Chemistry of *o*-Xylidene–Metal Complexes. Part 2.[1] Preparation and Properties of the *o*-Xylidene–Metal(IV) Complexes $[M(CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_4R)_2]$ (M = Ti, Zr, Hf, or Nb; R = H or $SiMe_3$) and $[\{M'(CH_2C_6H_4CH_2\text{-}o)_2(OC_4H_8)\}_n]$ (M′ = Ti, Zr, or Hf); *X*-Ray Crystal Structures of the Metallaindanes $[M(CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_4R)_2]$ (R = H, M = Ti, Zr, or Hf; R = $SiMe_3$, M = Nb) †

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Reaction of the di-Grignard reagent $o\text{-}C_6H_4(CH_2MgCl)_2$ (1) in tetrahydrofuran (thf) with the appropriate metallocene(IV) chloride, $[M(\eta\text{-}C_5H_4R)_2Cl_2]$, yields the corresponding crystalline, thermally robust metallaindane complexes $[M(CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_4R)_2]$ [R = H or $SiMe_3$, M = Ti, Zr, or Hf; R = $SiMe_3$, M = Nb]. The Zr-complex with R = H affords *o*-xylene either upon photolysis or pyrolysis. N.m.r. spectra of the d^0 complexes show magnetically equivalent pairs of C_5H_4R and CH_2 groups. The e.s.r. solution spectrum of the d^1 Nb complex was second order, with $g_{av} = 1.9986$ and $a(^{93}Nb) = 77.2$ G, calculated using a modified Breit–Rabi equation. Reduction of each of the d^0 Ti, Zr, or Hf compounds with $Na[C_{10}H_8]$ in thf results in scission of an $M\text{-}CH_2$ bond, as deduced by the appearance of a central triplet e.s.r. signal, with appropriate (except Hf) satellites, assigned to the d^1 complex $[M(\eta\text{-}C_5H_4R)_n(o\text{-}CH_2C_6H_4CH_2Na)(thf)_x]^{(2-n)+}$ (n = 1 or 2); cyclic voltammetry on one of the Ti^{IV} complexes shows a pseudo-reversible one-electron reduction, and hence the metallate(III) ion $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]^-$ may be a transient intermediate. Reactions of the Group 4A metallaindanes with CO under ambient conditions are sensitive to the nature of M: the Ti and Zr complexes yield $[M(\eta\text{-}C_5H_4R)_2(CO)_2]$ and indan-2-one; whereas the Hf complex affords two conformers of the seven-membered, bis-σ-acyl, the metallabenzocycloheptene-dione complex $[Hf\{C(O)CH_2C_6H_4CH_2CO\text{-}o\}(\eta\text{-}C_5H_4SiMe_3)_2]$, in which the two CO groups are believed to have an *anti* relationship. The two conformers coexist in equilibrium in solution in CH_2Cl_2 or $CHCl_3$ with one form (the less soluble) favoured at low temperature. Reaction of two equivalents of the di-Grignard reagent (1) with the appropriate Group 4A metal(IV) chloride in thf furnishes insoluble, pyrophoric powders of empirical formula $M(CH_2C_6H_4CH_2\text{-}o)_2(thf)$, which may well be oligomers having bridging *o*-xylidenes. The *X*-ray structures of the four title metallaindanes $[M(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (M = Ti, Zr, or Hf) and $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ confirm their formulae. Features of interest include (*i*) the bis-σ-co-ordinating mode of the chelating *o*-xylidene ligand; (*ii*) the bite angle (°) $C^{\alpha}MC^{\alpha'}$: 76.7(2) Ti, 77.3(2) Zr, 77.2(4) Hf, 72.4(7) Nb; (*iii*) the fold angle (°) [*i.e.* the angle subtended by the normals to (*a*) the $MC^{\alpha}C^{\alpha'}$ plane and (*b*) the C_4 plane of the MC_4 ring]: 41 Ti, 53 Zr, 53 Hf, 44 Nb; (*iv*) the $\langle M\text{-}C^{\alpha}\rangle$ distances (Å): 2.203(6) Ti, 2.300(8) Zr, 2.28(1) Hf, 2.286(9) Nb; (*v*) the $\langle M\text{-}C^{\beta}\rangle$ distances (Å): 2.913(6) Ti, 2.857(8) Zr, 2.91(1) Hf, 3.079(21) Nb; and (*vi*) the fact that the C_6 rings are planar while the α-CH_2's lie 0.10 (Ti), 0.12 (Zr), 0.12 (Hf), or 0.07 Å (Nb) out of this plane on the same side of the C_6 plane as the metal atoms.

The researches described in this paper concern *o*-xylidene complexes of some early transition metals, specifically those of titanium, zirconium, hafnium, and niobium in oxidation state +4. The starting material was a tetrahydrofuran (thf) solution of the di-Grignard reagent (1) [1] and either [for complexes (2)—(8)] the appropriate metallocene(IV) chloride or [for complexes (9)—(11)] the metal(IV) chloride. Reactions of the new complexes which we have studied include their thermolysis, carbonylation [especially of (4) leading to two isomers of formula (12)], and reduction [for (2)—(4) and (6)—(8)]. Single crystal *X*-ray data are also reported on the metallaindanes (or metallabenzocyclopentenes) (5)—(8).

The present work impinges on a number of areas which are of current prominence. First, there has been interest in the synthesis of five-membered metallacycles of transition elements of Groups 4A and 5A,[2–11] including their reactions with carbon monoxide.[3,4,8,10] Secondly, the Group 4A metal tetrabenzyls, $[M(CH_2Ph)_4]$, have attracted attention because of their unexpected high thermal stability, perhaps a consequence of their curious structures (M–C–Ph, *ca.* 90°) suggestive of π Ph–M interaction,[12] and their potential as α-olefin polymerisation catalysts.[13] Finally, there has been much activity concerned with transition-metal complexes of bulky hydrocarbyls; for example, the alkyl ligand $^-CH(SiMe_3)_2$ (R^-) has provided stable complexes in unusual metal oxidation states or with unexpected coligands, as in $[CrR_3]$ [14] or $[Zr(\eta\text{-}C_5H_5)_2(\eta\text{-}N_2)R]$.[15]

Of the new complexes, the majority [(2)—(8) and (12)] are metallacycles. The *o*-xylenediyl dianion, $o\text{-}^-CH_2C_6H_4CH_2^-$,

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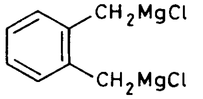
† Bis(η-cyclopentadienyl)(*o*-phenylenedimethylene-$C^{\alpha}C^{\alpha'}$)metal(IV).

