

## Organometallic compounds of the lanthanides

### XLVI \*. Synthesis and crystallographic characterization of $(C_5Me_5)_2Sm(DME)$

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#### Abstract

$(C_5Me_5)_2Sm(DME)$  has been obtained as green crystals by the reaction of  $SmCl_2$  with  $NaC_5Me_5$  in dimethoxyethane (DME). Its structure has been determined by an X-ray diffraction study. The crystals are orthorhombic with  $a$  1101.4(4),  $b$  2023.1(5),  $c$  1337.2(5) pm, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $\rho_{calc.}$  1.34 g cm<sup>3</sup>,  $R = 0.0574$  and 2524 observed data ( $I \geq 3\sigma(I)$ ).

#### Introduction

The organometallic compounds of divalent lanthanide metal ions have been of interest since the early 1970's because of their applications in organic synthesis [3–6], and a variety of new complexes and reaction patterns have been discovered [7–10]. Of the known organolanthanides of these divalent ions, those of ytterbium(II) have been investigated extensively because of their ability to form soluble complexes and their relevant reactivities. In contrast, those of samarium(II) (though the most reactive;  $Sm^{III} + e^- \rightarrow Sm^{II}$ :  $-1.5$  V [11]), were not much studied because the then known divalent organosamarium complexes  $[(C_5H_5)_2Sm(THF)_x]_y$  [12,13] and  $[(CH_3C_5H_4)_2Sm(THF)_x]_y$  [14] were insoluble.

Recently, Evans et al. reported a series of fully characterized soluble  $Sm^{II}$  derivatives  $(C_5Me_5)_2Sm(THF)_2$  [7,15],  $[C_5Me_5Sm(\mu-I)(THF)_2]_2$  [15] and  $(C_5Me_5)_2Sm$  [16]. We have prepared another soluble  $Sm^{II}$  derivative by using a bridged dicyclopentadienyl ligand  $[(C_5H_4)(CH_2)_3(C_5H_4)]^{2-}$  in THF [17]. Since

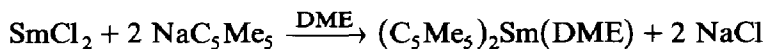
\* For part XLV see ref. 1

\*\* Present address see ref. 2.

Evans and his colleagues used either  $\text{SmI}_2(\text{THF})_2$  in THF or the metal vapor technique (in hexane/THF), they obtained only species containing coordinated THF. The solubilities of the  $\text{Sm}^{\text{II}}$  derivatives in solvents other than THF have not yet been examined. Further, chloride derivatives are known to be better starting materials than the iodides in the preparation of alkyl and hydride derivatives of the lanthanides owing to the lower solubility of  $\text{LiCl}$  than of  $\text{LiI}$  in organic solvents. We thus thought it of interest to find out whether  $\text{Sm}^{\text{II}}$  forms soluble organometallic derivatives in solvents other than THF, and to prepare the  $\text{Sm}^{\text{II}}$  analogues of the ytterbium complex  $(\text{C}_5\text{Me}_5)\text{YbCl}(\text{THF})_2/(\text{DME})$  that we reported recently [18].

## Results and discussion

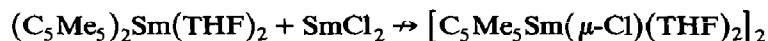
Metathetical reactions are common in organolanthanide chemistry [19] and have previously been employed in the preparation of soluble compounds such as  $(\text{C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2$  [20,21],  $(\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{L})_x$  [18],  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$  and  $[(\text{C}_5\text{Me}_5\text{Sm}(\mu\text{-I})(\text{THF})_2)_2]$  [15] and also of the insoluble compound  $(\text{C}_5\text{H}_5)_2\text{Sm}(\text{THF})_2$  [13]. The same metathetical reaction may also be expected to give isolable compounds of  $\text{Sm}^{\text{II}}$  in DME as follows:



