Synthesis and Structure of an Organosamarium Aryloxide Complex, $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$

WILLIAM J. EVANS*, TIMOTHY P. HANUSA and KEITH R. LEVAN

Department of Chemistry, University of California, Irvine, Calif. 92717, U.S.A.

Received March 21, 1985

Abstract

Bis(pentamethylcyclopentadienyl)samarium bis(tetrahydrofuranate), $(C_5Me_5)_2Sm(THF)_2$, reacts with 2,3,5,6-tetramethylphenol in toluene to yield $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$. The compound crystallizes in the space group $P2_1/c$ with a = 8.725(3) Å, b = 18.821(6) Å, c = 18.461(6) Å, β = 111.17(2)°, V = 2827(2) Å^3 and D_c = 1.340 g cm^{-3} for Z = 4. Molecules of the aryloxide complex are monomeric and exhibit a bent metallocene structure with a nearly linear Sm–O–C(aryloxide) linkage: Sm–O = 2.13(1) Å, O–C = 1.29(2) Å, and Sm–O–C = 172.3(13)°. Reaction of the samarium complex with phenyllithium produces the previously-characterized species $(C_5Me_5)_2Sm(C_6H_5)(THF)$.

Introduction

One of the most pervasive features of the chemistry of organolanthanide complexes is a marked affinity for oxygen and oxygen-containing substrates. Structural characterization of organometallic complexes containing Ln–O interactions is relatively limited, however, despite its importance to a comprehensive understanding of organolanthanide chemistry [1]. Only a few reports on the structure of organolanthanide complexes with formally charged oxygen-containing ligands (e.g., oxo, alkoxide, aryloxide, etc.) are available. These include the μ-oxo complex $[(C_5Me_5)_2Sm]_2O$ [2], the enediolate complexes, *cis*- and *trans*-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$ [3], and the ketenecarboxylate $\{[(C_5Me_5)_2Sm]_2(O_2CCCO)(THF)\}_2$ [4]. No structural information on a simple, unbridged organometallic alkoxide or aryloxide complex has been available for comparison with these more complex polymetallic species. The structure of the inorganic neodymium alkoxide $Nd_6(OCH(CH_3)_2)_{17}Cl$ [5] and of several organometallic and inorganic uranium alkoxides [6–8] provide the most closely related available data. We report here the synthesis and crystallographic characterization of a monomeric organosamarium complex containing a terminal aryloxide ligand which provides the basic structural information needed on M–O linkages in organolanthanide compounds.

Experimental

Preparation of $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$

All procedures were conducted using standard inert atmosphere techniques in a nitrogen-filled glovebox and solvents were distilled under nitrogen from sodium or potassium benzophenone ketyl as previously described [9]. A solution of $(C_5Me_5)_2Sm(THF)_2$ [10] (0.245 g, 0.43 mmol) in toluene (15 ml) was added to 2,3,5,6-tetramethylphenol (Aldrich) (0.065 g, 0.43 mmol) in toluene (15 ml) with stirring. The resulting deep greenish-black reaction mixture was filtered, and the filtrate reduced in volume to *ca.* 5 ml. Upon standing and slow evaporation for several days, the solution became yellowish-black and deposited a tacky orange-yellow solid. Hexanes were added to the solid, the solution was filtered, and evaporation of the solvent from the filtrate produced crystalline $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$, (0.137 g, 55%). ^{1}H NMR (C_6D_6, 250 MHz) δ 8.12(s,1,C_6*H*Me_4), 2.90(s,6,C_6H*Me*$_4$), 0.45(s,30,C_5*Me*$_5$), and −3.21(s,br,6,C_6H*Me*$_4$). IR (KBr, cm^{-1}): 2948(m), 2906(s,br), 2851(s), 1562(m), 1445(m,br), 1395(s), 1373(m), 1310(s), 1256(w), 1225(m), 1112(s), 1010(w,br), 917(w,br), 829(w,br), 688(w). *Anal.* Calcd. for $C_{30}H_{43}OSm$: Sm, 26.38. Found (complexometric): Sm, 26.5.

