

# A new method for the synthesis of $\text{Ln}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$ ( $\text{Ln} = \text{Nd, Sm, Gd, Yb}$ ), and the X-ray crystal structure of $\text{Yb}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$

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## Abstract

A series of neutral  $\eta^6\text{-C}_6\text{Me}_6$  complexes of lanthanide elements  $\text{Ln}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$  ( $\text{Ln} = \text{Nd, Sm, Gd, Yb}$ ) has been prepared directly in good yields from the reaction of  $\text{LnCl}_3$ ,  $\text{AlCl}_3$  and  $\text{C}_6\text{Me}_6$  in toluene. The complexes have been characterized by elemental analysis, IR and MS. Complex  $\text{Yb}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$  (1) crystallizes from toluene in monoclinic space group  $P2_1/a$ , with  $a = 12.203(4)$ ,  $b = 16.918(4)$ ,  $c = 18.718(3)$  Å,  $\beta = 100.84(3)^\circ$ ,  $V = 3795.37$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.63$  g cm<sup>-3</sup>. The X-ray diffraction study reveals that the Yb atom has distorted pentagonal bipyramidal geometry with  $\text{C}_6\text{Me}_6$  in an apical position. The average Yb–C bond length is 2.86(4) Å.

**Key words:** Neodymium; Samarium; Gadolinium; Ytterbium; Arene; X-ray diffraction

## 1. Introduction

The first neutral  $\eta^6$ -arene lanthanide complex  $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$  (2) was prepared and structurally characterized in 1986 [1,2]. Due to the differences in bonding properties between neutral  $\pi$ -arene complexes and ionic complexes, such as allyl-, cyclopentadienyl-, and cyclooctatetraenyl-derivatives, much attention has been paid to the synthesis and bonding properties of  $\eta^6$ -arene complexes of lanthanides [3,4]. Some new  $\eta^6$ -arene complexes have been synthesized and structurally characterized, including  $\text{Ln}(\eta^6\text{-m-Me}_2\text{C}_6\text{H}_4)(\text{AlCl}_4)_3$  [5],  $\text{Ln}(\eta^6\text{-C}_6\text{H}_6)(\text{AlCl}_4)_3$  [6] and  $(t\text{-Bu}_3\text{C}_6\text{H}_3)_2\text{Ln}$  [7]. All the complexes of  $\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_3$  reported so far were synthesized under reducing Friedel-Crafts conditions. During our study on the synthesis of  $\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_3$ , we hypothesized that reduction might not be necessary for the formation of  $\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_3$  in which the central metal is in the oxidation state +3. We tried to prepare such complexes by reaction in the absence of Al powders. We have now synthesized some complexes

$\text{Ln}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$  ( $\text{Ln} = \text{Nd, Sm, Gd, and Yb}$ ) by the new method.

## 2. Experimental section

All operations were carried out under argon in Schlenk-type glassware.

Toluene was refluxed over Na and distilled before use. Anhydrous  $\text{LnCl}_3$  ( $\text{Ln} = \text{Nd, Sm, Gd, Yb}$ ) was prepared according to the published procedure [8],  $\text{AlCl}_3$  was sublimed prior to use and  $\text{C}_6\text{Me}_6$  was used as purchased. The contents of Ln and Cl were analysed by EDTA titration and the Volhart method, respectively. IR spectra were recorded on an FTS-20E spectrometer as KBr pellets, and MS spectra were recorded on a VG Quattro MS spectrometer by the EI method.