The reaction of divalent lanthanide halides with the  $\text{C}_5\text{Me}_5^-$  anion is not always applicable. The combinations  $\text{YbCl}_2/\text{LiC}_5\text{Me}_5/\text{THF}$ ,  $\text{YbCl}_2/\text{NaC}_5\text{Me}_5/\text{Et}_2\text{O}$  and  $\text{EuCl}_2/\text{NaC}_5\text{Me}_5/\text{Et}_2\text{O}$  all failed to yield isolable  $(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{Et}_2\text{O})_n$  complexes [20], but we found that the above reaction does take place in refluxing DME with the formation of the green soluble complex  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$ . A thoroughly dried sample was used for the elemental analyses and NMR spectra. The analyses indicate that one DME molecule is coordinated to the metal ion. The integrals for the various proton signals in the NMR spectra are in the ratio 15/3/2, and confirm the analytical data. The X-ray study of a single crystal selected from those formed in the solution indicate the presence of a second DME molecule in the crystal lattice. This type of solvation is not uncommon in the case of organolanthanides [20]. The  $^1\text{H}$  NMR spectrum of the compound exhibits relatively sharp signals at 4.18 (30H), 1.9 (6H) and 1.84 ppm (4H). Evans et al. have reported that the position of the ring-methyl proton signal depends on the THF content of the complex  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_x$ , and that it moves downfield in  $\text{C}_6\text{D}_6$  as the THF content is lowered:  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ , 2.3–2.9;  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_{1.3}$ , 3.29;  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_{1.17}$ , –3.50 ppm. The ring-methyl protons in the present DME coordinated compound may thus be expected to resonate at low field. The resonance signals of  $\text{CH}_3\text{O}$  and  $\text{CH}_2\text{O}$  protons of DME are shifted towards high field. The  $^1\text{H}$  NMR spectrum of the hydrolyzed sample in  $\text{C}_6\text{D}_6$  exhibits free DME proton signals at  $\delta$  3.4 (4H) and 3.2 ppm (6H). This upfield shift is more pronounced than that observed in the case of  $(\text{C}_5\text{Me}_5)_2\text{La}(\mu\text{-Cl})_2\text{K}(\text{DME})_2$  and  $(\text{C}_5\text{Me}_5)_2\text{Pr}(\lambda\text{Cl})_2\text{Na}(\text{DME})_2$  [22] in which the DME molecules are coordinated to alkali metal ions.

As reported earlier, in the case of divalent lanthanides the metathetical reactions do not always yield the expected products. The reaction of a 1/1 mixture of  $\text{SmCl}_2$  and  $\text{NaC}_5\text{Me}_5$  did not give the chloride analogue of  $[(\text{C}_5\text{Me}_5\text{Sm}(\mu\text{-I})(\text{THF})_2)_2]$ . Even

though the reaction mixture was refluxed for 15 h, the purple compound  $(C_5Me_5)_2Sm(THF)_2$  formed did not react with the remaining unreacted  $SmCl_2$ . This indicates that the disproportionation reaction as used in the case of the iodide derivatives [15] does not work for the insoluble  $SmCl_2$ :



#### *Molecular structure of $(C_5Me_5)_2Sm(DME)$*

The molecular structure of  $(C_5Me_5)_2Sm(DME)(DME)$  consists of discrete molecules of  $(C_5Me_5)_2Sm(DME)$  with uncoordinated DME molecules in the lattice. There are no short intermolecular contacts. The samarium atom is pseudo-tetrahedrally coordinated by two cyclopentadienyl rings and the two oxygen atoms of one 1,2-dimethoxyethane molecule (Fig. 1). The  $C(\eta^5)$ -Sm angle is with  $140^\circ$  in the expected range and compares well with the ring centroid-metal-ring centroid angles in  $(C_5Me_5)_2Yb(THF)$ ,  $143.5(3)^\circ$  [20],  $(C_5Me_5)_2Yb(py)_2$ ,  $136.3(3)^\circ$  [23],  $(C_5Me_5)_2Sm(THF)_2$ ,  $137^\circ$  [7,15], and  $(C_5Me_5)_2Yb(NH_3)(THF)$ ,  $135.1^\circ$  [24], respectively. The angle  $O(1)-Sm-O(2)$  is considerably smaller,  $62.5(4)^\circ$ , but comparable with the corresponding angle,  $67.2(9)^\circ$ , in  $(C_5H_5)_2Yb(DME)$  [25]. The subtraction of the ionic radius of the octacoordinated samarium(II) ion (127 pm [26]) from the samarium-carbon bond length gives an effective ionic radius of 155 pm for the pentamethylcyclopentadienyl groups. This lends support to the view that the bonding in this type of complex is predominantly ionic.