Reaction of $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$ with C_6H_5Li

Phenyllithium (100 μl of a 1.9 M solution in toluene/diethyl ether, 0.19 mmol) was added via syringe to a solution of $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$ (58 mg, 0.10 mmol) in THF (15 ml). Within 5 min, the initially orange-yellow mixture became yellow and slightly turbid. The reaction was allowed to stir overnight, after which it was evaporated to a yellow

---

*Author to whom correspondence should be addressed.

TABLE I. Crystal Data for $(C_5Me_5)_2SmOC_6HMe_4$.

Formula	$C_{30}H_{43}OSm$
FW	570.08
Space group	$P2_1/c$
a	8.725(3) Å
b	18.821(6) Å
c	18.461(6) Å
β	111.17(2)°
V	2827(2) $Å^3$
Z	4
D_c	1.340 g cm^{-3}
T	24 °C
λ(Mo Kα)	0.71073 Å; graphite monochromator
μ	21.0 cm^{-1}
Scan type	$\theta - 2\theta$
Scan width	−1.2° in 2θ from $K\alpha_1$ to +1.2° from $K\alpha_2$
Scan speed	2–12° min^{-1}, variable
Background counting	Evaluated from 96-step peak profile
Data collection range	$0° \leqslant 2\theta \leqslant 45°$
Total unique data	3997
Unique data with $I \geqslant 2.33\sigma(I)$	1815
No. of parameters	289
$R(F)$	0.042
$R_w(F)$	0.054
GOF	1.560
Maximum Δ/σ in final cycle	0.05

oil. Hexane extraction of the oil left an off-white solid (*ca.* 15 mg) and a yellow solution which on evaporation left crude $(C_5Me_5)_2Sm(C_6H_5)(THF)$ (49 mg, 84%), identified by its characteristic ^1H NMR spectrum [11].

X-Ray Crystallography of $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6)

General procedures for data collection and reduction have been described previously [12]. A well-formed parallelepiped measuring 0.18 × 0.23 × 0.24 mm was sealed under N_2 in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections measured from $20° \leqslant 2\theta \leqslant 30°$. Relevant crystal and data collection parameters for the present study are given in Table I. The monoclinic space group was unambiguously determined as $P2_1/c$ (No. 14) from systematic absences (*OkO, k* odd; *hOl, l* odd). During the data collection, the intensities of 3 standard reflections measured every 100 reflections decreased by 8%; a decay correction was later applied. Intensities of the observed reflections were corrected for absorption. A combination of Patterson and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined anisotropically using full-matrix least-squares methods*. The comparatively high thermal motion of the methyl groups permitted the location of less than a fifth of the hydrogen atoms; consequently none were included. A final difference map contained no recognizable features and its largest peak was of height 1.45 e $Å^{-3}$ and was 1.18 Å from the samarium atom [10].

Tables of anisotropic thermal parameters and observed and calculated structure factor amplitudes have been deposited with the Editors-in-Chief in Padua; copies are available on request.

Results and Discussion

Addition of $(C_5Me_5)_2Sm(THF)_2$ to a solution of 2,3,5,6-tetramethylphenol in toluene results in the formation of deeply-colored solutions from which after several days orange crystals can be isolated in moderate yield. The ^1H NMR and IR spectra and complexometric analysis of the new organosamarium complex were consistent with the formula $(C_5Me_5)_2Sm(OC_6HMe_4)$. This formula was confirmed by an X-ray diffraction study as described below. Although reactions of transition metal metallocenes (e.g., $(C_5H_5)_2Co$, $(C_5H_5)_2Ni$) with phenol have been reported to generate phenoxide complexes, complete displacement of the cyclopentadienyl rings occurs in such cases [14].

Structure of $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6)

The molecule crystallizes in monomeric units which consist of a samarium atom bonded to a terminal aryloxide ligand and flanked by two canted C_5Me_5 rings. An ORTEP view of the complex illustrating the geometry and numbering scheme is presented in Fig. 1. Final positional parameters are listed in Table II and selected bond distances and angles are given in Table III.

