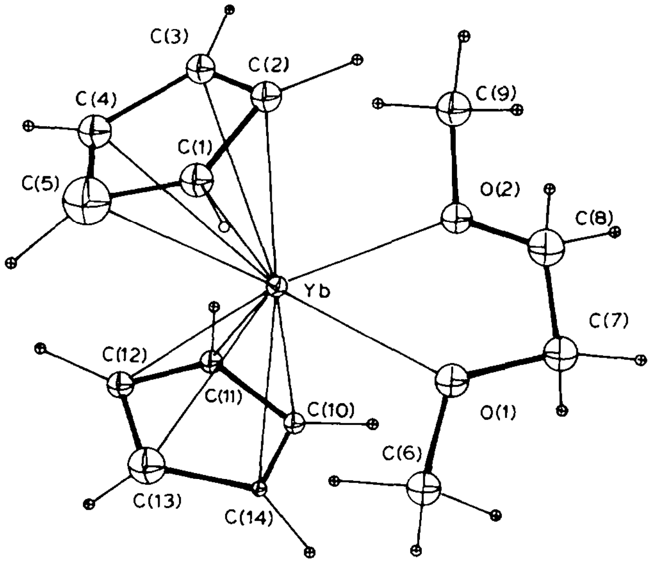

Fig. 1. Perspective diagram of the $Cp_2Yb(dme)$ molecule.

cannot be made from the ready conversion of $(\eta^5\text{-}Me_5C_5)_2Yb(Me_2PCH_2PMe_2)$ and $(\eta^5\text{-}Me_5C_5)_2Yb(Me_2PCH_2CH_2PMe_2)$ into $(\eta^5\text{-}Me_5C_5)_2Yb(OEt_2)$ and $(\eta^5\text{-}Me_5C_5)_2Yb(thf)$, respectively, on treatment with the appropriate ether [7].

The cyclopentadienyl rings of $Cp_2Yb(dme)$ are disordered and each can be described as two regular pentagons in an approximately staggered arrangement. Site occupancy factors determined for each ring are Cp(1) = 0.684(9), Cp(1′) = 0.316(9), Cp(2) = 0.404(10) and Cp(2′) = 0.596(10). The disorder pairs are not quite coplanar with dihedral angles between the planes of Cp(1) and Cp(1′) of 7(1)° and Cp(2) and Cp(2′) of 12(1)°.

Selected bond lengths and angles are given in Table 2. The angles around the ytterbium atom are displaced from the perfect tetrahedral in keeping with the steric requirements of the cyclopentadienyl ligands. The centroid–Yb–centroid angles range from 124 to 133° while the centroid–Yb–oxygen angles range from 107 to 114°. The angle O(1)–Yb–O(2) is considerably smaller, 67.2(9)°, but is comparable with the corresponding angle, 60.8(2)°, reported for $[(Me_3Si)_2N]_2Eu(dme)_2$ [15]. In $Cp_2Yb(dme)$ the O(1)...O(2) contact, 2.74 Å, is very close to the sum (2.80 Å) of two Van der Waal's radii of oxygen [16]. The close proximity of the oxygen atoms may be due to inter-ligand repulsion and reflect steric crowding of the ytterbium ion. The bonds Yb–O(1), 2.50(3), and Yb–O(2), 2.45(3) Å, are significantly shorter than those in $[(Me_3Si)_2N]_2Eu(dme)_2$, 2.756(4) and 2.638(4) Å. Six-coordinate Eu^{2+} is only 0.03 Å larger than eight-coordinate Yb^{2+} [17].

