

## Metalocene Derivatives of Early Transition Metals. Part 2.<sup>1</sup> Substituted Cyclopentadienyl Group 4A Dichloro-metalocene Complexes $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ ( $M = \text{Zr}$ or $\text{Hf}$ ; $\text{R} = \text{Me}$ , $\text{Et}$ , $\text{Pr}^i$ , $\text{Bu}^t$ , or $\text{SiMe}_3$ ), their Mono- and Di-alkyl Derivatives $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'\text{X}]$ ( $\text{X} = \text{Cl}$ or $\text{R}'$ ; $\text{R}' = \text{CH}_2\text{SiMe}_3$ or $\text{CH}_2\text{CMe}_3$ ), and their $d^1$ Reduction Products

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The substituted  $d^0$  metalocene dichloro-complexes  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$  ( $M = \text{Ti}^{\text{IV}}$ ,  $\text{Zr}^{\text{IV}}$ , or  $\text{Hf}^{\text{IV}}$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}^i$ ,  $\text{Bu}^t$ , or  $\text{SiMe}_3$ ), (1)–(11), have been prepared from  $\text{MCl}_4$  and  $2\text{Li}[\text{C}_5\text{H}_4\text{R}]$  in tetrahydrofuran (thf). From the appropriate dichloride and either (i)  $\text{MgR}'\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  there was obtained the chloro(alkyl)  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'\text{Cl}]$  ( $\text{R}' = \text{CH}_2\text{SiMe}_3$ ) or  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CMe}_3)\text{Cl}]$ , or (ii) alkyl-lithium in  $\text{OEt}_2$  the dialkyl  $[M'(\eta\text{-C}_5\text{H}_4\text{R}')_2(\text{CH}_2\text{XMe}_3)_2]$  ( $M' = \text{Zr}$  or  $\text{Hf}$ ;  $\text{R}' = \text{H}$ ,  $\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}^i$ , or  $\text{Bu}^t$ ;  $\text{X} = \text{C}$  or  $\text{Si}$ ), (13)–(16), was produced; treatment of  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{Cl}_2]$  with  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  gave  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{Br}_2]$ . The  $^1\text{H}$  n.m.r. spectra of each of the dichlorides (1)–(11) show the ring protons of the  $\text{C}_5\text{H}_4\text{R}$  group as an AA'BB' or  $\text{A}_2\text{B}_2$  ( $\text{R} = \text{SiMe}_3$ ) signal; the dialkyls (13)–(16) show this feature as an  $\text{A}_2\text{X}_2$  pattern, whereas in  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2(\text{CH}_2\text{SiMe}_3)\text{Cl}]$  it appears as ABCD. The  $^{13}\text{C}$  n.m.r. spectra show three signals for the corresponding carbon atoms ( $\text{C}_5\text{H}_4\text{R}$ ) and the chemical-shift data are compared with results on substituted ferrocenes or benzenes,  $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{R})_2]$  or  $\text{C}_6\text{H}_5\text{R}$ .

Treatment of the complex  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2]$  with an equimolar portion of  $\text{Na}[\text{C}_{10}\text{H}_8]$  in thf at  $20^\circ\text{C}$  yields an appropriate  $d^1$  dialkylmetal(III) complex, which is persistent for  $M = \text{Ti}$  or  $\text{Zr}$  but not for  $M = \text{Hf}$ , and is characterised by its e.s.r. spectrum [ $g_{\text{av.}}$ , 1.984–1.993;  $a(^1\text{H})$ , 0.175–0.360 mT;  $a(^{47/49}\text{Ti})$ , 0.720–1.05 mT;  $a(^{91}\text{Zr})$ , 1.000–2.410 mT] showing coupling with the  $\alpha$  protons of the alkyl group  $\text{R}'$ . As each of these (Zr) dialkyls undergoes irreversible one-electron reduction at a Pt electrode in  $0.2 \text{ mol dm}^{-3}$   $[\text{NBu}_4][\text{BF}_4]$  in thf the above  $d^1$  complexes are formulated as  $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{R})\text{R}'_2]$ . Cyclic voltammetry data are provided for several metalocene(IV) complexes: (i) dichlorides (reversible one-electron reduction leading to  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]^-$  ( $M = \text{Zr}$ ), and  $E_1^{\text{red}}$  is nearly 1 V more negative than for Ti); (ii) chloro(alkyls) (irreversible reduction); and (iii) dialkyls (irreversible reduction).

THIS paper extends the range of available zirconium(IV) and hafnium(IV) metalocene complexes of formula  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ ,  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{ClR}']$ , and  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2]$  ( $M = \text{Zr}$  or  $\text{Hf}$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}^i$ ,  $\text{Bu}^t$ , or  $\text{SiMe}_3$ ;  $\text{R}' = \text{CH}_2\text{CMe}_3$  or  $\text{CH}_2\text{SiMe}_3$ ). Such compounds have received relatively little attention, in contrast to the well studied complexes of some of the titanium analogues.<sup>2</sup> The zirconium and hafnium metalocenes  $[M(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$  ( $M = \text{Zr}$  or  $\text{Hf}$ ,  $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ) are known,<sup>3</sup> and a recent paper<sup>4</sup> deals with the synthesis of analogues ( $\text{R} = \text{Pr}^i$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{CHMePh}$ , or  $\text{CPhMe}_2$ ), obtained by reaction of the appropriate fulvalene ( $\text{C}_5\text{H}_4=\text{CR}_2$ ) derived cyclopentadienyl anion with the anhydrous metal(IV) chloride.<sup>4</sup> A further aspect of the present study relates to  $d^1$  organometal(III) complexes obtained from some of the above  $d^0$  metalocene(IV) precursors.

For the  $d^0$  dialkyl complexes  $[M(\eta\text{-C}_5\text{H}_5)_2\text{R}'_2]$  the following have been characterised:  $M = \text{Zr}$ , and  $\text{R}' = \text{Me}$ ,<sup>5</sup>  $\text{CH}_2\text{Ph}$ ,<sup>6</sup>  $\sigma$ -allyl,<sup>7</sup>  $\text{Ph}$ ,<sup>5</sup>  $\text{C}_6\text{F}_5$ ,<sup>8</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>9</sup> or  $\text{CHPh}_2$ ;<sup>10</sup>  $M = \text{Hf}$ , and  $\text{R}' = \text{Me}$ ,<sup>5</sup>  $\text{Ph}$ ,<sup>2</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>9</sup>  $\text{CHPh}_2$ ,<sup>10</sup> or  $\text{C}_6\text{F}_5$ .<sup>11</sup> A series of mixed dialkyl complexes  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{R}''\text{R}']$  has been prepared:  $\text{R}'' = \text{CH}(\text{SiMe}_3)_2$  and  $\text{R}' = \text{Me}$ ,<sup>12</sup>  $\text{Pr}^i$ ,<sup>12</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>12</sup>  $\text{Ph}$ ,<sup>12</sup> or  $\text{Bu}^t$ .<sup>10</sup> Alkyl(chloro)-complexes are less common, but the following have been reported:  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{ClR}']$  with  $\text{R}' = \text{Me}$ ,<sup>13</sup>  $\text{Et}$ ,<sup>14</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>9</sup> and  $\text{CH}(\text{SiMe}_3)_2$ ;<sup>10</sup> only the complexes containing the neopentyl type ligands exhibit appreciable stability.