The average Sm–C(ring) distance is 2.68(1) Å and the rings are tilted in a bent metallocene arrangement with a centroid–Sm–centroid angle of 139.1°. This angle, which lies between that of 140.1° found in unsolvated decamethylsamarocene [15] and the 136.8° angle observed in the disolvated $(C_5Me_5)_2Sm(THF)_2$ [10], reflects the intermediate steric demands of the aryloxide ligand. In previously reported trivalent bis(pentamethylcyclopentadienyl) lanthanide complexes, these angles have ranged from 131–138° [10b].

---

*A locally-modified version of the UCLA Crystallographic Computing Package and a VAX 11/780 computer system were used to perform all calculations [13].

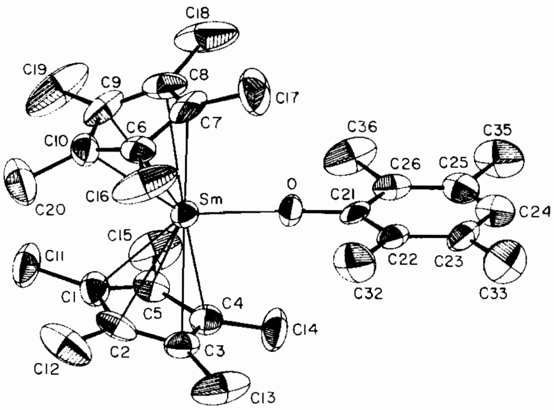

Fig. 1. ORTEP plot of $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$.

TABLE III. Selected Bond Lengths and Angles in $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$.

Bond distances (Å)	
Sm–O	2.13(1)
Sm–C	2.68(1) ave.
O–C(21)	1.29(2)
C–C (C_5Me_5)	1.40(2) ave.
C–CH_3	1.55(2) ave.
C–C (aryloxide)	1.40(2) ave.
C–CH_3 (aryloxide)	1.55(2) ave.
Bond angles (°)	
Sm–O–C(21)	172.3(13)
O–C(21)–C(22)	120.2(18)
O–C(21)–C(26)	122.5(17)
C(21)–C(22)–C(32)	117.7(15)
C(21)–C(26)–C(36)	116.7(16)

TABLE II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$.

Atom	*x*	*y*	*z*	$U_{eq} \times 10E4$[a]
Sm	0.57198(8)	0.24905(7)	0.00949(3)	501(5)
O	0.5496(18)	0.3254(6)	–0.0791(7)	740(125)
C(1)	0.6342(18)	0.2528(12)	0.1640(7)	669(113)
C(2)	0.4696(19)	0.2725(9)	0.1268(8)	654(149)
C(3)	0.4523(22)	0.3367(10)	0.0894(8)	673(148)
C(4)	0.6104(25)	0.3623(8)	0.1010(9)	702(156)
C(5)	0.7226(18)	0.3105(9)	0.1486(8)	612(129)
C(6)	0.4208(20)	0.1312(8)	–0.0642(10)	604(145)
C(7)	0.5255(33)	0.1528(9)	–0.1042(12)	838(214)
C(8)	0.6845(27)	0.1442(10)	–0.0537(16)	871(220)
C(9)	0.6844(23)	0.1147(9)	0.0119(12)	820(173)
C(10)	0.5201(27)	0.1065(9)	0.0084(9)	759(170)
C(11)	0.7171(28)	0.1934(9)	0.2204(10)	1055(196)
C(12)	0.3246(25)	0.2235(12)	0.1335(11)	1194(227)
C(13)	0.2872(24)	0.3751(12)	0.0452(11)	1281(218)
C(14)	0.6651(28)	0.4335(8)	0.0777(10)	978(195)
C(15)	0.9157(21)	0.3171(12)	0.1775(13)	1149(210)
C(16)	0.2302(22)	0.1325(11)	–0.1005(16)	1407(248)
C(17)	0.4614(34)	0.1812(11)	–0.1877(11)	1392(269)
C(18)	0.8284(29)	0.1609(12)	–0.0808(18)	1665(363)
C(19)	0.8401(27)	0.0896(12)	0.0806(14)	1741(272)
C(20)	0.4553(33)	0.0715(10)	0.0637(11)	1302(264)
C(21)	0.5481(23)	0.3773(8)	–0.1254(9)	583(152)
C(22)	0.3972(18)	0.4010(7)	–0.1813(8)	547(121)
C(23)	0.4021(23)	0.4572(8)	–0.2325(9)	740(151)
C(24)	0.5453(21)	0.4862(9)	–0.2320(11)	720(198)
C(25)	0.6893(24)	0.4646(9)	–0.1795(11)	719(169)
C(26)	0.6972(19)	0.4102(9)	–0.1266(9)	644(140)
C(32)	0.2394(21)	0.3657(10)	–0.1818(12)	1004(203)
C(33)	0.2330(21)	0.4827(12)	–0.2959(12)	1096(201)
C(35)	0.8474(22)	0.4974(10)	–0.1826(14)	1120(240)
C(36)	0.8626(21)	0.3803(11)	–0.0686(11)	1097(189)