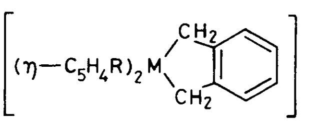
Supplementary data available (No. SUP 23751, 60 pp.): structure factor amplitudes, H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: G = 10^{-4} T, atm = 101 325 N m^{-2}.

No reprints available.



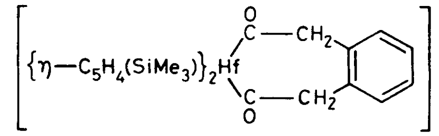
(1)



$[\{M(CH_2C_6H_4CH_2\text{-}o)_2(thf)\}_n]$

(2); M = Ti, R = $SiMe_3$
(3); M = Zr, R = $SiMe_3$
(4); M = Hf, R = $SiMe_3$
(5); M = Nb, R = $SiMe_3$
(6); M = Ti, R = H
(7); M = Zr, R = H
(8); M = Hf, R = H

(9); M = Ti
(10); M = Zr
(11); M = Hf



(12a), (12b)

from which all are derived, may be regarded as a substituted benzyl ligand, and especially in its metallacyclic complexes is expected to be sterically exceptionally undemanding; we shall return to this theme in Part 3, which will deal with complexes of W^V and W^{VI}. Acyl derivatives of metallacycles, such as the new complexes (12), are without precedent and are unlikely (for geometrical reasons) to involve the η^2-acyl–metal bonding mode, thus far characteristic of all previous acyls of early transition metals.

Some of the results presented herein have been briefly outlined in preliminary communications.[16,17] Only a small number of other papers have dealt with complexes derived from the *o*-xylidene ligand: the di-Grignard reagent (1) and chloride-free analogues $[\{Mg(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)(thf)_n\}_m]$ ($n = 2$ with $m = 3$, or $n = 1$ with m unknown; thf = tetrahydrofuran),[1] $[\{W(CH_2C_6H_4CH_2\text{-}o)O\}_2Mg(thf)_4]$,[18] $[W(CH_2C_6H_4CH_2\text{-}o)_3]$,[19] $[Fe(\eta^4\text{-}CH_2C_6H_4CH_2\text{-}o)(CO)_3]$,[20] $[\{Fe(CO)_3\}_2\{\mu\text{-}\eta^3{:}\eta'^3\text{-}C_6H_4(CH_2)_2\text{-}o\}]$ (and some CO insertion products),[21] $[Ru(\eta^4\text{-}CH_2C_6H_4CH_2\text{-}o)L_3]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, or PEt_3),[22] $[Pt(CH_2C_6H_4CH_2\text{-}o)L'_2]$ [L'_2 = cyclo-octa-1,5-diene[16] or $(PEt_3)_2$],[23] $[\{Co(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_2]$,[24a] and $[Pt_2(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)Me_4(\mu\text{-}Ph_2PCH_2PPh_2)]$.[24b] From these formulae, it is evident that the *o*-xylidene ligand is highly versatile, being capable of functioning not only in a chelating but also a bridging manner. As to the former, it may act as a chelating dicarbanion $CH_2C_6H_4CH_2^-$, as the neutral *o*-quinodimethide *o*-$C_6H_4(=CH_2)_2$, or in an intermediate fashion (W^V, W^{VI}, or Ru^0); while in the bridging mode it may behave as $^-CH_2C_6H_4CH_2^-$ or (for the iron complex $[\{Fe(CO)_3\}_2\{\mu\text{-}\eta^3{:}\eta'^3\text{-}C_6H_4(CH_2)_2\text{-}o\}]$) as $(CH_2 \cdots C \cdots CHCH{=}CHCH \cdots C \cdots CH_2)^{2-}$.

The oxidation state +3 is rather ill defined for organozirconium or -hafnium compounds.[25] Among the reactions now reported are reductions of the Group 4A metallabenzocyclopentenes (2)—(4) and (6)—(8), to give appropriate d^1 metal(III) complexes, characterised by means of their solution e.s.r. spectra. Apart from our preliminary publication on Group 4A metallabenzocyclopentenes,[17] other M^{IV} substrates for the reduction have included the metallocene(IV) dialkyls $[M(\eta\text{-}C_5H_5)_2R_2]$ and products of photolytic,[26] electrochemical,[27,28] or chemical reduction have been claimed as having formulae $[M(\eta\text{-}C_5H_5)_2R]$, $[M(\eta\text{-}C_5H_5)_2R_2]^-$, $[M(\eta\text{-}C_5H_5)R_2]$, and a Zr^{III} hydride.

Results and Discussion

Synthesis and Spectra of the Metallocene(IV) *Metallabenzocyclopentenes* (2)—(8).—In general, syntheses [equation (1),

$$[M(\eta\text{-}C_5H_4R)_2Cl_2] + (1) \xrightarrow{thf} [M(\eta\text{-}C_5H_4R)_2\{o\text{-}(CH_2)_2C_6H_4\}] + 2MgCl_2 \qquad (1)$$

R = H or $SiMe_3$] were carried out at low temperature in thf, using the di-Grignard reagent (1) in solution in thf, the reactions of the titanocene(IV) chlorides being performed in the dark to minimise the formation of Ti^{III} species; the formation of the latter was monitored by e.s.r. spectroscopy.

Each of the metallocene(IV) chlorides used gave the expected metallabenzocyclopentene as a crystalline material. Complexes (2)—(8) are exceedingly air-sensitive in solution, but only the Nb compound (5) and the diethyl etherate (6a) of $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (6b) showed marked air-sensitivity in the solid state. Complex (6a) contained solvent of crystallisation when obtained from diethyl ether, but OEt_2 was removed by recrystallisation from toluene–hexane.