The bonds  $Sm-O(1)$ , 252(1) pm and  $Sm-O(2)$ , 261(2) pm have lengths in the same range as the metal-oxygen bonds in  $(C_5H_5)_2Yb(DME)$ , 250(3) and 245(3) pm, respectively [25]. Notable is the  $O(1) \cdots O(2)$  contact of 267 pm, which is significantly smaller than the distance between the oxygen atoms of the uncoordinated DME molecule in the lattice (281 pm). This may be due to an interligand repulsion,

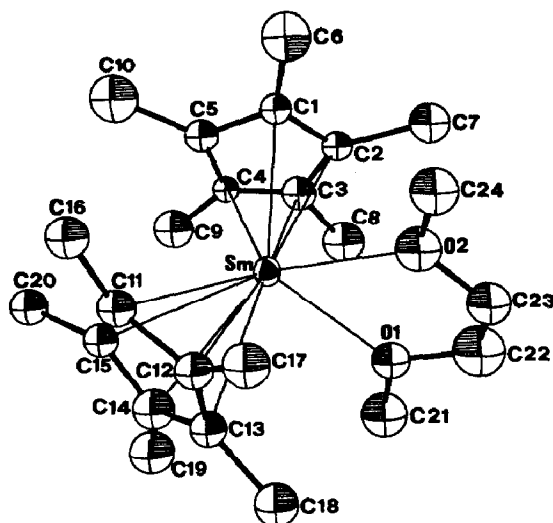


Fig. 1. Molecular structure of  $(C_5Me_5)_2Sm(DME)$  showing the atomic numbering.

and reflects the steric crowding of the samarium ion. As a result of the less bulky cyclopentadienyl groups the O...O distance in  $(C_5H_5)_2Yb(DME)$  (is, at 274 pm) is slightly shorter [25]. The uncoordinated DME molecule has the usual structure.

## Experimental

All operations were performed under purified argon by Schlenk techniques. Pre-dried THF, DME and pentane were distilled from sodium benzophenone ketyl, with the addition of some tetraglyme in the case of pentane. Benzene- $d_6$  was dried by refluxing over Na for several hours. Sodium pentamethylcyclopentadienide was prepared as described previously [22]. Anhydrous  $SmCl_2$  was prepared by reduction of  $SmCl_3$  in THF with lithium naphthalene [27]. Elemental analyses were performed on a Perkin-Elmer CHN analyzer 2400. Metal analyses were carried out by complexometric titration against dithiozone [28]. Infrared spectra were recorded for paraffin mulls between CsI plates, on a Perkin-Elmer 560 B ( $200-4000\text{ cm}^{-1}$ ) spectrometer.  $^1H$  NMR spectra were recorded for samples in sealed 5 mm tubes, on a Bruker WP80 SY instrument.

$(C_5Me_5)_2Sm(DME)$ . A suspension of 2.2 g (10 mmol) of red  $SmCl_2$  and 3.1 g (19.6 mmol) of  $NaC_5Me_5$  (free from THF) in 50 ml of DME was refluxed for about 4 h, during which time the solution became green and NaCl separated. The reaction

Table 1

Crystal and data collection parameters for  $(C_5Me_5)_2Sm(C_4H_{10}O_2) \cdot DME^a$