[a] U_{eq} (A^2) = 1/3 (trace of orthogonalized U_{ij} matrix).

TABLE IV. Structural Parameters of Lanthanide, Actinide and Early Transition Metal Complexes Containing Alkoxide and Aryloxide Ligands.

Complex	M–O (Å)	O–C (Å)	M–O–C (deg)	Reference
$[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$	2.094(1)		180[a]	2
trans-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$	2.107(7)	1.374(17)		3
	2.122(8)	1.334(15)		
$(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$	2.13(1)	1.29(2)	172.3(13)	this work
cis-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$	2.147(10)	1.319(19)		3
	2.179(10)	1.352(18)		
$[(C_5Me_5)_2Sm]_2(O_2CCCO)(THF)]_2$	2.25(1)	1.31(2)		4
$[TiCl_2(OPh)_2]_2$	1.74(1)	1.36(2)	165.9(6)	24
$[Ti(OPh_4]_2 \cdot 2PhOH$	1.789	1.36	175	17
	1.842	1.268	169	
	2.200	1.36	132	
$(C_5H_5)(1\text{-}Me\text{-}3\text{-}i\text{-}Pr\text{-}C_5H_3)TiCl(OC_6H_3Me_2\text{-}2,6)$	1.88	1.38	145	21
$(C_5H_5)(1\text{-}Me\text{-}3\text{-}i\text{-}Pr\text{-}C_5H_3)Ti(OC_6H_3Me_2\text{-}2,6)\text{-}$	1.91	1.32	147	21
$(OC_6H_4Cl\text{-}2)$	1.95	1.34	143	
$Nd_6(OCH(CH_3)_2)_{17}Cl$	2.05(2)	1.44(66)[b]	159–171	5
$[(C_5H_5)_2TiCl_2]_2O_2C_2Me_4$	1.750(2)	1.430(3)	166.2(2)	19
$(C_5H_5)_2TiCl(OEt)$	1.855(2)	1.415(4)	133.2(2)	19
$(C_5H_5)_2Ti[OC_6H_2(Me\text{-}4)(t\text{-}Bu)_2\text{-}2,6]$	1.892(2)	1.352(3)	142.3(2)	22
$[Ti(OCH_3)_4]_2$	1.745(9)	1.398(22)	160.6(15)	25
	1.751(10)	1.385(22)	152.4(13)	
	1.818(13)	1.383(22)	140.0(11)	
$U_2(OCHMe_2)_{10}$	2.03(1) (ave.)	1.41 (ave.)	163(3)	6
$[(C_5Me_5)_2UOMe]_2PH$	2.046(14)	1.44(3)	178(1)	7
$[(C_3H_5)_2U(O\text{-}i\text{-}Pr)_2]_2$	2.056(13)	1.41(3)	178.0(10)	8

[a] Required by the space group. [b] Idealized value.