The introduction of a substituent(s) into the cyclopentadienyl ring has given rise to a diverse chemistry particularly with complexes of chromium<sup>15</sup> and zir-

conium.<sup>16</sup> A ring substituent may affect the ease of displacement of chloride ligand, e.g. from  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{-}\{\text{CH}_2(\text{SiMe}_3)\text{Cl}\}]$ , see below, or the co-ordination of dinitrogen to give complexes of the type  $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{-}\{\text{CH}(\text{SiMe}_3)_2\}(\eta\text{-N}_2)]$ .<sup>17</sup>

### RESULTS AND DISCUSSION

The alkyl substituted cyclopentadienes,  $\text{C}_5\text{H}_5\text{R}$ , were synthesised by reaction of  $\text{Na}[\text{C}_5\text{H}_5]$  with the appropriate alkyl chloride in tetrahydrofuran (thf) (except for  $\text{R} = \text{Bu}^t$ , when it was necessary to use the alkyl bromide).<sup>18</sup> Metallation of the ligand with  $\text{LiBu}^n$ , followed by the reaction of the anion with the appropriate anhydrous metal(IV) chloride, gave the dichloro-metalocene complex [(1)–(11), Scheme] as white or cream air-stable crystals after recrystallisation from toluene-hexane. Metathesis with boron tribromide gave in one instance (cf. ref. 19) the corresponding bromide complex  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{Br}_2]$ , (12), in high yield.

The chloro(alkyl) complexes [(13)–(16), Scheme] were prepared by a 1:1 reaction of the dichloride with a Grignard reagent in methylene chloride. The dialkyl complexes [(18)–(23), Scheme] were prepared by reaction of the dichloride with the alkyl-lithium reagent in diethyl ether. Recrystallisation from hexane gave the chloro(alkyl) complexes as white crystals and the dialkyl complexes as pale yellow crystals. They are moderately air-stable in the solid state but somewhat more air-sensitive in solution. Analytical data, yields, and melting points are listed in Table 1.

Although the chemistry of zirconium and hafnium is

TABLE 1

Some data for substituted zirconocene(IV) and hafnocene(IV) dihalides, chloro(alkyls), and dialkyls (3)–(22) <sup>a</sup>

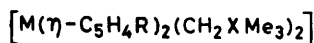
Complex	Analysis (%) <sup>b</sup>		M.p. <sup>c</sup> (θ <sub>c</sub> /°C)	Yield (%)
	C	H		
(3) [Zr(η-C <sub>5</sub> H <sub>4</sub> Et) <sub>2</sub> Cl <sub>2</sub> ]	48.9 (48.3)	5.4 (5.2)	96–98	50
(4) [Hf(η-C <sub>5</sub> H <sub>4</sub> Et) <sub>2</sub> Cl <sub>2</sub> ]	38.6 (38.6)	4.1 (4.1)	84–86	50
(5) [Zr(η-C <sub>5</sub> H <sub>4</sub> Pr) <sub>2</sub> Cl <sub>2</sub> ]	51.1 (51.0)	5.8 (5.8)	125–128	65
(6) [Hf(η-C <sub>5</sub> H <sub>4</sub> Pr) <sub>2</sub> Cl <sub>2</sub> ]	43.8 (41.4)	4.8 (4.9)	119–122	72
(7) [Zr(η-C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	53.5 (53.4)	6.1 (6.4)	187–188	63
(8) [Hf(η-C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	45.7 (44.0)	5.3 (5.3)	176–179	62
(9) [Ti(η-C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	49.3 (49.0)	6.2 (6.6)	175–177	85
(10) [Zr(η-C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	44.3 (44.0)	6.3 (6.0)	131–133	84
(11) [Hf(η-C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	36.7 (36.8)	4.9 (5.0)	125–126	80
(12) [Hf(η-C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> ]	31.4 (31.4)	4.3 (4.8)	127–130	95
(13) [Ti(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> )Cl]	55.9 (55.9)	6.8 (7.0)		85
(15) [Hf(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> )Cl]	39.0 (39.0)	4.9 (4.9)		78
(16) [Zr(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>2</sub> CMe <sub>3</sub> )Cl]	48.7 (48.8)	6.6 (6.8)	102–104	80
(17) [Hf(η-C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> )Cl]	54.0 (54.9)	6.3 (6.4)	141–143	76
(18) [Zr(η-C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> ]	56.7 (56.7)	8.5 (8.5)	103–106	82
(19) [Hf(η-C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> ]	47.2 (47.0)	6.9 (7.0)	97–100	85
(20) [Hf(η-C <sub>5</sub> H <sub>4</sub> Et) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> ]	47.4 (49.0)	7.1 (7.1)	45–47	80
(21) [Hf(η-C <sub>5</sub> H <sub>4</sub> Pr) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> ]	51.9 (50.8)	8.0 (7.8)	64–66	80
(22) [Zr(η-C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> ]	61.8 (61.5)	9.4 (9.5)	56–58	82

<sup>a</sup> All complexes are white or very pale yellow; see literature for complexes (1),<sup>4</sup> (2),<sup>4</sup> (14),<sup>9</sup> and (23).<sup>10</sup> <sup>b</sup> Calculated values are given in parentheses. <sup>c</sup> *In vacuo* in a sealed capillary.

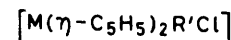
often quite similar, due to the closeness of their atomic radii (1.45 Å and 1.44 Å respectively),<sup>20</sup> it proved impossible to prepare the hafnium analogue of [Zr(η-C<sub>5</sub>H<sub>4</sub>Bu<sup>t</sup>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]; the product obtained was [Hf(η-C<sub>5</sub>H<sub>4</sub>Bu<sup>t</sup>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)Cl], (17), despite the forcing conditions employed (overnight reflux in thf or diethyl

ether). This behaviour has some precedent, in that similar substitution reactions have sometimes been shown to be subject to steric constraints. For example, it has been possible to replace only one chloride ligand in zirconocene dichloride by <sup>-</sup>CH(SiMe<sub>3</sub>)<sub>2</sub>.<sup>10</sup>

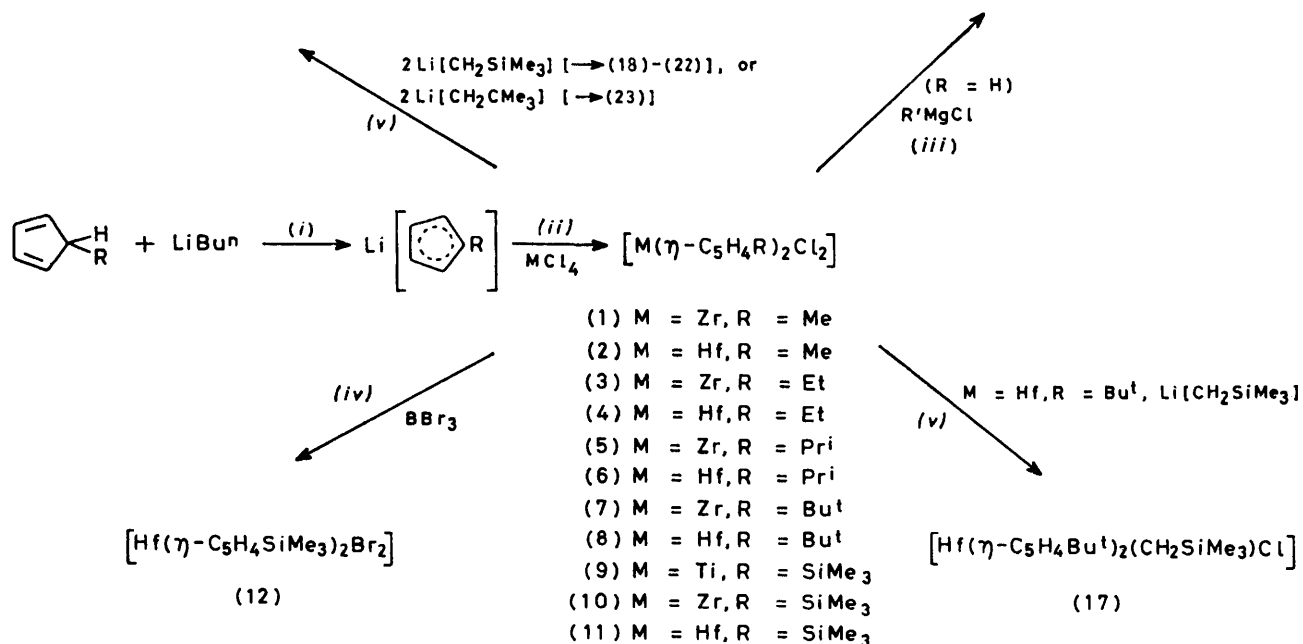
Examination of selected X-ray crystallographic data