Complexes (2)—(8) are thermally robust, melting without decomposition at up to 177 °C, Table 1. This contrasts markedly with the behaviour of other d^0 metallacycles. For example $[Ti(\eta\text{-}C_5H_5)_2(CH_2)_4]$ decomposes rapidly even at 0 °C (half-life in solution *ca.* 0.5 h), presumably as a result of β-elimination, although the metallacyclic structure makes this pathway less facile than for the related acyclic complex, $[Ti(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_2CH_3)_2]$.[8]

The synthesis of $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (5) adds a new member to the rare class of Group 5A metallacycles, previous examples of which included the product of equation (2) and the corresponding tantalum–propane

$$[TaCl_3(\eta\text{-}C_5H_5)(CHCMe_3)] + C_2H_4 \longrightarrow [Ta(CH_2CH_2CH_2CH_2)Cl_2(\eta\text{-}C_5H_5)] \qquad (2)$$

derivative;[9b,9c] attempts to prepare the Nb analogues were unsuccessful.[29] Further Nb^{IV}[30] (and Cr^{III}[31] or W[18,19]) metallacycles have been reported, as well as three cases of vanadium(IV) metallacycles.[9a]

A solution of the zirconium compound (7) in C_6D_6 showed (n.m.r.) no perceptible decomposition up to *ca.* 130 °C, but at 150 °C slow formation of *o*-xylene was observed. *o*-Xylene was also formed when a C_6D_6 solution of complex (7) was irradiated with u.v. light from a 250-W medium pressure mercury lamp. Decomposition may occur as shown in equation (3), and/or by a bimolecular pathway; similarly heating [Ti(η-

(3)

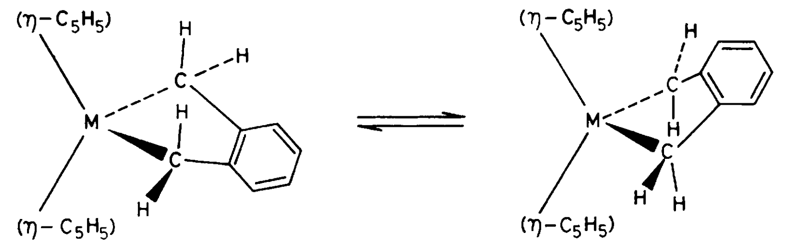
Table 1. Physical characteristics of the Group 4A and Nb^{IV} complexes (2)—(12a)

Compound	Colour	Analysis [a] (%) C	H	M.p.[b] (°C)	Yield [c] (%)
(2) $[Ti\{\eta-C_5H_4(SiMe_3)\}_2\{o-(CH_2)_2C_6H_4\}]$	Dark blue	67.7 (67.6)	8.5 (8.0)	130	43
(3) $[Zr\{\eta-C_5H_4(SiMe_3)\}_2\{o-(CH_2)_2C_6H_4\}]$	Red	61.2 (61.3)	7.7 (7.3)	133	63
(4) $[Hf\{\eta-C_5H_4(SiMe_3)\}_2\{o-(CH_2)_2C_6H_4\}]$	Yellow	51.8 (51.7)	5.9 (6.2)	128	43
(5) $[Nb\{\eta-C_5H_4(SiMe_3)\}_2\{o-(CH_2)_2C_6H_4\}]$	Purple	61.1 (61.0)	7.1 (7.3)	—	45
(6a) $[Ti(\eta-C_5H_5)_2\{o-(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$	Blue-black	72.0 (75.2)	7.3 (7.3)	132	59
(6b) $[Ti(\eta-C_5H_5)_2\{o-(CH_2)_2C_6H_4\}]$	Dark violet	75.6 (76.6)	6.7 (6.5)	153—154	
(7) $[Zr(\eta-C_5H_5)_2\{o-(CH_2)_2C_6H_4\}]$	Red	66.3 (66.4)	5.7 (5.6)	177	70
(8) $[Hf(\eta-C_5H_5)_2\{o-(CH_2)_2C_6H_4\}]$	Yellow	52.7 (52.4)	4.7 (4.4)	172—173	38
(9) $[\{Ti(CH_2C_6H_4CH_2-o)_2(thf)\}_n]$	Black-violet	72.7 (73.2)	7.4 (7.4)	130 (decomp.)	24
(10) $[\{Zr(CH_2C_6H_4CH_2-o)_2(thf)\}_n]$	Yellow	64.5 (64.6)	6.9 (6.5)	120 (decomp.)	34
(11) $[\{Hf(CH_2C_6H_4CH_2-o)(thf)\}_n]$	Pale yellow	52.1 (52.4)	5.8 (5.3)	130 (decomp.)	30
(12a) $[Hf\{\eta-C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$	Colourless	50.3 (50.9)	5.7 (5.6)	224	65

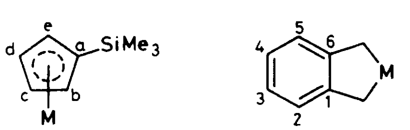
[a] Calculated values are given in parentheses. [b] Under vacuum in sealed capillaries and uncorrected. [c] These are not optimised, and refer to recrystallised material.

$C_5H_5)_2(CH_2M'Me_3)_2]$ (M' = Si or Sn) gave $M'Me_4$ as the sole isolated organic product.[32] {For H–D labelling experiments on $[Zr(\eta-C_5H_5)_2Me_2]$, see ref. 33.}

In the solid state the metallacyclopentene unit is not planar but contains a fold (Scheme 1), which is probably also present in the molecule in solution, whence magnetic inequivalence of the two cyclopentadienyl ligands is to be expected, as well as for the CH_2 protons (pseudo-axial or pseudo-equatorial). However, at room temperature such inequivalence in the solution n.m.r. spectra of the complexes was not observed, presumably because of rapid interconversion of the two environments, as shown in Scheme 1. (For the i.r. spectrum, comparisons were made with data from refs. 34 and 35.)