Of greatest interest is the geometry involving the samarium atom and the aryloxide ligand itself. The complex possesses an approximate C_2 symmetry, and the oxygen atom lies only 0.17 Å from the plane defined by the two ring centroids and the samarium atom. The Sm–O and O–C lengths and the Sm–O–C angle are compared in Table IV to analogous distances in a variety of organosamarium oxide complexes, early transition metal phenoxides and alkoxides [16], $Nd_6(OCH(CH_3)_2)_{17}Cl$, and uranium alkoxides. In the samarium aryloxide complex, the Sm–O distance of 2.13(1) Å is at the short end of the range previously observed for samarium–oxygen single bond distances (2.09–2.25 Å) in organometallic complexes, and is substantially less than the value of 2.4–2.5 Å typically found for oxygen donor–samarium distances in organometallic compounds [3, 4].

The C–O distance (1.29(2) Å) and Sm–O–C angle (172.3(13)°) along with the Sm–O length fit into a pattern observed with transition metal alkoxides and aryloxides: short M–O and, to a lesser extent, O–C separations are often coupled with wide M–O–C angles (see Table IV). The correlation is particularly evident in complexes such as $[Ti(OPh)_4]_2 \cdot 2PhOH$ [17], which contains several crystallographically-independent phenoxide ligands on a single metal center. Partial multiple bond character in the M–O–C linkage of the transition metal complexes has been suggested as an explanation for the short bond lengths and large angles [18, 19]. The oxygen-centered angles of the samarium aryloxide and μ-oxo dimer are among the widest known, however, and the extent of possible π-electron overlap, if any, in such complexes is unknown [2].

Undoubtedly, steric effects place significant constraints on the geometry of the metal–aryloxide interaction. The *ortho* methyl group C(36), for instance, is observed at 4.15 Å from the samarium atom and 3.82 Å from the pentamethylcyclopentadienyl ring methyl carbon C(14). Were the Sm–O–C angle to close to 150°, for example, C(36) would lie 3.77 Å and 3.47 Å from the samarium center and C(14), respectively*. Van der Waals repulsion would probably be substantial at such distances [20]. As a point of reference, the M–O–C angle is 145° in the titanium aryloxide complex $(C_5H_5)(1\text{-}Me\text{-}3\text{-}i\text{-}Pr\text{-}C_5H_3)TiCl(OC_6H_3Me_2\text{-}2,6)$ [21], which contains identical ortho substituents on the aryloxide ring

---

*These distances assume that the aryloxide ring remains in the same plane as the Sm–O–C angle is varied. Although some rotation of the ring could occur, the extent of possible movement is limited, as explained below.

but less bulky cyclopentadienyl rings. A complex with unsubstituted cyclopentadienyl rings and bulkier ortho substituents, $(C_5H_5)_2Ti[OC_6H_2(Me\text{-}4)(t\text{-}Bu)_2\text{-}2,6]$ [22], has a Ti–O–C angle of 142.3(3)°. These data suggest that the pentamethyl substitution of the cyclopentadienyl rings rather than the *ortho* substituents in $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$ may have the most important steric effects in this aryloxide complex.

The angle formed by the centroid-Sm-centroid plane and the plane of the aryloxide ring (C(21)–C(26)) is 85.1°, and the near perpendicularity of these two is also probably enforced by the proximity of the aryloxide methyl groups to those of the pentamethylcyclopentadienyl rings. The methyl groups themselves are not appreciably displaced from the aromatic ring plane (maximum distance = 0.08 Å), but both C(36) and C(32) approach within 4.0 Å of C(14) and C(17), respectively. Further tilt of the aryloxide ring relative to the C_5Me_5 units would be sterically unfavorable.

Since these steric influences are superimposed on whatever structural effects of electronic origin are present, the solid state geometry of the aryloxide complex, as well as of other organolanthanide and early transition metal phenoxide, alkoxide, and oxo species containing bulky ligands, can serve only as a weak gauge of the nature of the bonding present. Regardless of any ambiguities in the type of bonding, the samarium complex presents a simple, discrete, organometallic Sm–O system which may serve as a structural model for lanthanide–oxygen bonds in more complex organometallic compounds.