Formula	$C_{24}H_{40}O_2Sm \cdot C_4H_{10}O_2$
fw	601.10
Space group <sup>b</sup>	$P2_12_12_1$
a, pm	1101.4(4)
b, pm	2023.1(5)
c, pm	1337.2(5)
V, pm <sup>3</sup>	$2979.6 \times 10^6$
Z	4
$\rho_{calc}$ , g/cm <sup>3</sup>	1.34
$\mu$ , cm <sup>-1</sup>	18.82
F(000)	1248
Diffractometer	Enraf-Nonius CAD 4
Radiation, $\lambda$ , pm	Mo-K $\alpha$ , 71.069
Temperature, K	135(5)
Scan technique	$\omega-2\theta$
Data collected <sup>c</sup>	$0 \rightarrow h, \bar{k} \rightarrow k, \bar{l} \rightarrow l$
$2\theta$ limits	$1^\circ \leq 2\theta \leq 40^\circ$
No. of unique data	2716
No. of observed data, $I \geq 3\sigma(I)$	2524
$R = \sum[ F_o  -  F_c ] / \sum F_o  =$	0.0574
No. of parameters	192
Corrections	anomalous dispersion Lorentz and polarization effects

<sup>a</sup> Estimated standard deviations of the last significant digit are given in parentheses. <sup>b</sup> No. 19 of the International Tables. <sup>c</sup> Due to a failure of the low temperature unit the data collection was terminated after 4604 reflections measured.

mixture was cooled to room temperature and stirring was continued for 3 h. The mixture was then allowed to settle at a temperature of 10 °C, and the cold solution than filtered through a fine frit. The volume of the filtrate was slowly reduced under vacuum to 10 ml, and the solid filtered off, still cold. The resulting solid was rinsed twice with pentane to yield the title compound as microcrystals (3.6 g, 70%). Anal.: Found: C, 56.05; H, 7.63; Sm, 28.98.  $C_{24}H_{40}O_2Sm$  calcd.: C, 55.97; H, 7.83; Sm, 29.99%. IR (Nujol,  $cm^{-1}$ ): 3400, 2705, 1640, 1620, 1370, 1240, 1200, 1130, 1095, 1040, 860, 805.

*X-Ray crystal structure determination.* Suitable crystals of  $(C_5Me_5)_2Sm(DME)$  were obtained by recrystallization from DME. The crystals were stored under DME. A small amount of this suspension was transferred into a device similar to that reported by Veith and Bärninghausen [29]. An irregular shaped crystal with an approximate diameter of 0.30 mm was selected, attached with grease to the end of a glass fibre and placed in the cold nitrogen stream in the diffractometer.

Table 2

Final positional parameters for  $(C_5Me_5)_2Sm(O_2C_4H_{10}) \cdot DME^a$ 

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>eq</sub>
Sm	0.96863(8)	0.91057(4)	0.08384(7)	1.87
C(1)	1.0634(14)	0.7842(8)	0.0675(14)	2.11
C(2)	1.1277(17)	0.8190(9)	-0.0060(14)	2.05
C(3)	1.2037(18)	0.8631(10)	0.0489(15)	2.83
C(4)	1.1895(17)	0.8550(9)	0.1445(13)	1.63
C(5)	1.1014(18)	0.8048(10)	0.1626(15)	2.50
C(6)	0.9715(24)	0.7263(11)	0.0510(15)	4.71
C(7)	1.1182(19)	0.8029(11)	-0.1114(15)	3.58
C(8)	1.2880(19)	0.9115(14)	-0.0058(17)	4.40
C(9)	1.2624(20)	0.8910(11)	0.2265(17)	3.97
C(10)	1.0647(22)	0.7722(12)	0.2640(18)	5.00
C(11)	0.7911(16)	0.9211(10)	0.2376(14)	2.63
C(12)	0.7462(18)	0.9621(10)	0.1539(15)	2.57
C(13)	0.8203(17)	1.0190(9)	0.1466(14)	2.44
C(14)	0.9111(20)	1.0151(10)	0.2200(16)	3.41
C(15)	0.8932(17)	0.9543(9)	0.2743(14)	2.33
C(16)	0.7351(19)	0.8604(10)	0.2764(16)	3.05
C(17)	0.6336(16)	0.9470(10)	0.0906(19)	3.42
C(18)	0.7972(18)	1.0745(9)	0.0769(18)	3.57
C(19)	1.0055(20)	1.0651(10)	0.2369(17)	4.32
C(20)	0.9657(20)	0.9332(9)	0.3654(13)	2.87
O(1)	1.0024(11)	0.9924(6)	-0.0559(9)	3.03
O(2)	0.8544(11)	0.8890(6)	-0.0842(13)	3.73
C(21)	1.0775(22)	1.0496(11)	-0.0494(18)	4.68
C(22)	0.9740(28)	0.9793(13)	-0.1540(18)	5.60
C(23)	0.8686(20)	0.9345(10)	-0.1602(17)	3.58
C(24)	0.7672(19)	0.8389(10)	-0.0974(19)	3.70
O(3)	0.6232(16)	0.2953(9)	0.0636(16)	6.99
O(4)	0.8160(17)	0.3554(9)	-0.0390(13)	5.69
C(25)	0.5666(30)	0.2520(17)	0.1377(25)	8.64
C(26)	0.6946(24)	0.2580(14)	-0.0062(22)	4.88
C(27)	0.7362(23)	0.3064(13)	-0.0780(24)	5.54
C(28)	0.8605(21)	0.4008(13)	-0.1101(17)	4.73