### 2.1. Preparation of $\text{Ln}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$

#### 2.1.1. $\text{Nd}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3 \cdot \text{MeC}_6\text{H}_5$

$\text{NdCl}_3$  (251 mg, 1.0 mmol),  $\text{AlCl}_3$  (133 mg, 3.0 mmol) and  $\text{C}_6\text{Me}_6$  (200 mg, 1.2 mmol) were placed in a flask containing 35 ml toluene. The mixture was stirred at 90–95°C for three days. During the period of the reaction, the colour of the solution changed to blue. After the unreacted halides had been removed by

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centrifugation, the solution was cooled slowly to room temperature. Some days later, blue crystals were isolated from the solution, washed in toluene and dried *in vacuo*. Yield was 426 mg (47%). Anal. found: Nd 15.18, Cl 46.83; calcd. for NdC<sub>19</sub>H<sub>26</sub>Al<sub>3</sub>Cl<sub>12</sub>: Nd 15.93, Cl 47.01%. The crystals decomposed at 103°C. IR: 1567s, 1488s, 1250w, 1020w, 900b, 777s, 710s cm<sup>-1</sup>. MS: *m/z* 249 (< 1%, NdCl<sub>3</sub>), 230(83%, 2AlCl<sub>3</sub> - Cl), 162(100%, C<sub>6</sub>Me<sub>6</sub>), 132(42%, AlCl<sub>3</sub>).

### 2.1.2. Sm( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>·MeC<sub>6</sub>H<sub>5</sub>

In essentially the same way as described in 2.1.1, SmCl<sub>3</sub>(257 mg, 1.0 mmol), AlCl<sub>3</sub>(133 mg, 3.0 mmol) and C<sub>6</sub>Me<sub>6</sub>(200 mg, 1.2 mmol) were mixed. During the period of the reaction, the colour of the solution changed to yellow. After the workup, yellow crystals were isolated from the solution. Yield: 574 mg, 63%; T<sub>decomp</sub>: 104°C. Anal. found: Sm 16.82, Cl 46.95; calcd. for SmC<sub>19</sub>H<sub>26</sub>Al<sub>3</sub>Cl<sub>12</sub>: Sm 16.50, Cl 46.68%. IR: 1570s, 1549s, 1475s, 1245w, 1018w, 905b, 780s, 715s cm<sup>-1</sup>. MS: *m/z* 546 (< 1%, M - 2AlCl<sub>3</sub>), 418 (< 1%, M - 3AlCl<sub>3</sub>), 472 (< 1%, M - 2Al - Cl<sub>3</sub> - 5CH<sub>3</sub>), 396 (< 1%, 3AlCl<sub>3</sub>), 326 (< 2%, 3AlCl<sub>3</sub> - 2Cl), 264(3%, 2Al - Cl<sub>3</sub>), 259(18%, SmCl<sub>3</sub>), 231(36%, 2AlCl<sub>3</sub> - Cl), 162(100%, C<sub>6</sub>Me<sub>6</sub>), 147(100%, C<sub>6</sub>Me<sub>6</sub> - Me), 132(78%, AlCl<sub>3</sub>).

### 2.1.3. Gd( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>·MeC<sub>6</sub>H<sub>5</sub>

In essentially the same way as described for 2.1.1, GdCl<sub>3</sub>(264 mg, 1.0 mmol), AlCl<sub>3</sub>(133 mg, 3.0 mmol) and C<sub>6</sub>Me<sub>6</sub>(200 mg, 1.2 mmol) were mixed. During the period of the reaction, the colour of the solution changed to yellow. After the workup, yellow crystals were isolated from the solution. Yield: 542 mg, 59%; T<sub>decomp</sub>: 103°C. Anal. found: Gd 16.77, Cl 46.35; calcd. for GdC<sub>19</sub>H<sub>26</sub>Al<sub>3</sub>Cl<sub>12</sub>: Gd 17.13, Cl 46.34%. IR: 1570s, 1490s, 1540s, 1440s, 1390w, 1250w, 1030w, 1010w, 905b, 818m, 770m, 710m, 675m cm<sup>-1</sup>. MS spectra: *m/z* 262 (< 1%, GdCl<sub>3</sub>), 230(28%, 2AlCl<sub>3</sub> - Cl), 162(23%, C<sub>6</sub>Me<sub>6</sub>), 147(64%, C<sub>6</sub>Me<sub>6</sub> - Me), 132(100%, AlCl<sub>3</sub>).