- (18) M = Zr, R = Me, X = Si  
 (19) M = Hf, R = Me, X = Si  
 (20) M = Hf, R = Et, X = Si  
 (21) M = Hf, R = Pri, X = Si  
 (22) M = Zr, R = Bu<sup>t</sup>, X = Si  
 (23) M = Zr, R = H, X = C



- (13) M = Ti, R' = CH<sub>2</sub>SiMe<sub>3</sub>  
 (14) M = Zr, R' = CH<sub>2</sub>SiMe<sub>3</sub>  
 (15) M = Hf, R' = CH<sub>2</sub>SiMe<sub>3</sub>  
 (16) M = Zr, R' = CH<sub>2</sub>CMe<sub>3</sub>



SCHEME (i) In n-hexane, 20 °C, 2 h, (ii) in thf, 0–20 °C, 24 h, (iii) in CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, 1 h, (iv) in CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, 6 min, (v) in OEt<sub>2</sub>, 20 °C, 12 h

(Table 2) reveals the following trends, (i) and (ii). (i) The cyclopentadienyl (cp) ligand-metal distance (cp-M) increases in the order  $M = \text{Zr} > \text{Hf} \gg \text{Ti}$ . Although the ionic radii of Zr and Hf are similar (but larger than that of Ti), the shorter cp-Hf distance is attributed to the fact that the heavier members of a transition-metal group form stronger and hence shorter bonds than the lighter members.<sup>20</sup> (ii) The introduction of a substituent(s) into the cyclopentadienyl ring causes an increase in the cp-M-cp angle. Strong steric interactions of the rings in Group 4 metallocenes are demonstrated by the out-of-plane bending of the substituents in  $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)_2\text{Cl}_2]$ <sup>21</sup> or  $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{R}')_2(\text{CH}(\text{SiMe}_3)_2)\text{Cl}]$

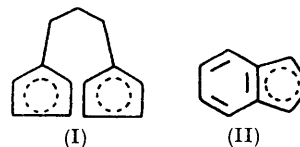
those of the iso-electronic  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{SiMe}_3)_2]^-[\text{BF}_4]$  ( $M = \text{Nb}$  or  $\text{Ta}$ ).<sup>24</sup>

The cyclopentadienyl region of the <sup>1</sup>H n.m.r. spectra of the complexes  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$  ( $M = \text{Zr}$  or  $\text{Hf}$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}^i$ , or  $\text{Bu}^t$ ), (1)–(8), shows the ring protons as a complex AA'BB' signal; although the two protons  $\alpha$  to the group R are in identical environments they are not equivalent with respect to their interactions with a given  $\beta$  proton. When the ring substituent is  $\text{SiMe}_3$  the signal approximates to  $\text{A}_2\text{X}_2$ , comprising two triplets,  $J_{\text{AX}} \approx J_{\text{AX}'} \approx 3$  Hz. A complicated pattern was observed by Samuel<sup>25</sup> for  $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ , but this was said to give way to  $\text{A}_2\text{B}_2$  in the more polar solvent

TABLE 2  
Selected X-ray crystallographic data for some Group 4 metallocene dihalides and dialkyls

Complex	Mean M-C (Å) of $\eta\text{-C}_5\text{H}_4\text{R}$	M-centroid (Å) of $\eta\text{-C}_5\text{H}_4\text{R}$	cp'-M-cp' ° (°)	Ref.
$[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$	2.370	2.058	131	<i>b</i>
$[\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$	2.293	2.067	130.2	<i>c</i>
$[\text{Ti}(\eta\text{-C}_5\text{Me}_5)_2\text{Cl}_2]$		2.12	137.4	21
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{F}_2]$	2.50		127.8	10
$[\text{Zr}(\eta\text{-C}_5\text{H}_4)_2\text{Cl}_2]$	2.52	2.20	134	10
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$	2.48		126.3	10
$[\text{Zr}(\eta\text{-C}_5\text{H}_4)_2(\text{CH}_3)_2\text{Cl}_2]$ <sup>d</sup>	2.49	2.19	129.5	10
$[\text{Hf}(\eta\text{-C}_5\text{H}_4)_2(\text{CH}_3)_2\text{Cl}_2]$ <sup>d</sup>	2.48	2.17	129.5	10
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{Ph})_2]$	2.51	2.22	128.4	10
$[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{Ph})_2]$	2.46	2.16	128.2	10
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)_2\text{Me}_2]$ <sup>e</sup>	2.54	2.23	120.8	10
$[\text{Hf}(\eta^5\text{-C}_9\text{H}_7)_2\text{Me}_2]$ <sup>e</sup>	2.52	2.22	121.0	10
$[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$		2.21	132.1	<i>f</i>
$[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2(\text{C}_4\text{Ph}_4)]$	2.49	2.20	134	10
$[\text{Ti}(\eta\text{-C}_5\text{Me}_5)_2\text{N}_2]$		2.06	145	<i>g</i>
$[\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2\text{N}_2]$		2.23	141	<i>h</i>
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2(\text{CH}(\text{SiMe}_3)_2)\text{Cl}]$	2.56	2.26	129.1	22
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{CH}(\text{SiMe}_3)_2)\text{Cl}]$	2.54	2.24	128.1	22

<sup>a</sup> cp'-M-cp' refers to the angle made by the two ring centroids and the central metal atom. <sup>b</sup> A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, *Can. J. Chem.*, 1975, **53**, 1622. <sup>c</sup> J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 6422. <sup>d</sup> The cyclopentadienyl ligand in this complex is as shown, (I). <sup>e</sup> The  $\eta^5\text{-C}_9\text{H}_7$  ligand is as shown, (II). <sup>f</sup> F. N. Fronczek, E. C. Baker, P. R. Sharp, K. N. Raymond, H. G. Alt, and M. D. Rausch, *Inorg. Chem.*, 1976, **15**, 2284. <sup>g</sup> R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8358. <sup>h</sup> R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351.



( $\text{R} = \text{Bu}^t$  or  $\text{SiMe}_3$ ).<sup>22</sup> Relief of steric strain in such complexes is probably a balance of the opening of the cp-M-cp angle and the out-of-plane bending of the ring substituent(s). The resistance of  $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{Cl}_2]$  towards dialkylation by  $\text{Li}[\text{CH}_2\text{SiMe}_3]$  is consistent with trends (i) and (ii).

The i.r. spectra of the new Group 4 metallocenes are unexceptional, showing the expected bands for an  $\eta$ -cyclopentadienyl ligand<sup>23</sup> and the alkyl groups.

**Hydrogen-1 Nuclear Magnetic Resonance Spectral Data.**—The <sup>1</sup>H n.m.r. spectral parameters for the new complexes are listed in Table 3. The spectra show the expected simplicity both for the cyclopentadienyl ring substituent R and, where applicable, the  $\text{-CH}_2\text{XMe}_3$  ( $\text{X} = \text{C}$  or  $\text{Si}$ ) group. The methylene protons of the zirconocene- $\text{CH}_2\text{XMe}_3$  complexes are more acidic than those of the hafnocene analogues, but less acidic than

acetone. The substituted dialkyls, (18)–(23), all exhibit the  $\text{A}_2\text{X}_2$  pattern with  $J = 3$  Hz for the ring protons. The cyclopentadienyl protons are all inequivalent, giving rise to an ABCD system, for which eight lines per proton are expected, although accidental equivalence gives rise to the observed quartets. The cyclopentadienyl resonances of the hafnium complexes are consistently found to be 0.1 p.p.m. upfield of the zirconocene analogues. The cyclopentadienyl resonances of the mono-alkyl complexes are at  $\tau$  ca. 4.0, those of the dihalides are to slightly lower field, and those of the dialkyls are to slightly higher field, indicating a monotonic increase in shielding of the ring protons upon alkylation at the metal.