The ytterbium–carbon distances range from 2.60(3) to 2.91(5) Å and average 2.68(7), 2.69(6), 2.80(10) and 2.72(6) Å for Cp(1), Cp(1′), Cp(2) and Cp(2′), respectively. A recent systematic study of many *f*-block organometallics [18] (mainly lanthanoid(III) and actinoid(IV)) has correlated metal–carbon bond lengths with the type of metal–ligand bonding. Subtraction of the ionic radius of a lanthanoid or actinoid ion for a given oxidation state and coordination number from the

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) [a]

Cyclopentadienyl [b]

Ring 1		Ring 2		Ring 1′ [c]	
Yb–C(1)	2.68(3)	Yb–C(10)	2.76(4)	Yb–C(1′)	2.62(4)
Yb–C(2)	2.60(3)	Yb–C(11)	2.91(5)	Yb–C(2′)	2.67(4)
Yb–C(3)	2.63(3)	Yb–C(12)	2.90(4)	Yb–C(3′)	2.75(4)
Yb–C(4)	2.73(3)	Yb–C(13)	2.75(4)	Yb–C(4′)	2.76(4)
Yb–C(5)	2.76(3)	Yb–C(14)	2.67(4)	Yb–C(5′)	2.67(4)
Av.	2.68(7)	Av.	2.80(10)	Av.	2.69(6)
Yb–cent [d]	2.41	Yb–cent	2.54	Yb–cent	2.43

Ring 2′		1,2-Dimethoxyethane			
Yb–C(10′)	2.78(3)	Yb–O(1)	2.50(3)	Yb–O(2)	2.45(3)
Yb–C(11′)	2.70(3)	C(6)–O(1)	1.32(4)	O(1)–C(7)	1.55(4)
Yb–C(12′)	2.65(3)	C(7)–C(8)	1.30(5)	C(8)–O(2)	1.29(5)
Yb–C(13′)	2.70(3)	O(2)–C(9)	1.55(4)		
Yb–C(14′)	2.78(3)				
Av.	2.72(6)				
Yb–cent	2.46				

Pseudo-tetrahedral angles around ytterbium

Cent(1)–Yb–Cent(2)	131	Cent(1)–Yb–O(1)	114
Cent(1)–Yb–O(2)	113	Cent(2)–Yb–O(2)	107
Cent(2)–Yb–O(1)	107	Cent(1′)–Yb–Cent(2′)	133
Cent(1′)–Yb–O(1)	111	Cent(1′)–Yb–O(2)	110
Cent(2′)–Yb–O(1)	109	Cent(1)–Yb–Cent(2′)	129
Cent(1′)–Yb–Cent(2)	124	O(1)–Yb–O(2)	67.2(9)

Dihedral angles between planes

Cp(1)–Cp(1′)	7(1)	Cp(2)–Cp(2′)	12(1)

[a] A complete list of bond lengths and angles, positional and thermal parameters, and observed and calculated structure factor amplitudes are available from the authors on request. [b] Carbon–carbon bond lengths of the cyclopentadienyl ligands were constrained to 1.38 Å. [c] Primed atoms or groups are the disorder pairs of the unprimed atoms or groups. [d] Cent denotes the centre of the rings described by the carbon atoms, C(1) → C(5), C(10) → C(14), C(1′) → C(5′) and C(10′) → C(14′).

metal–carbon bond length gives a fairly invariant value (1.64 ± 0.04 Å) for the effective ionic radius of the cyclopentadienyl or substituted cyclopentadienyl ligand. This lends support for the view of predominantly ionic bonding in these complexes. However, only one divalent organolanthanoid, $(\eta^5\text{-Me}_5C_5)_2$Yb(pyridine)$_2$ [5] was included, and only one other $(\eta^5\text{-Me}_5C_5)_2$Yb(thf) [2] has been subsequently examined by this method. Subtracting the ionic radius of eight-coordinate Yb^{2+} (1.14 Å) [17] from the average ytterbium–carbon bond distance of Cp_2Yb(dme) (2.72 Å) gives 1.58 Å as the effective ionic radius of the cyclopentadienyl ligand. Values of 1.60 and 1.58 Å have been reported for $(\eta^5\text{-Me}_5C_5)_2$Yb(pyridine)$_2$ [5] and $(\eta^5\text{-Me}_5C_5)_2$Yb(thf) [2], respectively, and a value of 1.61 Å is calculated for $(\eta^5\text{-Me}_3SiC_5H_4)_2$Yb(thf)$_2$ [4]. Thus, bonding in Cp_2Yb(dme) appears to be predominantly ionic. However, the accuracy of the analysis in the present work may be