### 2.1.4. Yb( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>·MeC<sub>6</sub>H<sub>5</sub>

In essentially the same way as described for 2.1.1, YbCl<sub>3</sub>(279 mg, 1.0 mmol), AlCl<sub>3</sub>(133 mg, 3.0 mmol) and C<sub>6</sub>Me<sub>6</sub>(200 mg, 1.2 mmol) were mixed. During the period of the reaction, the colour of the solution changed to brown. After the workup, deep blue crystals were isolated from the solution. Yield: 579 mg, 62%; T<sub>decomp</sub>: 104°C. Anal. found: Yb 17.57, Cl 44.47; calcd. for YbC<sub>19</sub>H<sub>26</sub>Al<sub>3</sub>Cl<sub>12</sub>: Yb 18.24, Cl 45.56%. IR: 1560w, 1490w, 1520w, 1480s, 1390s, 1258b, 1020w, 900b, 810w, 770m, 715m cm<sup>-1</sup>. MS: *m/z* 569 (< 1%, M - 2AlCl<sub>3</sub>), 440 (< 1%, M - 3AlCl<sub>3</sub>), 493 (< 1%, M - 2AlCl<sub>3</sub> - 5Me), 396 (< 1%, 3AlCl<sub>3</sub>), 326(4%, 3AlCl<sub>3</sub> -

TABLE 1. Crystal data for complex 1

Formula	Yb( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )(AlCl <sub>4</sub> ) <sub>3</sub> ·MeC <sub>6</sub> H <sub>5</sub>
FW	933.77
Space group	P2 <sub>1</sub> /a
<i>a</i> (Å)	12.203(4)
<i>b</i> (Å)	16.918(4)
<i>c</i> (Å)	18.718(8)
$\beta$ (°)	100.84(3)
<i>V</i> (Å <sup>3</sup> )	3795.37
<i>Z</i>	4
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.63
Crystal size (mm <sup>3</sup> )	0.16 × 0.08 × 0.2
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	35.1
Temp. (°C)	23
Scan method	w
Data collection range, $2\theta$ (°)	3–45
No. of unique data	4772
$F_o^2 > 3\sigma(F_o^2)$	1619
No. of parameters refined	286
<i>f</i> (000)	1812
<i>R</i>	0.081
<i>R</i> <sub>w</sub>	0.073

2Cl), 276(20%, YbCl<sub>3</sub>), 264(6%, 2AlCl<sub>3</sub>), 231(18%, 2AlCl<sub>3</sub> - Cl), 162(92%, C<sub>6</sub>Me<sub>6</sub>), 147(100%, C<sub>6</sub>Me<sub>6</sub> - Me), 132(69%, AlCl<sub>3</sub>).

## 2.2. X-ray crystallography

All geometrical and intensity data were obtained on an R3M/E automatic four circle diffractometer. A single crystal of 1 was sealed in a Lindemann glass capillary under argon.

The crystal data were collected using graphite monochromated Mo K $\alpha$  radiation, in  $\omega$  scan mode. 4772 reflections were collected within the range of  $3^\circ \leq 2\theta \leq 45^\circ$ , of which 1619 reflections with  $F_o^2 > 3\sigma(F_o^2)$  were observed. The crystal data were corrected for Lorentz and polarization factors but not for absorption. The heavy atom positions were derived from a three-dimensional Patterson map and the remainder of the structure developed by consecutive least-squares procedures and difference Fourier maps. All positional parameters and temperature factors for non-hydrogen atoms were refined anisotropically. The refinement converged at residuals  $R = 0.081$  and  $R_w = 0.073$ . Details of the crystal data collections and refinement are listed in Table 1. Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2.