**Carbon-13 N.M.R. Spectral Data.**—The <sup>13</sup>C n.m.r. spectra of a series of substituted ferrocenes have been recorded,<sup>26</sup> and the preparation of the substituted zir-

TABLE 3

Hydrogen-1 chemical shifts ( $\tau$ ) for zirconocene(IV) and hafnocene(IV) dihalides, chloro(alkyls), and dialkyls in  $\text{CDCl}_3$  at 34 °C

Complex	Chemical shift for $\text{C}_5\text{H}_4\text{R}^a$	Chemical shift for alkyl substituent	Chemical shift of the alkyl group
$[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$	3.45 (s)		
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$	3.48 (s)		
$[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$	3.54 (s)		
(1) <sup>b</sup>	3.7 (m)	7.7 (s), $\text{CH}_3$	
(2) <sup>b</sup>	3.8 (m)	7.7 (s), $\text{CH}_3$	
(3)	3.8 (m)	7.4 (q) ( $J = 7$ Hz), $\text{CH}_2$ ; 8.9 (t) ( $J = 7$ Hz), $\text{CH}_3$	
(4)	3.8 (m)	7.3 (q) ( $J = 7$ Hz), $\text{CH}_2$ ; 8.8 (t) ( $J = 7$ Hz), $\text{CH}_3$	
(5)	3.7 (m)	5.8 (sept) ( $J = 7$ Hz), $\text{CH}$ ; 8.7 (d) ( $J = 7$ Hz), $\text{CH}_3$	
(6)	3.9 (m)	6.8 (sept) ( $J = 7$ Hz), $\text{CH}$ ; 8.7 (d) ( $J = 7$ Hz), $\text{CH}_3$	
(7)	3.7 (m)	8.75 (s), $\text{CH}_3$	
(8)	3.8 (m)	8.70 (s), $\text{CH}_3$	
(9)	3.4 <sup>c</sup>	9.65 (s), $\text{CH}_3$	
(10)	3.4 <sup>c</sup>	9.70 (s), $\text{CH}_3$	
(11)	3.6 <sup>c</sup>	9.65 (s), $\text{CH}_3$	
(12)	3.5 <sup>c</sup>	9.70 (s), $\text{CH}_3$	
(13) <sup>d</sup>	4.1		7.9 (s) ( $\text{CH}_2$ ), 9.9 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(14) <sup>d</sup>	4.0		9.0 (s) ( $\text{CH}_2$ ), 9.7 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(15) <sup>d</sup>	4.1		9.4 (s) ( $\text{CH}_2$ ), 9.8 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(16) <sup>d</sup>	4.0		8.6 (s) ( $\text{CH}_2$ ), 8.8 (s) [ $\text{C}(\text{CH}_3)_3$ ]
(17) <sup>d</sup>	4.0 <sup>e</sup>	8.50 (s), $\text{CH}_3$	9.2 (s) ( $\text{CH}_2$ ), 9.6 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(18) <sup>d</sup>	4.2	7.9 (s), $\text{CH}_3$	9.6 (s) ( $\text{CH}_2$ ), 9.5 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(19) <sup>d</sup>	4.2	7.8 (s), $\text{CH}_3$	9.7 (s) ( $\text{CH}_2$ ), 10.2 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(20) <sup>d</sup>	4.1	7.2 (q) ( $J = 7$ Hz), $\text{CH}_2$ ; 8.5 (t) ( $J = 7$ Hz), $\text{CH}_3$	9.9 (s) ( $\text{CH}_2$ ), 9.5 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(21) <sup>d</sup>	3.9	6.8 (sept) ( $J = 7$ Hz), $\text{CH}$ ; 8.6 (d) ( $J = 7$ Hz), $\text{CH}_3$	10.2 (s) ( $\text{CH}_2$ ), 9.6 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(22)	4.0	8.5 (s), $\text{CH}_3$	9.8 (s) ( $\text{CH}_2$ ), 9.6 (s) [ $\text{Si}(\text{CH}_3)_3$ ]
(23)	4.0 (s)		9.3 (s) ( $\text{CH}_2$ ), 8.9 (s) [ $\text{C}(\text{CH}_3)_3$ ]

<sup>a</sup> Complex multiplet; midpoint value quoted. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet. <sup>b</sup> Ref. 1. <sup>c</sup> Two triplets  $J = 3$  Hz; midpoint value quoted. <sup>d</sup> Solvent  $\text{C}_6\text{D}_6$ . <sup>e</sup> Four quartets; midpoint value quoted.

conocene and hafnocene dichloro-complexes (1)–(11) now provides an opportunity to make comparisons. The carbon atoms of the cyclopentadienyl rings of the Group 4 metal complexes resonate downfield from the uncomplexed  $\text{C}_5\text{H}_5^-$  ligand, whereas in the substituted ferrocenes they are observed upfield of free  $\text{C}_5\text{H}_5^-$ . This demonstrates that there is little, if any, back-donation of electron density from the Group 4 metal to

the ligand. Typically three resonances are observed: one for  $\text{C}^1$ , the unique carbon bearing the substituent, one for the two carbon atoms  $\alpha$  to  $\text{C}^1$  ( $\text{C}^2$  and  $\text{C}^5$ ), and one for the two carbon atoms  $\beta$  to  $\text{C}^1$  ( $\text{C}^3$  and  $\text{C}^4$ ). Chemical-shift data are in Table 4.

Carbon-13 chemical shifts for the substituted ferrocenes show that when R in  $\text{C}_5\text{H}_4\text{R}$  is an electron-donating group,  $\text{C}^1$  is deshielded and resonates at lower field,

TABLE 4

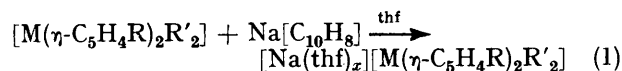
Carbon-13 chemical-shift data (p.p.m. ref. to  $\text{SiMe}_4 = 0$  p.p.m.) for some metallocene(IV) dichlorides in  $\text{CDCl}_3$  at 34 °C

Complex (or ligand)	Chemical shift of cyclopentadienyl ring carbon atoms			Chemical shift of alkyl substituent carbon atoms
	$\text{C}^1$ <sup>b</sup>	$\text{C}^{2,5}$ <sup>b</sup>	$\text{C}^{3,4}$ <sup>b</sup>	
$\text{C}_5\text{H}_5^-$ <sup>a</sup>		103.8		
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$		115.7		
$[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$		114.4		
$\text{C}_5\text{H}_4\text{SiMe}_3^-$ <sup>a</sup>	112.6	112.5	105.7	–3.8 $\text{CH}_3$
(1)	130.1	117.5	112.3	15.7 $\text{CH}_3$
(2)	128.1	116.0	111.0	15.3 $\text{CH}_3$
(3)	136.7	115.9	112.0	23.1 $\text{CH}_2$
(4)	134.5	114.4	111.0	23.0 $\text{CH}_2$
(5)	142.8	114.6	112.0	28.5 $\text{CH}$
(6)	139.9	113.0	110.8	28.5 $\text{CH}$
(7)	144.4	115.7	112.3	33.3 $\text{CMe}_3$
(8)	142.0	114.1	111.1	33.4 $\text{CMe}_3$
(9)	132.7	129.7	119.6	0.1 $\text{CH}_3$
(10)	126.4	125.6	116.1	0.1 $\text{CH}_3$
(11)	124.0	124.7	114.9	0.2 $\text{CH}_3$