Scheme 1. Conformations of metallabenzocyclopentenes



Scheme 2. Labelling schemes used for assignment of the n.m.r. spectra of complexes (2)—(4), (6)—(8), (12a), and (12b)

N.m.r. data are collected in Tables 2 (^1H) and 3 (^{13}C), and the appropriate atom-labelling schemes are indicated in Scheme 2. Each of the complexes (2)—(4) showed a single signal for the trimethylsilyl protons, confirming their equivalence.

It had previously been observed in compounds such as $[M\{\eta-C_5H_4(SiMe_3)\}_2R_2]$ (R = Cl, M = Ti, Zr, or Hf; R = Br, M = Hf) that $J(H^bH^c) \simeq J(H^bH^d) \simeq 3$ Hz so that each equivalent pair of protons appeared as a triplet.[27] Complexes (3) and (4) showed such an expected spectrum, but for the titanium derivative (2) a singlet was recorded. This is attributed to a fortuitous equivalence of environments for the two pairs of protons in complex (2).

The ^{13}C n.m.r. signals were assigned on the basis of their intensities and positions, and by comparison with the spectra of other metallocene complexes.[27]

Complex (5) and the related complex $[Nb(\eta-C_5H_5)_2\{o-(CH_2)_2C_6H_4\}]$ afforded the 10-line e.s.r. spectra expected of a Nb d^1 species (100% ^{93}Nb, $I = \frac{9}{2}$) but with no hyperfine coupling to α-^1H. This absence of coupling has previously been noted in the case of a number of niobocene(IV) alkyls $[Nb(\eta-C_5H_4R)_2R'_2]$ (R' ≠ Me).[36] The spectra were second order, and isotropic g_{av} and $a(^{93}Nb)$ values were calculated (Table 4) using a modification[37] of the Breit–Rabi equation.[38]

It has been suggested (and supported by e.s.r. and X-ray data) that for a $[M(\eta-C_5H_4R)_2L_2]$ system the a_1 orbital which is the lowest unoccupied molecular orbital for a d^0 and the

Table 2. ^{1}H N.m.r. chemical shift data [a] for selected Group 4A metallocene(IV) metallacycles

Complex	CH_2	C_6H_4	C_5H_5	C_5H_4	$Si(CH_3)_3$	Other
(2) $[Ti\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [b]	7.72 (s)	2.98 (m)		4.1 (s)	9.69 (s)	
(3) $[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [b]	8.04 (s)	2.95 (m)		4.15 (t), 4.62 (t)	9.63 (s)	
(4) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [b]	8.2 (s)	2.85 (m)		4.09 (t), 4.37 (t)	9.12 (s)	
(6a) $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$ [b]	8.06 (s)	3.3 (m)	4.69 (s)			6.83 (q), 8.94 (t)
(7) $[Zr(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [b]	8.3 (s)	3.13 (m)	4.9 (s)			
(8) $[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [c]	8.57 (s)	3.1 (m)	4.78 (s)			
(12a) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$ [d]	6.45 (s) [e]	2.82 (s)		3.48 (t), 3.72 (t)	9.72 (s)	
(12b) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$ [d]	6.52 (s)	2.75 (s)		3.72 (t)	9.78 (s)	

[a] Values quoted in τ relative to internal $SiMe_4$ = 10. [b] In C_6D_6. [c] In $[^2H_8]$toluene. [d] In CD_2Cl_2. [e] $^2J(^{13}CO\text{-}CH_2)$ = 4 Hz.

Table 3. ^{13}C N.m.r. chemical shift data [a] for selected Group 4A metallocene(IV) metallacycles

Compound	Solvent	CH_2	C_6H_4 [b]		C_5H_5
			$C^{1,6}$	$C^{2,5}\text{-}C^{3,4}$	
(2) $[Ti\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	63.4	147.1	125.9, 124.7	
(3) $[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	52.0	138.9	128.6, 125.1	
(4) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	52.5	141.2	128.0, 124.6	
(6a) $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$	C_6D_6	62.1	146.6	126.4, 124.8	112.5
(7) $[Zr(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	50.4	138.1	128.0, 125.5	107.9
	$CDCl_3$	49.9	137.6	128.5, 125.0	107.8
(8) $[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	$CDCl_3$	50.2	140.2	127.7, 124.1	108.1
(12a) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$	$CDCl_3$	36.3 [c]	134.8	128.1, 125.6	
(12b) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$	$CDCl_3$	33.8	133.8	128.6, 125.7	

Compound	Solvent	C_5H_4 [b]		$Si(CH_3)_3$	Other
		C^a	$C^{b,e}\text{-}C^{c,d}$		
(2) $[Ti\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	121.7	119.1, 116.4	0.04	
(3) $[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	117.6	114.4, 112.7	0.3	
(4) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6	118.8	114.6, 112.9	0.2	
(6a) $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$	C_6D_6				65.9, 15.5 (OEt_2)
(7) $[Zr(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	C_6D_6				
	$CDCl_3$				
(8) $[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	$CDCl_3$				
(12a) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$	$CDCl_3$	117.0	123.4, 113.0	0.3	135.0 (CO)
(12b) $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{(CO)_2(CH_2)_2C_6H_4\}]$	$CDCl_3$	121.3	118.2, 112.6	0.27	130.8 (CO)

[a] Values in p.p.m. relative to $SiMe_4$ = 0, calculated from solvent resonances: C_6D_6 = 128.0, $CDCl_3$ = 77.0. [b] For numbering, see Scheme 2. [c] $^1J(^{13}CO\text{-}CH_2)$ = 61 Hz.