## 3. Results and discussion

### 3.1. Synthesis

It has been reported that the reaction of SmCl<sub>3</sub>, AlCl<sub>3</sub> and C<sub>6</sub>Me<sub>6</sub> in the molar ratio of 1:7.5:2.5

TABLE 2. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) and their estimated standard deviations for Yb( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>·MeC<sub>6</sub>H<sub>5</sub>

Atom	x	y	z	U <sub>eq</sub>
Yb	1017(1)	5720(1)	7842(1)	40(1)
Cl(1)	898(8)	5586(7)	9319(5)	72(5)
Cl(2)	-757(7)	6680(6)	7925(5)	52(5)
Cl(3)	-749(8)	4729(7)	8011(6)	78(5)
Cl(4)	2094(8)	6992(6)	8603(5)	67(5)
Cl(5)	-382(7)	5442(6)	6489(5)	63(5)
Cl(6)	-3237(8)	5650(9)	7194(7)	108(6)
Cl(7)	3004(10)	6608(9)	10501(7)	111(7)
Cl(8)	1283(8)	6940(7)	6886(5)	68(5)
Cl(9)	-2341(9)	5797(8)	9088(6)	100(6)
Cl(10)	429(10)	7553(8)	9845(7)	112(7)
Cl(11)	-1423(10)	7284(8)	5822(8)	127(8)
Cl(12)	659(10)	6359(9)	5055(6)	103(6)
Al(1)	-1895(8)	5720(9)	8103(7)	68(5)
Al(2)	1600(10)	6754(8)	9647(7)	72(6)
Al(3)	-1(11)	6554(8)	5986(7)	70(6)
C(1)	1684(25)	4273(23)	7402(19)	60(15)
C(2)	2167(25)	4747(21)	6856(30)	111(23)
C(3)	2896(30)	5240(22)	7208(19)	66(18)
C(4)	3346(25)	5342(25)	8008(26)	85(21)
C(5)	3013(28)	4842(25)	8504(18)	58(17)
C(6)	2088(23)	4309(22)	8186(18)	55(15)
C(7)	892(30)	3660(21)	7140(22)	72(19)
C(8)	1986(45)	4632(32)	6143(21)	146(31)
C(9)	3511(31)	5849(28)	6758(19)	84(20)
C(10)	4353(30)	5974(27)	8412(31)	124(29)
C(11)	3501(33)	4793(29)	9353(18)	87(21)
C(12)	1693(33)	3690(55)	8697(29)	110(27)
C(13)	1162(33)	7643(30)	2230(26)	108(27)
C(14)	402(35)	8126(29)	1695(30)	352(76)
C(15)	11(39)	8517(31)	2274(26)	123(29)
C(16)	262(35)	8577(25)	3074(29)	107(28)
C(17)	1055(36)	7993(32)	3462(26)	111(28)
C(18)	1583(34)	7454(30)	3010(22)	136(33)
C(19)	2212(43)	6894(37)	3359(39)	183(41)

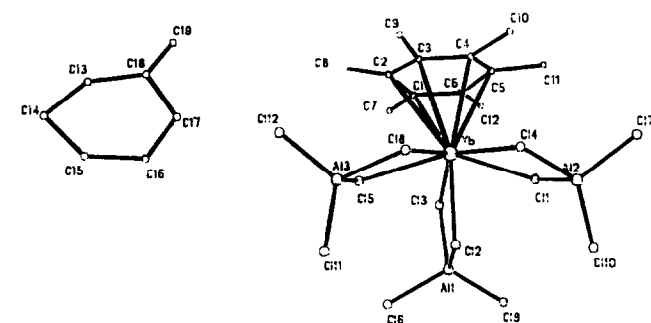
complexes. If the reaction temperature is higher than 95°C or the reaction lasts longer than three days at 90–95°C, the tarry residues will increase markedly and the yield of the complex will decrease dramatically, to the extent that the pure complex cannot be isolated. When the reaction temperature is much lower than 90°C, it is difficult to get pure products. It is interesting that when EuCl<sub>3</sub> reacts with AlCl<sub>3</sub> and C<sub>6</sub>Me<sub>6</sub> under the same reaction conditions, the desired trivalent Eu complex cannot be isolated. When the molar ratio of EuCl<sub>3</sub> to AlCl<sub>3</sub> decreases to 1:1, an unexpected reaction occurs and a new divalent neutral arene complex of Eu, [Eu(C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>2</sub>]<sub>4</sub> is isolated [9].