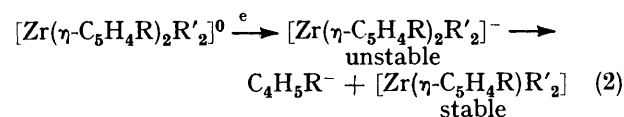
<sup>a</sup> Solvent thf. <sup>b</sup> Numbering from  $\text{C}^1$ , the carbon atom bearing the substituent R.

whereas C<sup>2,5</sup> and C<sup>3,4</sup> are shielded and resonate at high field. Although these results appeared to be in conflict with expectations based simply on inductive effects, it was argued<sup>26</sup> that accumulation of charge at C<sup>1</sup> causes repulsion of the  $\pi$ -electron density at C<sup>1</sup> and consequently an increase in  $\pi$ -electron density at C<sup>2,5</sup> and C<sup>3,4</sup>, thus deshielding C<sup>1</sup> and shielding C<sup>2,5</sup> and C<sup>3,4</sup>. The cyclopentadienyl ligand can be treated in a similar fashion to a substituted benzene, for which good quantum mechanical calculations are available and which show similar trends to those postulated to occur in substituted cyclopentadienyl groups. Values of  $\Delta C^1$ ,  $\Delta C^{2,5}$ , and  $\Delta C^{3,4}$  for substituted benzenes, ferrocenes, and Group 4 metallocene dichloro-complexes are in Table 5 ( $\Delta C^2$  is the difference in <sup>13</sup>C chemical shift for C<sup>2</sup> between the  $\eta$ -C<sub>5</sub>H<sub>5</sub> and the  $\eta$ -C<sub>5</sub>H<sub>4</sub>R complex). We note that C<sup>1</sup> in the Group 4 metal complexes is deshielded with respect to C<sup>2,5</sup> and C<sup>3,4</sup>, the  $\Delta C^1$  values being 1–2 p.p.m. less than for the iron analogues; this is consistent with the lower  $\pi$ -electron density in the ring of the *d*<sup>0</sup> metallocenes. Although the resonance of C<sup>1</sup> moves downfield in an almost monotonic linear fashion with increasing  $\alpha$ -branching in the substituent, there is no simple cor-

*Chemical or Electrochemical Reduction of Some Group 4 Metallocene(IV) Dichlorides, Chloro(alkyls), and Dialkyls.*— In a preliminary communication<sup>29</sup> we described e.s.r. observations on the products of addition of sodium dihydronaphthylide in thf to certain metallocene(IV) dialkyls at



20 °C, whence we inferred that reaction according to equation (1) had taken place. We now provide details of these findings and extensions, including data from cyclic voltammetry, which lead, *inter alia*, to revision in the interpretation as to the nature of the stable organometal(III) products, see equation (2).



Neutral *d*<sup>1</sup> metallocene(III) alkyls are known for Ti: [Ti( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>R'] with R' = aryl, CH<sub>2</sub>Me<sub>3</sub>, or CH<sub>2</sub>Ph, but not R' = Me, Et, Pr<sup>i</sup>, Bu<sup>n</sup>, Bu<sup>t</sup>, n-C<sub>5</sub>H<sub>11</sub>,<sup>30</sup> or CH<sub>2</sub>-SiMe<sub>3</sub>,<sup>31</sup> the unstable methyl<sup>32</sup> [*g*<sub>av.</sub>, 1.981, *a*(Ti), 0.44

TABLE 5

$\Delta^{13}\text{C}$  values<sup>a</sup> for substituted ferrocenes,<sup>b</sup> metallocene dichlorides, and substituted benzenes<sup>b</sup>

Substituent R	$\Delta^{13}\text{C}$ from [Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>b</sup>			$\Delta^{13}\text{C}$ from [Zr( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sup>c</sup>			$\Delta^{13}\text{C}$ from [Hf( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sup>c</sup>			$\Delta^{13}\text{C}$ from C <sub>6</sub> H <sub>6</sub> <sup>b</sup>		
	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>1</sup>	C <sup>2</sup>	C <sup>4</sup>
Me	-16.1	-1.3	0.7	-14.4	-1.8	3.4	-13.7	-1.6	3.4	-8.9	-0.7	2.9
Et	-22.9	0.6	1.0	-21.0	-0.2	3.4	-20.1	0	3.4	-15.7	0.5	2.5
Pr <sup>i</sup>	-28.7	2.0	1.2	-27.1	1.1	3.7	-25.5	1.4	3.6	-20.0	2.4	3.0
Bu <sup>t</sup>	-33.9	3.1	1.2	-28.7	0	3.4	-27.6	0.3	3.3	-22.4	3.2	
SiMe <sub>3</sub>				-10.7	-9.9	-0.4	-9.6	-10.3	-0.5			

<sup>a</sup>  $\Delta^{13}\text{C}$  is defined as the difference in chemical shift (p.p.m.) between the appropriate ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> metal complex (or C<sub>6</sub>H<sub>6</sub>) and the corresponding ( $\eta$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub> metal complex (or C<sub>6</sub>H<sub>5</sub>R). <sup>b</sup> Data from ref. 26. <sup>c</sup> Solvent CDCl<sub>3</sub>.

relation between the charge density at C<sup>1</sup> and a substituent parameter (*e.g.*  $\sigma$ ), but also a dependence on the relative disposition of the ring and substituent.<sup>27</sup>

The shielding of the *ortho*-carbons of alkyl-substituted benzenes has a significant contribution from magnetic anisotropy, and this is also to be expected for C<sup>2</sup> and C<sup>5</sup> of metallocenes. The values of  $\Delta C^{2,5}$  show that C<sup>2</sup> and C<sup>5</sup> are deshielded by comparison with the unsubstituted complexes. However, C<sup>3,4</sup> and the *para* atoms of unsubstituted benzenes do not experience a contribution from magnetic anisotropy and accordingly their <sup>13</sup>C n.m.r. shifts more closely reflect electron density.<sup>28</sup> For the Group 4 metallocenes, the extent of shielding for C<sup>3</sup> and C<sup>4</sup> is invariant with the substituent group.

The zirconium and hafnium complexes containing the SiMe<sub>3</sub> group as the ring substituent all show C<sup>1</sup>, C<sup>2,5</sup>, and C<sup>3,4</sup> substantially downfield from the parent C<sub>5</sub>H<sub>5</sub> complex. This deshielding is attributed to a net electron withdrawal by the SiMe<sub>3</sub> group, the  $-M$  effect involving Si *3d* orbitals being dominant compared with the  $+I$  effect. In general, the hafnium <sup>13</sup>C resonances are slightly upfield from those of the zirconium complexes.

mT; in thf at -80 °C] being stabilised as the tetramethylaluminate [Ti( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(Me<sub>2</sub>AlMe<sub>2</sub>)].<sup>33</sup> For Zr or Hf, only two bulky alkyls are reported, as the dinitrogen complexes [Zr( $\eta$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>{CH(SiMe<sub>3</sub>)<sub>2</sub>}( $\eta$ -N<sub>2</sub>)] (R = H or Me).<sup>17</sup> These compounds were obtained by sodium amalgam reduction of the appropriate zirconium(IV) complex [Zr( $\eta$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>{CH(SiMe<sub>3</sub>)<sub>2</sub>Cl}] in thf under dinitrogen [*g*<sub>av.</sub>, *ca.* 2.004; *a*(<sup>91</sup>Zr), *ca.* 0.4 mT, *a*(<sup>14</sup>N), *ca.* 0.36 mT]; by contrast when R was more bulky (Pr<sup>i</sup>, Bu<sup>t</sup>, or SiMe<sub>3</sub>) incorporation of N<sub>2</sub> was not observed although a zirconium(III) signal was noted in the e.s.r. spectrum [*g*<sub>av.</sub>, *ca.* 1.992; *a*(<sup>91</sup>Zr), *ca.* 1.7 mT]. Anionic *d*<sup>1</sup> alkyls were represented by [Ti( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>R']<sup>-</sup> (R' = Me, Et, or Pr), obtained from [{Ti( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl}]<sub>2</sub> and a large excess of MgR'X.<sup>34</sup>