<sup>a</sup> Estimated standard deviations of the last significant digit are given in parentheses.

Initial investigations showed the crystal system to be orthorhombic. The intensities  $0 \rightarrow h$ ,  $\bar{k} \rightarrow k$ ,  $\bar{l} \rightarrow l$  in the  $2\theta$  range  $1^\circ \leq 2\theta \leq 40^\circ$  were measured at 135(5) K, by use of  $\omega$ - $2\theta$  scans with Mo- $K_\alpha$  radiation ( $\lambda$  71.069 pm). Three reflections were checked every 2 h, and the maximum fluctuation found to be 12.2%. Corresponding corrections were applied to the raw intensities. The crystal orientation was checked after each 200 intensity measurements by scanning three orientation check reflections. In case of an angular change greater than  $0.1^\circ$  an array of 20 reflections was recentered and a new orientation matrix was calculated. A failure of the low temperature device resulted in decomposition of the crystal after 4600 reflections had been collected. The subsequent calculations were made on the basis of these reflections.

The data were corrected for Lorentz and polarization effects. No absorption correction was made ( $\mu$  18.82  $\text{cm}^{-1}$ ). From systematic absent reflections ( $h00$ ,  $h = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ;  $00l$ ,  $l = 2n + 1$ ) the space group was determined to be  $P2_12_12_1$  (No. 19 of the International Tables).

The positional parameters of the samarium atom were calculated from the Patterson map. A difference Fourier map based on the metal atom phase revealed the positions of all non-hydrogen atoms in the asymmetric unit. The positional parameters of these atoms were refined by full-matrix least squares with anisotropic thermal parameters for Sm and isotropic ones for all carbon and oxygen atoms. Hydrogen positions were calculated but not refined ( $d(\text{C-H})$  108 pm) and added to

Table 3

Selected interatomic distances (pm) for  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{O}_2\text{C}_4\text{H}_{10}) \cdot \text{DME}^a$ . Cp denotes the centroids of the cyclopentadienyl groups (C(1)–C(5), Cp(1); C(11)–C(15), Cp(2))