Table 4. A comparison of e.s.r. parameters and L–Nb–L bond angles (θ) for some niobocene(IV) complexes

	$a(^{93}Nb)/G$	g_{av}	$\theta/°$	Ref.
$[Nb(\eta\text{-}C_5H_5)_2Cl_2]$	116.5	1.9770	85.0(1)	*a*
$[Nb(\eta\text{-}C_5H_5)_2Cl(CH_2SiMe_3)]$	106.6	1.9839	*b*	*c*
$[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2Cl(CH_2SiMe_3)]$	98.0	1.9912	84.3(3)	*c*
$[Nb(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)_2]$	87.6	1.9956	79.0(4)	*c*
$[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	77.2	1.9986	72.9(2) 71.9(2)	This work
$[Nb(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	76.3	1.9957	*b*	This work

[a] R. Broussier, H. Normant, and B. Gautheron, *J. Organomet. Chem.*, 1978, **155**, 337; (*X*-ray) K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290. [b] Not determined. [c] P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1980, 180.

highest occupied molecular orbital of a d^1 system is primarily metal centred (for bibliography, see ref. 36), the energy and nature (% ligand character *versus* % metal character) of which is related to the angle L–M–L (θ); addition of *d* electrons to the system (*i.e.*, $d^0 \longrightarrow d^1 \longrightarrow d^2$) results in decreasing both the metal character of the a_1 orbital and also L–M–L. The new data of Table 4 provide further evidence for this model; thus a fall in the magnitude of $a(^{93}Nb)$, and concomitant rise in g_{av}, is accompanied by a lowering of the angle θ.

Some Reactions of the Metallocene(IV) *Metallabenzocyclopentenes* (2)—(8).—In view of the e.s.r. and *X*-ray correlations outlined above it was considered of interest to attempt the synthesis of the d^1 complexes $[M^{III}(\eta\text{-}C_5H_4R)_2\{o\text{-}(CH_2)_2C_6H_4\}]^-$ from their M^{IV} d^0 precursors (2)—(4) and (6)—(8), using $Na[C_{10}H_8]$ in thf as an electron-transfer reagent. The results obtained were unexpected: e.s.r. spectra showed that instead of a central quintet resulting from coupling to four α-hydrogens, signals of the black or brown reduction products

Table 5. E.s.r. data for the complexes obtained from the reduction of $[M(\eta\text{-}C_5H_4R)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ with $Na[C_{10}H_8]$ in thf at 0 °C

Complex used as substrate for reduction	Central signal	g_{av}	$a(^1H)/G$	$a(M)/G$
$[Ti\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Triplet	1.985	4.75	10.9
$[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Triplet	1.986	5.0	15.0
$[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Broad singlet	1.961	—	*
$[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Triplet	1.985	5.0	13.3
$[Zr(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Triplet	1.983	5.5	14.8
$[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$	Triplet	1.985	5.25	*

* Hyperfine coupling $a(^{179}Hf$ or $^{177}Hf)$ not observed.

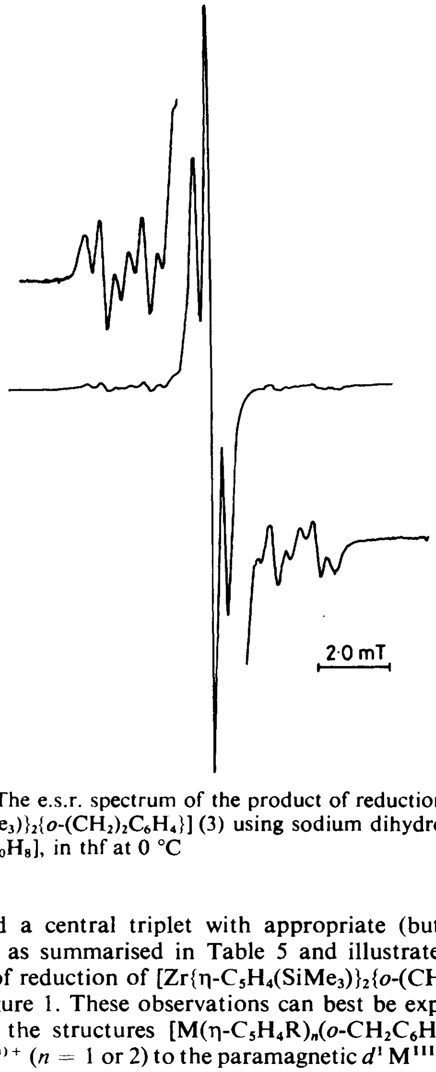


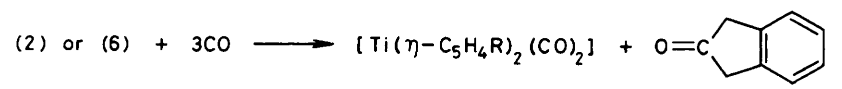
Figure 1. The e.s.r. spectrum of the product of reduction of $[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (3) using sodium dihydronaphthylide $Na[C_{10}H_8]$, in thf at 0 °C

comprised a central triplet with appropriate (but not Hf) satellites, as summarised in Table 5 and illustrated for the product of reduction of $[Zr\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (3) in Figure 1. These observations can be explained by assigning the structures $[M(\eta\text{-}C_5H_4R)_n(o\text{-}CH_2C_6H_4CH_2Na)\text{-}(thf)_x]^{(2-n)+}$ ($n = 1$ or 2) to the paramagnetic d^1 M^{III} reduction products. The e.s.r. data serve to show the presence of d^1 complexes with a CH_2^- ligand attached to the metal centre, but not whether or not a cyclopentadienyl anion is ($n = 1$) or is not ($n = 2$) lost upon reduction. The formation of such compounds, rather than the more usual products of $Na[C_{10}H_8]$ reduction of Group 4A metallocene dialkyls, $[M(\eta\text{-}C_5H_4R)\text{-}R'_2]$,[27] is attributed to steric strain in the metallacyclopentene ring of the initially formed unstable d^1 metallate(III) complexes $[M(\eta\text{-}C_5H_4R)_2\{o\text{-}(CH_2)_2C_6H_4\}]^-$. For example, for such an anion with M = Zr, the bite angle θ would be expected to fall below even the low value of 77.3(2)° found in the d^0 precursor (7) (Table 7). The electrochemical reduction of $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$ (6a) provides an indication that the species $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]^-$, although unstable and undetected by e.s.r. experiments at low temperature, is actually the precursor of the observed species. This is suggested by the pseudo-reversibility of the reduction step, with the ratio of the peak currents, $i_{ox}/i_{red} = 0.85$ ($i_{ox}/i_{red} = 1.0$ for a fully reversible process). At low scan speeds the voltammogram indicated that the reduced species reacts to form another reducible species. This can be explained in terms of reductions followed by the opening of the metallacyclopentene ring.