All complexes have been characterized by IR and MS. The IR skeletal C=C vibrations within the phenyl ring appear in the ranges 1558–1570 and 1440–1488 cm<sup>-1</sup>, and out-of-plane ring bendings at 710–675 cm<sup>-1</sup>. No MS spectra showed the parent molecular ions, but AlCl<sub>3</sub>, LnCl<sub>3</sub>, C<sub>6</sub>Me<sub>6</sub> ions and some fragments which are attributed to the moieties containing AlCl<sub>3</sub>, C<sub>6</sub>Me<sub>6</sub> groups connected with the central metal could be observed clearly. Furthermore, we also found that the contents of the higher molecular weight fragments were very low (<1%), indicating instability of the neutral arene complexes under measurement conditions (vacuum up to 10<sup>-6</sup> mbar).

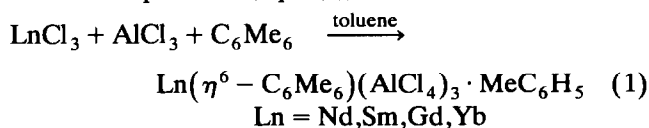
These arene complexes are hardly soluble in aromatic solvents and they decompose in electron-donor solvents such as diethyl ether and THF. <sup>1</sup>H-NMR spectra of these complexes were not measured because most Ln<sup>3+</sup> ions are paramagnetic.

### 3.2. Structure of Yb( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>·MeC<sub>6</sub>H<sub>5</sub>

The molecular structure of **1** is shown in Fig. 1. Important bond lengths and angles are listed in Table 3. The coordination polyhedra of the centre metal can be described as a distorted pentagonal bipyramid which is the same as that for **2** [1,2]. Cl(1), Cl(3), Cl(4), Cl(5) and Cl(8) are located in an equatorial plane with

Fig. 1. Molecular structure of **1**.

under reducing Friedel-Crafts conditions gives a blood red solution from which a low yield of neutral arene complex Sm( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub> **2** was obtained leaving a tarry red residue [1,2]. Although the red colour of the solution is indicative of formation of Sm<sup>2+</sup> complex, only the trivalent compound **2** was obtained and characterized. We have found that under appropriate conditions, the neutral arene complex Ln( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub> can be synthesized by the reaction of LnCl<sub>3</sub> with AlCl<sub>3</sub> and C<sub>6</sub>Me<sub>6</sub> in the molar ratio of 1:3:1.2 without Al powders (eqn. (1)):



Control of the reaction temperature and reaction times is the key point for success in isolating the title

TABLE 3. Important bond lengths and angles in complex **1**

Bond lengths			
Yb–Cl(1)	2.804(10)	Yb–Cl(1)	2.755(39)
Yb–Cl(2)	2.734(10)	Yb–Cl(2)	3.010(48)
Yb–Cl(3)	2.795(10)	Yb–Cl(3)	2.889(40)
Yb–Cl(4)	2.772(10)	Yb–Cl(4)	2.873(35)
Yb–Cl(5)	2.815(9)	Yb–Cl(5)	2.923(35)
Yb–Cl(8)	2.791(11)	Yb–Cl(6)	2.739(35)
Bond angles			
Cl(1)–Yb–Cl(2)	78.3(3)	Cl(3)–Yb–Cl(8)	134.5(3)
Cl(1)–Yb–Cl(3)	69.9(3)	Cl(4)–Yb–Cl(5)	137.8(3)
Cl(1)–Yb–Cl(4)	70.0(3)	Cl(4)–Yb–Cl(8)	69.8(3)
Cl(1)–Yb–Cl(5)	137.6(3)	Cl(5)–Yb–Cl(8)	70.8(3)
Cl(1)–Yb–Cl(8)	136.6(3)	C(1)–Yb–C(2)	29.8(11)
Cl(2)–Yb–Cl(3)	73.4(3)	C(2)–Yb–C(3)	25.4(9)
Cl(2)–Yb–Cl(4)	79.3(3)	C(3)–Yb–C(4)	30.3(12)
Cl(2)–Yb–Cl(5)	78.3(3)	C(4)–Yb–C(5)	27.4(12)
Cl(2)–Yb–Cl(8)	77.6(3)	C(5)–Yb–C(6)	30.1(10)
Cl(3)–Yb–Cl(4)	135.1(3)	C(6)–Yb–C(1)	30.8(10)
Cl(3)–Yb–Cl(5)	69.6(3)		