Atoms	Distance (pm)	Atoms	Distance (pm)
Sm–O(1)	252(1)	C(1)–C(5)	140(3)
Sm–O(2)	261(2)	C(1)–C(6)	157(3)
Sm–C(1)	277(2)	C(2)–C(3)	143(3)
Sm–C(2)	282(2)	C(2)–C(7)	145(3)
Sm–C(3)	280(2)	C(3)–C(4)	130(2)
Sm–C(4)	280(2)	C(3)–C(8)	154(3)
Sm–C(5)	280(2)	C(4)–C(5)	143(3)
Sm–C(11)	285(2)	C(4)–C(9)	154(3)
Sm–C(12)	282(2)	C(5)–C(10)	156(3)
Sm–C(13)	286(2)	C(11)–C(12)	148(3)
Sm–C(14)	286(2)	C(11)–C(15)	140(3)
Sm–C(15)	282(2)	C(11)–C(16)	147(3)
O(1)–C(21)	143(2)	C(12)–C(13)	141(3)
O(1)–C(22)	138(3)	C(12)–C(17)	153(3)
O(2)–C(23)	138(2)	C(13)–C(14)	141(3)
O(2)–C(24)	141(2)	C(13)–C(18)	148(3)
O(3)–C(25)	146(3)	C(14)–C(15)	144(3)
O(3)–C(26)	144(3)	C(14)–C(19)	147(3)
O(4)–C(27)	142(3)	C(15)–C(20)	152(3)
O(4)–C(28)	141(3)	C(22)–C(23)	148(4)
C(1)–C(2)	140(3)	C(26)–C(27)	145(4)
Sm–Cp(1)	254	Sm–Cp(2)	257
O(1) $\cdots$ O(2)	268	O(3) $\cdots$ O(4)	281

<sup>a</sup> Estimated standard deviations of the last significant digit are given in parentheses.

Table 4

Selected interatomic angles (deg) for  $(C_5Me_5)_2Sm(O_2C_4H_{10}) \cdot DME^a$ . Cp denotes the centroids of the cyclopentadienyl groups (C(1)–C(5), Cp(1); C(11)–C(15), Cp(2))

Atoms	Angle	Atoms	Angle
O(1)–Sm–O(2)	62.8(4)	C(11)–C(12)–C(17)	125(2)
C(2)–C(1)–C(5)	110(2)	C(13)–C(12)–C(17)	126(2)
C(2)–C(1)–C(6)	127(2)	C(12)–C(13)–C(14)	109(2)
C(5)–C(1)–C(6)	123(2)	C(12)–C(13)–C(18)	124(2)
C(1)–C(2)–C(3)	104(2)	C(14)–C(13)–C(18)	127(2)
C(1)–C(2)–C(7)	122(2)	C(13)–C(14)–C(15)	108(2)
C(3)–C(2)–C(7)	133(2)	C(13)–C(14)–C(19)	125(2)
C(2)–C(3)–C(4)	111(2)	C(15)–C(14)–C(19)	127(2)
C(2)–C(3)–C(8)	121(2)	C(11)–C(15)–C(14)	110(2)
C(4)–C(3)–C(8)	128(2)	C(11)–C(15)–C(20)	125(2)
C(3)–C(4)–C(5)	110(2)	C(14)–C(15)–C(20)	125(2)
C(3)–C(4)–C(9)	125(2)	C(21)–O(1)–C(22)	110(2)
C(5)–C(4)–C(9)	125(2)	C(23)–O(2)–C(24)	118(2)
C(1)–C(5)–C(4)	105(2)	O(1)–C(22)–C(23)	111(2)
C(1)–C(5)–C(10)	126(2)	O(2)–C(23)–C(22)	117(2)
C(4)–C(5)–C(10)	129(2)	C(25)–O(3)–C(26)	111(2)
C(12)–C(11)–C(15)	105(2)	C(27)–O(4)–C(28)	115(2)
C(12)–C(11)–C(16)	127(2)	O(3)–C(26)–C(27)	104(2)
C(15)–C(11)–C(16)	128(2)	O(4)–C(27)–C(26)	115(3)
C(11)–C(12)–C(13)	108(2)	Cp(1)–Sm–Cp(2)	140
Cp(1)–Sm–O(1)	110	Cp(1)–Sm–O(2)	104
Cp(2)–Sm–O(1)	103	Cp(2)–Sm–O(2)	111

<sup>a</sup> Estimated standard deviations of the last significant digit are given in parentheses.

the structure model with a constant isotropic temperature factor ( $U_{iso,H}$  400 pm<sup>2</sup>). Unit weights were used throughout the refinement.

All calculations were performed with the program SHELX [30]. Atomic scattering factors for Sm were taken from ref. 31, and anomalous dispersion terms from ref. 32.