The values of $a(^1H)$ in Table 5 may be subject to small errors as not all spectra gave fully resolved triplets. In calculating coupling to Ti it was assumed that (*i*) coupling to each spin-active isotope is equal[39] (^{47}Ti $I = \frac{5}{2}$, 7.3%; ^{49}Ti $I = \frac{7}{2}$, 5.3%); (*ii*) the outermost observed satellites are due to coupling with states of spin quantum number $\frac{5}{2}$;[40] and (*iii*) the outer satellites due solely to ^{49}Ti are too weak to detect. In no case was coupling with ^{23}Na[41] or cyclopentadienyl hydrogens[42] found. It may be that the hafnium complex (4) reacted with $Na[C_{10}H_8]$ in a different fashion from that of the other metallacycles, as indicated by the anomalous value for g_{av} observed in this case; however, as this e.s.r. spectrum was otherwise uninformative we are unable to offer further comment.

The e.s.r. triplet signals of Table 5 may be compared with those for the species $[M(\eta\text{-}C_5H_4R)R'_2]$ (M = Ti, Zr, or Hf; R = H, Me, or Pr^i; R′ = Me, CH_2Ph, CH_2SiMe_3, $CHPh_2$, or CH_2Bu^t);[27] similar g_{av} and $a(M)$ values are found, but proton hyperfine couplings $a(^1H)$ are higher in the case of the metallocene–metallacycle reduction products and approach those found for $[M^{III}(\eta\text{-}C_5H_5)_2Me]$ [7.0 (M = Zr) or 6.75 G (M = Hf)].[43]

The products of the reactions of the Group 4A metallabenzocyclopentenes with carbon monoxide were found to be sensitive to the nature of the metal. The Ti complexes (2) and (6) on reaction with CO appeared to undergo reactions analogous to that of the titanacyclopentane, $[\overline{Ti(CH_2CH_2CH_2C}H_2)(\eta\text{-}C_5H_5)_2]$.[3] For the case of complex (6), both the products of equation (4) (R = H) were well characterised; with ν(C=O) i.r. bands identical to those found[44] for $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$, and a band at 1 755 cm⁻¹ corresponding to that of authentic indan-2-one. When the reaction was carried out in C_6D_6, prominent signals in the ¹H n.m.r. spectra were assignable to $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$ and indan-2-one, whilst removal of

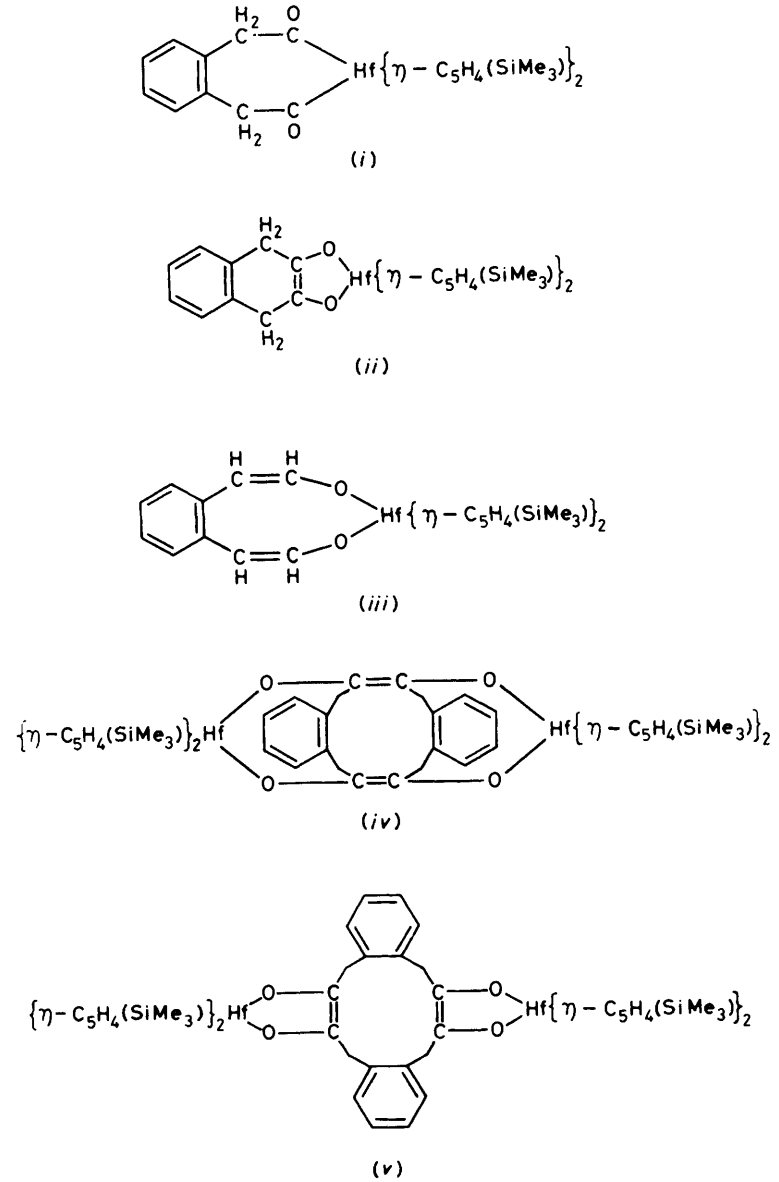

$$(2) \text{ or } (6) + 3CO \longrightarrow [Ti(\eta\text{-}C_5H_4R)_2(CO)_2] + O{=}C_9H_8 \qquad (4)$$

solvent followed by extraction with diethyl ether and g.l.c. of the resulting solution gave a major peak corresponding to that of an authentic sample of indan-2-one. Similarly, complex (2) with CO gave a mixture with i.r. bands attributable to indan-2-one and [Ti{η-$C_5H_4(SiMe_3)$}$_2$(CO)$_2$].