Upon dropwise addition of a thf solution of Na-[C<sub>10</sub>H<sub>8</sub>] to a solution of a bis(cyclopentadienyl)dialkylmetal(IV) complex [M( $\eta$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>R']<sub>2</sub> (M = Ti, R = H, R' = Me, CH<sub>2</sub>Ph, or CH<sub>2</sub>SiMe<sub>3</sub>; M = Zr, R = H, R' = CH<sub>2</sub>Ph, CH<sub>2</sub>CMe<sub>3</sub>, CHPh<sub>2</sub>, or CH<sub>2</sub>SiMe<sub>3</sub>; M = Zr, R = Me, R' = CH<sub>2</sub>SiMe<sub>3</sub>; or M = Hf, R = Pr<sup>i</sup>, R' = CH<sub>2</sub>SiMe<sub>3</sub>) at room temperature the initial

TABLE 6

E.s.r. data on the reduction product obtained from the reaction between  $\text{Na}[\text{C}_{10}\text{H}_8]$  and  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2]$  in thf at 20 °C

[M( $\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2$ ] complex			Multiplicity of central signal <sup>a</sup>	$g_{\text{av}}$	$a(\text{H})/\text{mT}$	$a(\text{M})/\text{mT}$
M	R	R'				
Ti	H	Me	sept <sup>b</sup>	1.986	0.360	0.720
Ti	H	$\text{CH}_2\text{Ph}$	q	1.998	0.212	0.837
Ti	H	$\text{CH}_2\text{SiMe}_3$	q	1.985	0.275	1.025
Zr	H	$\text{CH}_2\text{Ph}$	q	1.986	0.245	1.750
Zr	H	$\text{CH}_2\text{CMe}_3$	q	1.993	0.175	1.725
Zr	H	$\text{CHPh}_2$	c	1.987	d	1.000
Zr	H	$\text{CH}_2\text{SiMe}_3$	q	1.984	0.300	2.375
Zr	Me	$\text{CH}_2\text{SiMe}_3$	q	1.987	0.350	2.400
Zr	Pr <sup>i</sup>	$\text{CH}_2\text{SiMe}_3$	q	1.984	0.250	2.350
Hf	Pr <sup>j</sup>	$\text{CH}_2\text{SiMe}_3$	q <sup>e</sup>	1.987	0.350	f

<sup>a</sup> q = Puintet. <sup>b</sup> Resolved only at -20 °C. <sup>c</sup> Broad signal. <sup>d</sup> Not resolved. <sup>e</sup> Part of an octet overlapping with zirconium analogue. <sup>f</sup> <sup>177</sup>Hf ( $I = \frac{3}{2}$ , 18.5%) or <sup>178</sup>Hf ( $I = \frac{3}{2}$ , 13.7%) hyperfine coupling was not observed.

green colour due to  $\text{Na}[\text{C}_{10}\text{H}_8]$  was discharged. The addition was stopped when the colour of the  $\text{Na}[\text{C}_{10}\text{H}_8]$  was not immediately dispersed; at this point the solution was yellow-brown and the e.s.r. spectrum was recorded (Table 6).

When the central metal atom was Ti or Zr, a strong e.s.r. signal with hyperfine splitting was observed, except for the case of M = Zr with R =  $\text{CHPh}_2$  when a broad signal was noted. When the central metal atom was Hf, reaction with  $\text{Na}[\text{C}_{10}\text{H}_8]$  followed by immediate scanning of the e.s.r. spectrum showed a complex eight-line spectrum. Upon setting the mixture aside overnight the signal largely decayed and only a weak spectrum identical with that of the analogous zirconium complex remained. This was due to a zirconium impurity in the commercial hafnium tetrachloride from which the complex was prepared.

For the titanium or zirconium compounds, the central e.s.r. signal was flanked by satellites arising from the interaction of the unpaired electron with spin-active isotopes of <sup>47</sup>Ti ( $I = \frac{5}{2}$ , 17.3%), and <sup>49</sup>Ti ( $I = \frac{3}{2}$ , 5.5%), or <sup>91</sup>Zr ( $I = \frac{5}{2}$ , 11.3%). A typical spectrum is shown in the Figure.

Attempts to obtain crystals from the reduction of  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{SiMe}_3)_2]$  were unsuccessful.

The complexes obtained in the above reductions are clearly  $d^1$ , shown by the relevant (Ti or Zr) satellites and

the  $g_{\text{av}}$  values in the e.s.r. spectra. The observation of a quintet for the e.s.r. signal when  $\text{R}' = \text{CH}_2\text{R}'$ , or a septet when  $\text{R}' = \text{Me}$ , due to coupling to four or six equivalent protons demonstrates unequivocally that two alkyl groups are associated with the metal(III) centre. These observations lead to two alternative formulations:  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2]^-$  or  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{R}'_2]$ ; in the latter the metal has a formal 11-electron count and hence it is likely that one or more thf molecules would lie within the metal co-ordination sphere.

No evidence was found for the interaction of the  $d^1$  metal centre with a solvated sodium cation [<sup>23</sup>Na ( $I = \frac{3}{2}$ , 100%)], although this had been observed in  $[\text{Na}(\text{thf})_x][\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ .<sup>35</sup> The absence of alkali metal coupling in the e.s.r. spectrum of the dialkyl-metal(III) or -metallate(III) complexes may be the result of steric hindrance to ion-pair formation by the relatively bulky alkyl groups; similarly, absence of sodium splitting was observed in  $[\text{Na}(\text{thf})_x][\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{PPh}_2)]$ .<sup>35</sup>

Hyperfine interaction due to the protons of the cyclopentadienyl group(s) was not noted in our e.s.r. spectra, although it had been observed for the complex  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]^-$ .<sup>34</sup> For  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{R}'_2]^-$  ( $\text{R}' = \text{Me, Et, or Pr}^i$ ), the absence of coupling to the cyclopentadienyl protons was attributed to hindrance to free rotation of the cyclopentadienyl rings due to steric interaction with the alkyl groups, an effect which may also prevail in our complexes.

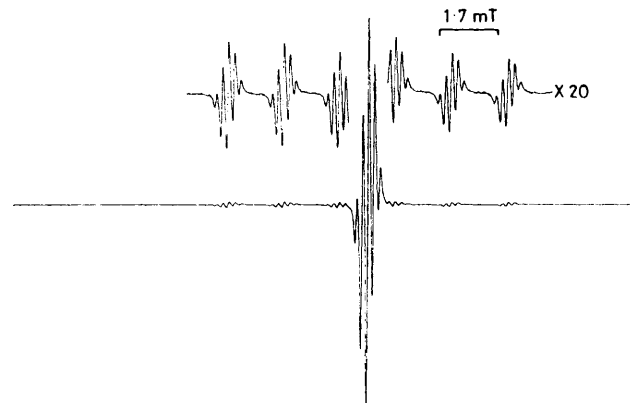


FIGURE The e.s.r. spectrum of the product of the reaction between equimolar portions of  $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{CH}_2\text{SiMe}_3)_2]$  and  $\text{Na}[\text{C}_{10}\text{H}_8]$  in thf at 20 °C

TABLE 7

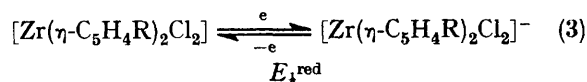
Reduction potential data for various zirconium(IV) complexes

Complex	$-E_1^{\text{red}}/\text{V}^a$
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$	1.59
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$	1.70
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$	1.73
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Et})_2\text{Cl}_2]$	1.74
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{Ph})_2]$	1.90 <sup>b</sup>
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CHPh}_2)_2]$	1.97 <sup>b</sup>
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{ClR}']^c$	2.06 <sup>b</sup>
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClR}']^c$	2.09 <sup>b</sup>
$[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{ClR}']^c$	2.08 <sup>b</sup>

<sup>a</sup> Reduction potential versus the saturated calomel electrode: potentials were internally referenced using the  $[\text{Mo}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{0/+1}$  couple,  $E_1^{\text{ox}} = -0.16$  V, as a standard. <sup>b</sup> Irreversible: potentials quoted are for  $E_p^{\text{red}}$ . <sup>c</sup>  $\text{R}' = \text{CH}(\text{SiMe}_3)_2$ .