This Sm–O complex may also be useful as a simple fully-characterized system upon which to study the reactivity of the lanthanide-oxygen bond. In preliminary studies, we have found that $(C_5Me_5)_2Sm(OC_6HMe_4)$ reacts with LiC_6H_5 in THF to yield the phenyl complex $(C_5Me_5)_2Sm(C_6H_5)(THF)$ [11]. This reaction parallels the previously-described conversion of $(C_5H_5)_2SmO(t\text{-}Bu)$ into $(C_5H_5)_2SmCH_2SiMe_3$ via treatment with $LiCH_2SiMe_3$ [23]. In the presently-described case, the reaction occurs in a much more sterically congested environment. The full extent to which the Sm–O linkage can be used as a precursor to Sm–C bonds is under investigation.

Acknowledgements

We thank the National Science Foundation for support of this research and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.). We also thank Professor R. J. Doedens for his help and advice with the crystal structure determination.

References

1 W. J. Evans, *Adv. Organomet. Chem., 24,* 131 (1985).
2 W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc., 107,* 405 (1985).
3 W. J. Evans, J. W. Grate and R. J. Doedens, *J. Am. Chem. Soc., 107,* 1671 (1985).
4 W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang and J. L. Atwood, *J. Am. Chem. Soc., 107,* 3728 (1985).
5 R. A. Anderson, D. H. Templeton and A. Zalkin, *Inorg. Chem., 17,* 1962 (1978).
6 F. A. Cotton, D. O. Marler and W. Schwotzer, *Inorg. Chem., 23,* 4211 (1984).
7 M. R. Duttera, V. W. Day and T. J. Marks, *J. Am. Chem. Soc., 106,* 2907 (1984).
8 M. Brunelli, G. Perego, G. Lugli and A. Mazzei, *J. Chem. Soc., Dalton Trans.,* 861 (1979).
9 W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc., 104,* 2008 (1982).
10 (a) W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc., 103,* 6507 (1981);
(b) W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc., 107,* 941 (1985).
11 W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, *Organometallics, 4,* 112 (1985).
12 D. B. Sams and R. J. Doedens, *Inorg. Chem., 18,* 153 (1979).
13 'UCLA Crystallographic Computing Package', Univ. Calif. Los Angeles; C. E. Strouse personal communication to R. J. Doedens.
14 K. Taniguchi and T. Arakawa, *Chem. Abstr., 78,* 135871r (1973).
15 W. J. Evans, L. A. Hughes and T. P. Hanusa, *J. Am. Chem. Soc., 106,* 4270 (1984).
16 K. C. Malhotra and R. L. Martin, *J. Organomet. Chem., 239,* 159 (1982).
17 G. W. Svetich and A. A. Voge, *J. Chem. Soc., Chem. Commun.,* 676 (1971).
18 T. W. Coffindaffer, I. P. Rothwell and J. C. Huffman, *Inorg. Chem., 22,* 2906 (1983).
19 J. C. Huffman, K. G. Moloy, J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc., 102,* 3009 (1980).
20 L. Pauling, 'The Nature of the Chemical Bond, 3rd. edn.', Cornell University Press, Ithaca, New York, 1960, p. 260.
21 J. Besancon, S. Top, J. Tirouflet, Y. Dusausoy, C. Lecomte and J. Protas, *J. Organomet. Chem., 127,* 153 (1977).
22 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, S. Torroni, J. L. Atwood, W. E. Hunter and M. J. Zaworotko, *J. Organomet. Chem., 188,* C31 (1980).
23 H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, *Organometallics, 1,* 1194 (1982).
24 K. Watenpaugh and C. N. Caughlan, *Inorg. Chem., 5,* 1782 (1966).
25 D. A. Wright and D. A. Williams, *Acta Crystallogr., Sect. B:, 34,* 1107 (1968).