The reaction of CO with each of the zirconium complexes (3) or (7) gave products which were inadequately identified. Prolonged reaction of a solution of (3) with CO gave a brown solution having i.r. bands assignable to ν(C=O) of indan-2-one and [Zr{η-$C_5H_4(SiMe_3)$}$_2$(CO)$_2$]. There appears not to be a precedent for the conversion of a zirconocene(IV) complex by means of CO into the corresponding zirconocene(II) carbonyl. Reaction of complex (7) with CO gave two products, neither of which was particularly soluble in common organic solvents. *in situ* Experiments in CD_2Cl_2 in n.m.r. tubes showed that these two compounds did not react further with CO at 1 atm and 25 °C or interconvert even on heating. Mass spectrometry of the two compounds showed that one (the less soluble) contained two Zr atoms and indicated that the other may have been of empirical formula [Zr(C_5H_5)$_2${(CO)$_2$-(CH_2)$_2C_6H_4$}]. A compound isomeric with (3), [Zr(η-C_5H_5)$_2$($CH_2CH_2C_6H_4$-*o*)], also reacted with CO in a complicated fashion;[11] hydrolysis products indicated the formation of dinuclear complexes.

In contrast to previous reports of carbonylation of zirconocene(IV) alkyls, which are slow[32] or reversible,[45] the reactions of carbon monoxide with the Group 4A metallabenzocyclopentene complexes were generally facile and irreversible. This is probably due to the ease with which the initial coordination of carbon monoxide can occur, adjacent to the small *o*-xylidene ligand, and to the relief of strain in the *o*-xylidene ligand that is effected by a subsequent ring expansion upon CO insertion.

The reaction of the hafnium complex (4) with CO in pentane gave a precipitate of colourless microcrystals which proved to be the product (12a) of CO insertion into *both* Hf–CH_2 bonds. Complex (12a) has both acyl groups σ bonded. Thus ν(C=O) at 1 668 cm^{-1} is at a higher wavenumber than expected if the acyl groups were η^2 bonded, as in [Zr(η-C_5H_5)$_2$(η^2-$COCH_2Ph$)-



Scheme 3. Possible structures of complexes (12a) and (12b)

$(CH_2Ph)]$ [ν(CO) at 1 540 cm^{-1}].[45] A value of 1 720 cm^{-1} was observed for $[Ti(\eta\text{-}C_5H_5)_2\{CO(CH_2)_3CH_2\}]$ for which the σ configuration has been assigned.[8] On heating a solution of (12a), an isomer, (12b), was formed which may also have σ acyl–Hf bonds, with ν(CO) at 1 620 cm^{-1}. Consistent with the ν(CO) assignment, when the insertion reaction and subsequent isomerisation were carried out using ^{13}C-enriched CO, the bands at 1 668 in (12a) and 1 620 cm^{-1} in (12b) shifted to an appropriately lower wavenumber.

Various possible structures for the adducts of complex (4) with two CO groups are shown in Scheme 3. Structures (*ii*)—(*v*) cannot be ruled out from the cited data, as the bands assigned above to ν(CO) could arise from ν(C=C), as is case for the compounds $[Th(\eta\text{-}C_5Me_2)_2\{OC(Me)C(Me)O\}]$ and $[Th(\eta\text{-}C_5Me_5)_2\{OC(CH_2SiMe_3)C(CH_2SiMe_3)O\}]$ which have such CC modes at 1 655 and 1 632 cm^{-1}, respectively.[46] However, structures (*ii*)—(*v*) are inconsistent with the ^{1}H n.m.r. data which show complexes (12a) and (12b) to have CH_2 resonances at τ, 6.45 and 6.52 respectively. Whilst such chemical shifts are acceptable for CH_2 groups attached to the carbon atom of an M–C=O unit, *e.g.*, τ 6.27 for $COCH_2$ in $[Hf(\eta\text{-}C_5H_5)_2(COCH_2C_6H_5)(CH_2C_6H_5)]$,[45] they are inappropriate if [as in (*ii*)] the CH_2's are attached to MOC, as in $[Zr(\eta\text{-}C_5Me_5)_2\{OC(Me)C(Me)O\}]$ with Me peaks at τ 8.09.[4] Structure (*ii*) in Scheme 3 is unlikely because it is not obvious that alternative conformers are possible. However, we find that a solution of complex (12a) in CD_2Cl_2 was slowly converted at ambient temperature into a mixture of (12a) and (12b), and the similarities in the n.m.r. and i.r. spectra of complexes (12a) and (12b) suggest that they are more likely to be conformers [*e.g.*, as in Scheme 4 for (*i*) of Scheme 3] rather than isomers.

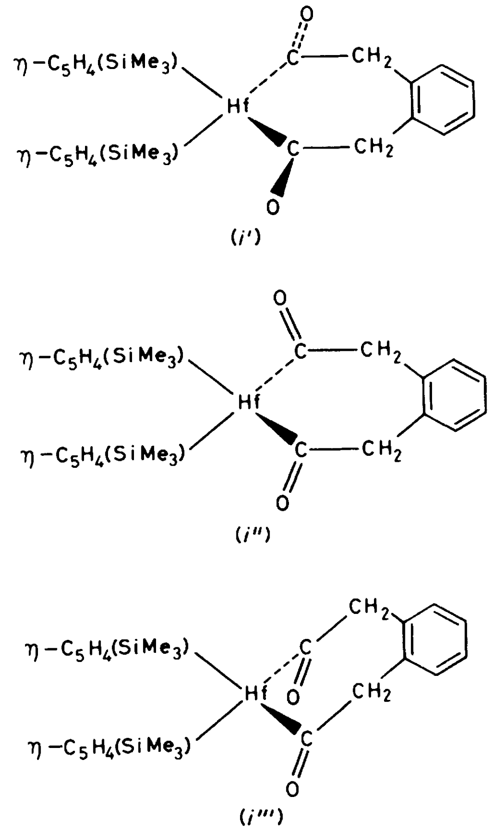
Using ^{13}CO the derived complex shows a $^{1}J(^{13}CO{-}^{13}C)$ coupling of 61 Hz and $^{2}J(^{13}CO{-}CH_2)$ of 4 Hz, consistent with structures (*i′*)—(*i‴*) of Scheme 4.