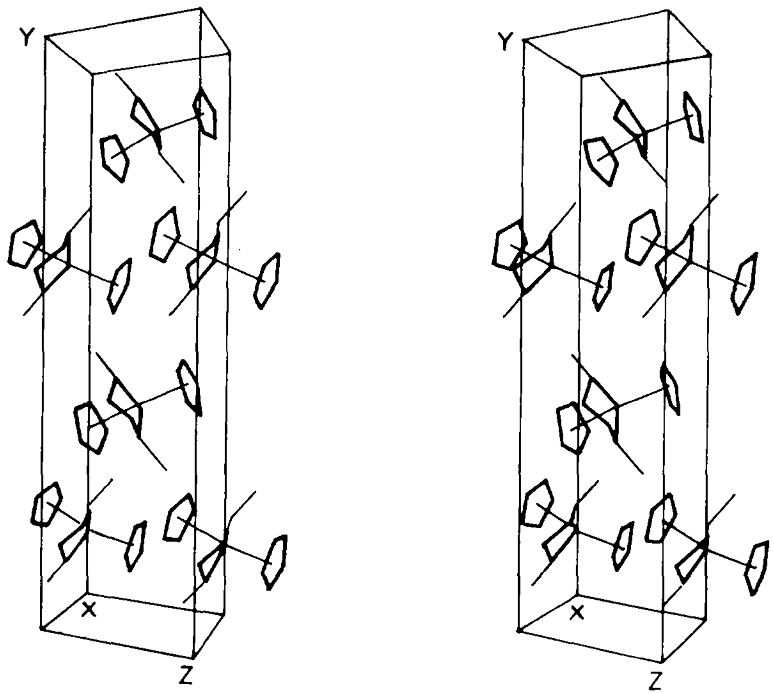

Fig. 2. Stereo-diagram of the unit cell of $Cp_2Yb(dme)$.

TABLE 3

COMPARISON OF SOME ORGANOLANTHANOID-OXYDONOR BOND LENGTHS

	Coord. No. [a]	Ionic [b] radius Ln^{n+} (Å)	Bond length Ln–O(A)	Ln–O minus ionic radius (Å)	Ref.
$Cp_2Yb(dme)$	8	1.14	2.45	1.31	This work
			2.50	1.36	
$(\eta^5\text{-}Me_5C_5)_2Yb(thf)$	7	1.08	2.41	1.33	2
$(\eta^5\text{-}Me_3SiC_5H_4)_2Yb(thf)_2$	8	1.14	2.42	1.28	4
			2.39	1.25	
$(\eta^5\text{-}MeC_5H_4)_2Yb(thf)$	10	1.19	2.53	1.34	3
$Cp_2LuCH_2SiMe_3(thf)$	8	0.977	2.29	1.31	19
$Cp_2Lu(C_6H_4\text{-}p\text{-}Me)(thf)$	8	0.977	2.27	1.29	19
$Cp_2LuBu^t(thf)$	8	0.977	2.31	1.33	20
$Cp_3Y(thf)$	10	1.07	2.45	1.38	21
$Cp_3La(thf)$	10	1.27	2.57	1.30	21
$Cp_3Gd(thf)$	10	1.11	2.49	1.38	22
$CpErCl_2(thf)_3$	8	1.00	2.37 [c]	1.37	23
			2.35 [c]	1.35	
			2.45 [d]	1.45	
$[(\eta^5\text{-}MeC_5H_4)_2Y(\mu\text{-}H)(thf)]_2$	9	1.08	2.46	1.39	24
			Average =	1.34(5) [e]	