Additional data pertinent to the crystal structure determination are summarized in Table 1. Final positional parameters are listed in Table 2. The atomic numbering scheme used is shown in Fig. 1. Selected interatomic distances and angles are listed in Tables 3 and 4, respectively. Further details are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, West Germany on quoting the depository number CSD 53204, the authors, and the full journal citation.

## References

- 1 H. Schumann, C. Janiak and J. Pickardt, *J. Organomet. Chem.*, 349 (1988) 117.
- 2 Present address: Department of Chemistry, Katiya University, Warangal 506 009, India.
- 3 D.F. Evans, G.V. Fazakerley and R.F. Philips, *J. Chem. Soc., Chem. Commun.*, (1970) 244.
- 4 D.F. Evans, G.V. Fazakerley and R.F. Philips, *J. Chem. Soc. A*, (1970) 1931.
- 5 P. Girard, J.L. Namy and H.B. Kagan, *J. Am. Chem. Soc.*, 102 (1980) 2693.
- 6 P. Girard, R. Couffignal and H.B. Kagan, *Tetrahedron Lett.*, 22 (1981) 3959.
- 7 W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 103 (1981) 6507.
- 8 P.L. Watson, *J. Chem. Soc., Chem. Commun.*, (1980) 652.

- 9 C.J. Burns and R.A. Andersen, *J. Am. Chem. Soc.*, 109 (1987) 915 and 941.
- 10 S.J. Swamy and H. Schumann, unpublished results; M.N. Bochkarev, A.A. Trifonov, G.A. Razuvaev, M.A. Ilatovskaya and V.B. Shur, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1986) 1898; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1986) 1726.
- 11 L.R. Morss, *Chem. Rev.*, 76 (1976) 827.
- 12 G.W. Whatt and E.W. Gillow, *J. Am. Chem. Soc.*, 91 (1969) 775.
- 13 J.L. Namy, P. Girard and H.B. Kagan, *Nouv. J. Chim.*, 5 (1981) 479.
- 14 W.J. Evans and H.A. Zinnen, unpublished results.
- 15 W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 107 (1985) 941.
- 16 W.J. Evans, L.A. Hughes and T.P. Hanusa, *Organometallics*, 5 (1986) 1285.
- 17 S.J. Swamy, J. Loebel and H. Schumann, to be submitted for publication.
- 18 S.J. Swamy and H. Schumann, *J. Organomet. Chem.*, 334 (1987) 1.
- 19 W.J. Evans in: F.R. Hartley and S. Patai, Eds., *The Chemistry of the Metal-Carbon Bond*, Wiley, New York, 1982, p. 489.
- 20 T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 19 (1980) 2999.
- 21 P.L. Watson, J.F. Whitney and R.L. Harlow, *Inorg. Chem.*, 20 (1981) 3271.
- 22 H. Schumann, I. Albrecht, J. Loebel, E. Hahn, M.B. Hossain and D. van der Helm, *Organometallics*, 5 (1986) 1296.
- 23 T.D. Tilley, R.A. Andersen, B. Spencer and A. Zalkin, *Inorg. Chem.*, 21 (1982) 2647.
- 24 A.L. Wayda, J.L. Dye and R.D. Rogers, *Organometallics*, 3 (1984) 1605.
- 25 G.P. Deacon, P.I. Mackinnon, T.W. Hambley and J.C. Taylor, *J. Organomet. Chem.*, 259 (1983) 91.
- 26 R.D. Shannon, *Acta Cryst. A*, 32 (1976) 751.
- 27 K. Rossmann, *Monatsh. Chem.*, 110 (1979) 109.
- 28 G. Jander and H. Blasius, *Einführung in das Anorganisch-Chemische Praktikum*, S. Hirzel, Stuttgart, 1973; p. 351.
- 29 M. Veith and H. Bärninghausen, *Acta Cryst. B*, 30 (1974) 1806.
- 30 G.M. Sheldrick, *SHELX-76 System of Programs*, 1976.
- 31 D.T. Cromer and J.B. Mann, *Acta Cryst. A*, 24 (1968) 321.
- 32 D.T. Cromer and D.J. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.