Reduction potential data obtained by cyclic voltammetry for the various zirconium(IV) complexes at a Pt electrode in 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]-thf are listed in Table 7. For comparison, a value of  $-E_{1}^{\text{red}} = 0.75$  V for the complex [Ti(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] was obtained under similar conditions.

Each of the dichloro-zirconium(IV) complexes reduces in a reversible diffusion-controlled one-electron process. Thus, the ratios of their peak currents,  $i_p^{\text{ox}} : i_p^{\text{red}}$ , were close to 1:1; the peak current function  $i_p^{\text{red}}/v^{1/2}$  was essentially independent of the scan rate,  $v$ , over the range 0.03–0.3 V s<sup>-1</sup>, whilst their peak potential separations  $|E_p^{\text{red}} - E_p^{\text{ox}}|$  were ca. 70–90 mV. The primary electron-transfer process for these dichloro-complexes is therefore defined according to equation (3).<sup>36</sup>



Pt electrode, 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]-thf

The reduction potentials,  $E_1^{\text{red}}$ , equation (3), are sensitive to the nature of R and become more positive in the order R = Et < Me < H < SiMe<sub>3</sub>. This order is consistent with a decreasing electron-donating influence and the results emphasise the poor inductive influence of the SiMe<sub>3</sub> group on the cyclopentadienyl ligand compared to H. The complex [Zr(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] reduces at a potential of nearly 1 V more negative than its titanium(IV) analogue: this substantial difference of ca. 20–25 kcal mol<sup>-1</sup> \* in the energies of their lowest unoccupied molecular orbitals (l.u.m.o.) may be compared with the 1–5 kcal mol<sup>-1</sup> difference in the l.u.m.o. energies of iso-electronic Group 6 closed-shell complexes.<sup>37</sup>

Sodium dihydronaphthylide reduction of the dialkyl zirconium(IV) complexes in thf gave solutions whose e.s.r. spectra were originally interpreted in terms of the formation of *stable* [Zr<sup>III</sup>(η-C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>R'<sub>2</sub>]<sup>-</sup> anions.<sup>29</sup> However, this is at variance with the cyclic voltammetry data which we now have for these zirconium(IV) dialkyls. The dialkyls undergo *irreversible* one-electron reductions at a Pt electrode at scan rates up to 1.0 V s<sup>-1</sup>. Thus, under the conditions of the cyclic voltammetry experiments, the lifetimes of the zirconium(III) anions must be less than 100 ms. El Murr and co-workers<sup>38</sup> have shown that certain [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>R'<sub>2</sub>] complexes undergo one-electron reduction followed by loss of C<sub>5</sub>H<sub>5</sub><sup>-</sup> which generates complexes [Ti(C<sub>5</sub>H<sub>5</sub>)R'<sub>2</sub>]. Cyclic voltammetry of the zirconium(IV) alkyls reveals the formation of an anodic wave upon scan reversal which we attribute to the free C<sub>5</sub>H<sub>5</sub><sup>-</sup> ligand. These data and reinterpretation of the e.s.r. spectra suggest that the dialkyls reduce in a fashion analogous to the titanium(IV) complexes, according to equation (2).

The chloro(alkyl)zirconium(IV) complexes also undergo *irreversible* electrochemical reduction at a platinum electrode. Their reduction potentials and overall behaviour show little sensitivity to the nature of the sub-

stituent of the cyclopentadienyl ligand and each complex shows an oxidation wave for a *product* of the reduction in the region associated with free cyclopentadienyl anion ligands, *viz.* (3) above. This behaviour is somewhat surprising as the MeC<sub>5</sub>H<sub>4</sub> and C<sub>5</sub>H<sub>5</sub> derivatives have been shown to yield dinitrogen complexes, presumably *via* chloride loss. We are investigating these reductions further.

#### EXPERIMENTAL

**General Procedures.**—These have, for the most part, been described in Part 1,<sup>1</sup> and in ref. 10. Cyclic voltammetry was carried out in thf containing 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>] at a platinum working electrode under an atmosphere of dinitrogen according to procedures described earlier.<sup>37</sup> Measurements were made using a Hi-Tek Instruments Ltd. Potentiostat type DT2101, a Chemical Electronics (Birtley) waveform generator type 01 and recorded on a Philips X-Y recorder type 24000 A4.

Hydrogen-1 n.m.r. spectra were obtained on Varian T60 or Perkin-Elmer R32 spectrometers. Carbon-13 n.m.r. data were recorded on a JEOL PFT 100 instrument. Electron spin resonance spectra were recorded on a Varian E3 spectrometer,  $g_{\text{av}}$  values being measured relative to polycrystalline 2,2-diphenylpicrylhydrazine.

**Synthetic Procedures.**—As the preparation of many of the complexes is similar, only representative examples are described below in detail. Further data on the complexes (1)–(23) are in the Tables.

**Dichlorobis(η-t-butylcyclopentadienyl)zirconium(IV), (7).**—To a stirred solution of Na[C<sub>5</sub>H<sub>5</sub>] (44 g, 0.5 mol) in thf (600 cm<sup>3</sup>) (prepared from sodium sand and cyclopentadiene in thf), t-butyl bromide (68.5 g, 0.5 mol) was added over 1 h at 0 °C. The mixture was stirred for 24 h at 20 °C. Addition of water (200 cm<sup>3</sup>) gave two layers; the thf layer was removed and the aqueous layer was extracted with diethyl ether (2 × 100 cm<sup>3</sup>). The thf and combined ether extracts were dried over Mg[SO<sub>4</sub>]. Removal of the thf and diethyl ether (water aspirator) followed by fractional distillation of the residue gave the product, t-butylcyclopentadiene (Found: C, 88.5; H, 11.4. Calc. for C<sub>9</sub>H<sub>14</sub>: C, 88.5; H, 11.5%).

To freshly cracked t-butylcyclopentadiene (3 g, 24.6 mmol) in n-hexane (100 cm<sup>3</sup>), n-butyl-lithium (24.6 mmol) as a solution in hexane was slowly added (ca. 0.5 h) at room temperature with mechanical stirring. The solution became viscous and then deposited a white precipitate of t-butylcyclopentadienyl-lithium. Solvent was removed under vacuum and the white residue was dissolved in thf (100 cm<sup>3</sup>). To this solution at 0 °C a solution of zirconium tetrachloride (2.86 g, 12.3 mmol) in thf (30 cm<sup>3</sup>) was added with stirring over 0.5 h. The mixture was stirred for a further 12 h at 20 °C. Tetrahydrofuran was removed under vacuum and the residue was extracted with boiling toluene (100 cm<sup>3</sup>) and a little activated charcoal; filtration of the hot mixture gave a yellow filtrate which, upon the addition of hexane and cooling to -30 °C, gave crystals of the *title compound* (7).

**Bis(η-t-butylcyclopentadienyl)bis(trimethylsilylmethyl)-zirconium(IV), (22).**—Trimethylsilylmethyl-lithium (4.94 mmol) in diethyl ether was added to a stirred suspension of dichlorobis(η-t-butylcyclopentadienyl)zirconium in diethyl ether (50 cm<sup>3</sup>) at room temperature. The mixture was stirred for 12 h and volatiles were removed under vacuum.

\* Throughout this paper: 1 cal = 4.184 J.

Extraction of the residue with hexane (40 cm<sup>3</sup>) and concentration of the filtrate to ca. 10 cm<sup>3</sup>, followed by cooling to -30 °C, gave white crystals of the *title compound* (22).