[a] The cyclopentadienyl ligand is regarded as formally tridentate. [b] From Ref. 17 or calculated by the method of ref. 18. [c] Pseudo *trans*-thf. [d] Pseudo *cis*-thf. [e] The figure in parentheses is the sample standard deviation. The correlation coefficient between ionic radius and metal-oxygen bond length is 0.85.

limited by the disorder of the cyclopentadienyl ligands. The bonds Yb–C(11) and Yb–C(12), 2.91 and 2.90 Å, respectively, are significantly longer than the average (2.72 Å) and are similar to bridging Yb–C bonds (2.87 and 2.91 Å) of (η^5-$MeC_5H_4)_2$Yb(thf), which is polymeric with both terminal and bridging methylcyclopentadienyl groups [3]. However, Cp_2Yb(dme) is monomeric with no significant intermolecular contacts under 3.5 Å. The unit cell is shown in Fig. 2.

The metal–oxygen distances of Cp_2Yb(dme) are compared with those of other oxydonor-organolanthanoid complexes in Table 3. Subtraction of the metal ion radius from the bond distance leaves a reasonably constant value in all but one case, indicating little systematic variation in metal–oxygen bonding in these compounds. The exception is $CpErCl_2(thf)_3$, which has *trans*-chlorines and *mer*-tetrahydrofuran ligands [23]. Whilst the pseudo-*trans*-Er–O distances are unexceptional (Table 3), the *cis*-tetrahydrofuran has an elongated Er–O owing to inter-ligand repulsion [23].

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References

1 G.B. Deacon, P.I. MacKinnon and Tran D. Tuong, Aust. J. Chem., 36 (1983) 43.
2 T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D.H. Templeton, Inorg. Chem., 19 (1980) 2999.
3 H.A. Zinnen, J.L. Pluth and W.J. Evans, J. Chem. Soc., Chem. Commun., (1980) 810.
4 M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir and J. Holton, J. Chem. Soc., Chem. Commun., (1980) 987.
5 T.D. Tilley, R.A. Andersen, B. Spencer and A. Zalkin, Inorg. Chem., 21 (1982) 2647.
6 P.L. Watson, J. Chem. Soc., Chem. Commun., (1980) 652.
7 T.D. Tilley, R.A. Andersen and A. Zalkin, Inorg. Chem., 22 (1983) 856.
8 G.B. Deacon, A.J. Koplick and T.D. Tuong, Polyhedron, 1 (1982) 423, and unpublished results.
9 G.B. Deacon, W.D. Raverty and D.G. Vince, J. Organomet. Chem., 135 (1977) 103.
10 M.M. Elcombe, G.W. Cox, A.W. Pryor and F.H. Moore, AAEC/TM578 1971
11 G.M. Sheldrick, SHELX-76 Program System, University of Cambridge, 1976.
12 D.T. Cromer and J.T. Waber, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV, Tables 2.2A and 2.3.1.
13 T.J. Marks and R.D. Ernst, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, England, 1982, Vol. 3, pp. 173.
14 P.L. Watson, J.F. Whitney and R.L. Harlow, Inorg. Chem., 20 (1981) 3271.
15 T.D. Tilley, A. Zalkin, R.A. Andersen and D.H. Templeton, Inorg. Chem., 20 (1981) 551.
16 L. Pauling, The Nature of the Chemical Bond, Cornel Univ. Press, New York, 1960, p. 260.
17 R.D. Shannon, Acta Cryst., A, 32 (1976) 751.
18 K.N. Raymond and C.W. Eigenbrot, Jr., Acc. Chem. Res., 13 (1980) 276.
19 H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, Organometallics, 1 (1982) 1194.
20 W.J. Evans, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Chem. Soc., Chem. Commun., (1981) 292.
21 R.D. Rogers, J.L. Atwood, A. Emad, D.J. Sikora and M.D. Rausch, J. Organomet. Chem., 216 (1981) 383.
22 R.D. Rogers, R. Vann Bynum and J.L. Atwood, J. Organomet. Chem., 192 (1980) 65.
23 C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, Organometallics, 1 (1982) 998.
24 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 2008.