deviations of  $-0.0962$  to  $0.0924$  Å. The sixth chlorine atom Cl(2) occupies one apical position and C<sub>6</sub>Me<sub>6</sub> occupies the other one.

**1** and **2** are isostructural while the number of solvent molecules in the crystal lattice is different, there being one toluene in **1** and 1.5 toluene in **2**. So it is reasonable to compare the corresponding bond lengths between **1** and **2**. The mean distances of Ln–Cl<sup>p</sup> (chlorine in the plane) and Ln–Cl<sup>a</sup> (chlorine in the apical position) in **1** are 2.795(7) and 2.734(10) Å, respectively, while the corresponding distances in **2** are 2.853(6) and 2.826(6) Å, respectively. The differences of bond lengths result from the difference in ionic radii of Yb<sup>3+</sup> (1.042 Å) and Sm<sup>3+</sup> (1.132 Å) [10]. The average Yb–C distance in **1** is 2.86(4) while Sm–C in **2** is 2.89(5) Å. Considering the difference in ionic radii of Yb<sup>3+</sup> and Sm<sup>3+</sup>, it seems that the Yb–C bond is a little weaker than the Sm–C bond. The Cl–Ln–Cl bond angles for adjacent chlorine atoms in the plane, which range from 69.6 to 70.8° in **1**, are comparable to the range 69.4–71.1° in **2**.

Synthesis of the trivalent lanthanide complexes of neutral arene other than C<sub>6</sub>Me<sub>6</sub> is currently in progress. We have successfully synthesized and structurally characterized a series of arene complexes such as Nd( $\eta^6$ -(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)(AlCl<sub>4</sub>)<sub>3</sub> and Ln( $\eta^6$ -(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)(AlCl<sub>4</sub>)<sub>3</sub> (Ln = Pr, Nd). So it seems practicable to synthesize various  $\eta^6$ -arene complexes of lanthanides by this method.

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Supplementary Material Available: Tables of thermal parameters, and observed and calculated structure factors are available from the authors.

### References

- 1 F.A. Cotton and W. Schowtzer, *J. Am. Chem. Soc.*, **108** (1986) 4657.
- 2 F.A. Cotton and W. Schowtzer, *Organometallics*, **6** (1987) 1275.
- 3 D.M. Anderson, F.G.N. Cloke, P.A. Cox, N. Edelstein, J.C. Green, T. Pang, A.A. Sameh and G. Shalimoff, *J. Chem. Soc., Chem. Commun.*, (1989) 53.
- 4 W.A. King, T.J. Marks, D.M. Anderson, D.J. Duncalf and F.G. Cloke, *J. Am. Chem. Soc.*, **114** (1992) 9221.
- 5 B.C. Fan, Q. Shen and Y.H. Lin, *J. Organomet. Chem.*, **376** (1989) 61.
- 6 B.C. Fan, Q. Shen and Y.H. Lin, *J. Organomet. Chem.*, **377** (1989) 51.
- 7 J.G. Brennan, F. Geoffrey, A.A. Sameh and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, (1987) 1668.
- 8 M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.*, **24** (1962) 287.
- 9 H.Z. Liang, Q. Shen, S.C. Jin and Y.H. Lin, *J. Chem. Soc., Chem. Commun.*, (1992) 480.
- 10 R.D. Shannon, *Acta Cryst.*, **A37** (1976) 751.