*Chlorobis(η-cyclopentadienyl)(trimethylsilylmethyl)hafnium(IV)*, (15).—To a stirred solution of dichlorobis(η-cyclopentadienyl)hafnium(IV) (0.38 g, 1.0 mmol) in dichloromethane (30 cm<sup>3</sup>) a solution of (trimethylsilylmethyl)magnesium chloride (1.1 mmol), as a solution in diethyl ether, was added at room temperature over a period of 10 min. After 12 h, solvents were removed under vacuum and the residue was extracted with benzene (10 cm<sup>3</sup>) to give a very pale yellow solution. Concentration of the filtrate to ca. 5 cm<sup>3</sup> and addition of hexane (5 cm<sup>3</sup>), followed by cooling to -30 °C, gave white crystals of the *title compound* (15).

*Dibromobis(η-trimethylsilylcyclopentadienyl)hafnium(IV)*, (12).—To a stirred solution of dichlorobis(η-trimethylsilylcyclopentadienyl)hafnium(IV) (0.8 g) in dichloromethane (10 cm<sup>3</sup>) boron tribromide (0.25 cm<sup>3</sup>) was added and the solution was stirred for 5 min. Volatiles were removed under vacuum and the residue was extracted with hexane (20 cm<sup>3</sup>). After filtration and reduction of volume to ca. 10 cm<sup>3</sup>, cooling to -30 °C gave colourless crystals of the *title compound* (12).

*Reduction of Some Metallocene(IV) Dialkyls by Treatment with Sodium Dihydronaphthylide*.—Only a representative reaction is described. Sodium dihydronaphthylide was prepared as an approximately 0.25 mol dm<sup>-3</sup> solution by stirring the appropriate amounts of clean sodium and naphthalene in dry degassed thf under an argon atmosphere for 4 h. The strength of the green solutions was estimated by quenching a 1 cm<sup>3</sup> aliquot with 0.1 mol dm<sup>-3</sup> hydrochloric acid solution (10 cm<sup>3</sup>) and back-titrating the resulting solution with standard sodium hydroxide solution using phenolphthalein as an indicator.

*Reduction of Bis(η-cyclopentadienyl)bis(neopentyl)zirconium(IV)*.—The zirconium(IV) complex (ca. 0.1 g) was dissolved in dry degassed thf (2 cm<sup>3</sup>). A thf solution of Na[C<sub>10</sub>H<sub>8</sub>], prepared as above, was added dropwise with stirring until the green colour of the reagent was no longer dispersed. The solution was then stirred for a further 2 min and its e.s.r. spectrum was recorded.

*Attempted Isolation of a Zirconium(III) Dialkyl*.—Bis(η-cyclopentadienyl)bis(trimethylsilylmethyl)zirconium(IV) (0.79 g, 2 mmol) was dissolved in dry degassed thf (10 cm<sup>3</sup>). Sodium dihydronaphthylide (2 mmol) was added as a solution in thf and the resulting mixture was stirred for 15 min to give a dark brown solution. The volume of solvent was concentrated to ca. 2.5 cm<sup>3</sup> and the solution was cooled to -30 °C. After 24 h no solid product was observed; hexane (10 cm<sup>3</sup>) was floated on the surface of the thf solution. After 48 h insignificant solid product was obtained and thus the solvent was removed *in vacuo* to give a brown amorphous powder. To this powder was added toluene (1 cm<sup>3</sup>) followed by thf until the powder had just dissolved. The solution was filtered and cooled to -78 °C for 40 h, but again no useful solid product was obtained. The solvent was then removed *in vacuo* to give a brown powder which was washed with toluene (2 × 20 cm<sup>3</sup>) to remove naphthalene and then the powder was pumped to dryness. An e.s.r. spectrum of the powder showed that it contained a mixture of products.

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#### REFERENCES

- Part 1, P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.
- P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium and Hafnium,' Academic Press, New York, 1974; R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243.
- E. M. Brainina, M. Kh. Minacheva, B. V. Lokshin, E. I. Fedin, and P. V. Petrovski, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 1969, 2492; E. Samuel, *Bull. Soc. Chim. Fr.*, 1966, 3548.
- P. Renaut, G. Tainturier, and B. Gautheron, *J. Organomet. Chem.*, 1978, **148**, 35.
- E. Samuel and M. D. Rausch, *J. Am. Chem. Soc.*, 1973, **95**, 6263.
- G. Facinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1972, 654.
- H. A. Martin, P. J. Lemaire, and F. J. Jellinek, *J. Organomet. Chem.*, 1968, **14**, 149.
- M. A. Chaudhari and F. G. A. Stone, *J. Chem. Soc. A*, 1966, 838.
- M. R. Collier, M. F. Lappert, and R. Pearce, *J. Chem. Soc., Dalton Trans.*, 1973, 445.
- J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Am. Chem. Soc.*, 1977, **99**, 6645.
- M. D. Rausch, H. B. Gordon, and E. Samuel, *J. Coord. Chem.*, 1971, **1**, 141.
- J. Jeffery, M. F. Lappert, N. T. Luong-Thi, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1978, 1081; Part 4, in preparation.
- J. R. Surtees, *Chem. Commun.*, 1965, 567.
- H. Sinn and G. Oppermann, *Angew. Chem. Int. Ed. Engl.*, 1966, **5**, 962.
- J. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, 1978, **100**, 3939.
- P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121.
- J. Jeffery, M. F. Lappert, and P. I. Riley, *J. Organomet. Chem.*, 1979, **181**, 25.
- K. Alder and H.-J. Ache, *Chem. Ber.*, 1962, **95**, 503; E. W. Abel and M. O. Dunster, *J. Organomet. Chem.*, 1971, **33**, 161.
- P. M. Druce, D. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc. A*, 1969, 2106.
- M. F. Lappert, D. S. Patil, and J. B. Pedley, *J. Chem. Soc., Chem. Commun.*, 1975, 830.
- T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.
- Part 3, M. F. Lappert, P. I. Riley, P. I. W. Yarrow, J. L. Atwood, W. E. Hunter, and M. J. Zaworotko, following paper.
- H. P. Fritz, *Adv. Organomet. Chem.*, 1964, **1**, 239.
- M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Chem. Commun.*, 1978, 925.
- E. Samuel, *Bull. Soc. Chim. Fr.*, 1966, 3548.
- A. N. Nesmeyanov, P. V. Petrovskii, L. A. Fedorov, V. I. Robas, and E. I. Fedin, *J. Struct. Chem. (Engl. Trans.)*, 1973, **14**, 42.
- D. T. Clark and J. W. Emsley, *Mol. Phys.*, 1967, **12**, 365.
- H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.
- M. F. Lappert, P. I. Riley, and P. I. W. Yarrow, *J. Chem. Soc., Chem. Commun.*, 1979, 305.
- J. H. Teuben, *J. Organomet. Chem.*, 1974, **69**, 241; F. W. van der Weij, H. Scholtens, and J. H. Teuben, *ibid.*, 1977, **127**, 299.
- T. Chivers and E. D. Ibrahim, *J. Organomet. Chem.*, 1974, **77**, 241.
- E. Klei and J. H. Teuben, *J. Organomet. Chem.*, 1980, **188**, 97.
- J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 45.
- H. H. Brintzinger, *J. Am. Chem. Soc.*, 1967, **89**, 6871.



<sup>35</sup> J. G. Kenworthy, J. Myatt, and P. F. Todd, *Chem. Commun.*, 1969, 263.

<sup>36</sup> N. El Murr, A. Chaloyard, and J. Tirouflet, *J. Chem. Soc., Chem. Commun.*, 1980, 446.

<sup>37</sup> C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 1975, 879.

<sup>38</sup> A. Chaloyard, A. Dormond, J. Tirouflet, and N. El Murr, *J. Chem. Soc., Chem. Commun.*, 1980, 214.