As the n.m.r. spectra of both complexes (12a) and (12b) show equivalence of the two CH_2 groups and of the two CO's, any mixed-bonding modes, such as σ for one acyl group and η^2 for the other, are ruled out. The equivalence of the two trimethylsilyl units within each compound argues against the *syn* arrangement of the two CO's, *i.e.* (*i‴*) in Scheme 4.

Finally, we rule out structures other than mononuclear because the mass spectrum of complex (12a) shows a parent ion at *m/e* = 614, corresponding to $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CO)_2(CH_2)_2C_6H_4\}]^+$. We conclude that complexes (12a) and (12b) are conformers (*i′*) and (*i″*) of Scheme 4, with the 2 CO's having an *anti* relationship.

Complexes (12a) and (12b) in solution in CD_2Cl_2 or $CDCl_3$ coexist in equilibrium, with the former favoured at low and the latter at higher temperature. Their interconversion was carried out in CD_2Cl_2 or $CDCl_3$ in an n.m.r. tube sealed under an atmosphere of carbon monoxide (gentle heating in an open n.m.r. tube resulted in loss of CO and irreversible decomposition). Cooling to *ca.* 0 °C in CD_2Cl_2 gave almost exclusively (12a), while heating to 35 °C gradually afforded the equilibrium mixture of (12a) and (12b) in *ca.* 1 : 1 ratio (Figure 2), with equilibrium reached after *ca.* 4 h. In $CDCl_3$ at 35 °C, equilibrium was attained in *ca.* 3 h (Figure 3) and the ratio of (12a) : (12b) was then *ca.* 1 : 3. Cooling of the warmed solutions gradually restored the primacy of (12a) at low temperature. Although Figures 2 and 3 refer to ^{1}H n.m.r. spectra, similar features were also discernible in the proton-decoupled ^{13}C spectra.

The reason that complex (12a) was obtained exclusively as the initial product from carbonylation of the metallacycle (4) is considered to be attributable to its precipitation from the reaction medium; the high temperature-favoured conformer (12b) was not isolated pure.



Scheme 4. Possible conformers of complexes (12a) and (12b) having the structure (*i*) as illustrated in Scheme 3

To summarise, carbonylation of the Hf^{IV} metallacycle (4) yields $[Hf\{\eta\text{-}C_5H_4(SiMe_3)_2\}\{o\text{-}(CO)_2(CH_2)_2C_6H_4\}]$, which has two conformers (12a) and (12b) in equilibrium in solution, both with a high degree of symmetry, and hence are best represented by structures (*i′*) and (*i″*) of Scheme 4.

Reactions of the Di-Grignard Reagent (1) *with Group* 4A *Metal Tetrachlorides.*—The compounds $[M(CH_2Ph)_4]$ (M = Ti, Zr, or Hf) [47,48] are generally prepared in diethyl ether, then extracted with, and crystallised from, hexane. However, at low temperature the reaction of the di-Grignard reagent (1) with a metal(IV) chloride MCl_4 (M = Ti, Zr, or Hf) in thf gave an insoluble solid, or for M = Zr an orange solution which darkened to brown on warming above 10 °C and attempts to isolate a compound from the solution at low or ambient temperatures were unsuccessful. On washing (thf) the precipitate from each reaction and drying *in vacuo*, pyrophoric powders (9)—(11) were obtained with i.r. spectra and microanalyses indicative of products having the composition $M(CH_2C_6H_4CH_2\text{-}o)_2(thf)$. The insolubility of compounds (9)—(11) indicates that their structures are unlikely to be those of the metallaspirobicycle (13) but rather of an oligomer having bridging *o*-xylidenes. The i.r. spectra of complexes (9)—(11) showed aromatic ring-breathing modes [34] in the range 1 532—1 588 cm^{-1}, and a characteristic strong band in the region 1 010—1 020 cm^{-1} assigned to $\nu_{asym}(COC)$ of co-ordinated thf; in free thf, this band is at 1 069 cm^{-1} but shifts to lower wavenumber in metal-co-ordinated thf.

It has been observed that co-ordination of thf to $[Zr(CH_2Ph)_4]$ leads to reduced solubility of the tetrabenzyl compound.[49]

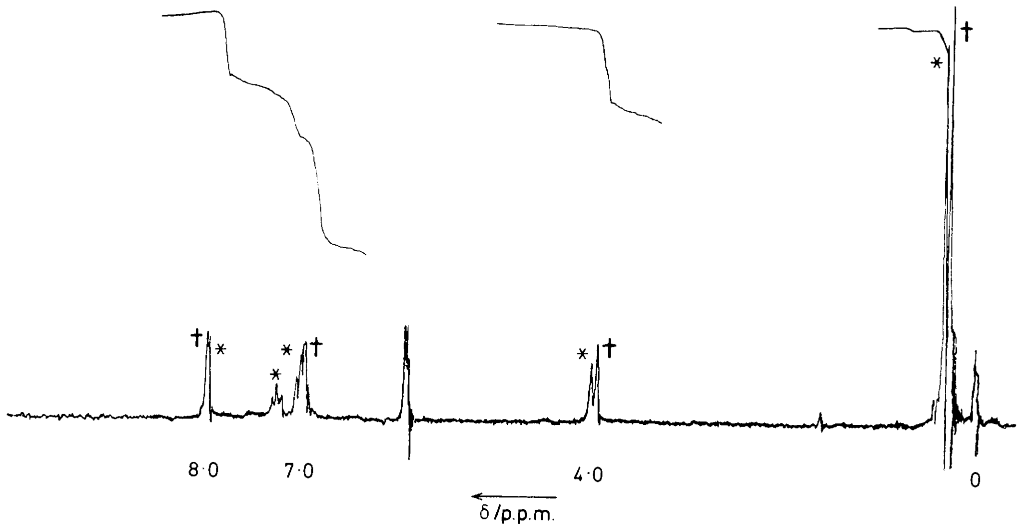


Figure 2. The ^1H n.m.r. spectrum at 90 MHz of an equilibrium mixture of the two conformers (12a) and (12b) of formula $[Hf\{C(O)CH_2C_6H_4CH_2CO\text{-}o\}\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$, in CD_2Cl_2 after 4 h at 35 °C, showing signals due to (12a) (*) and (12b) (†)

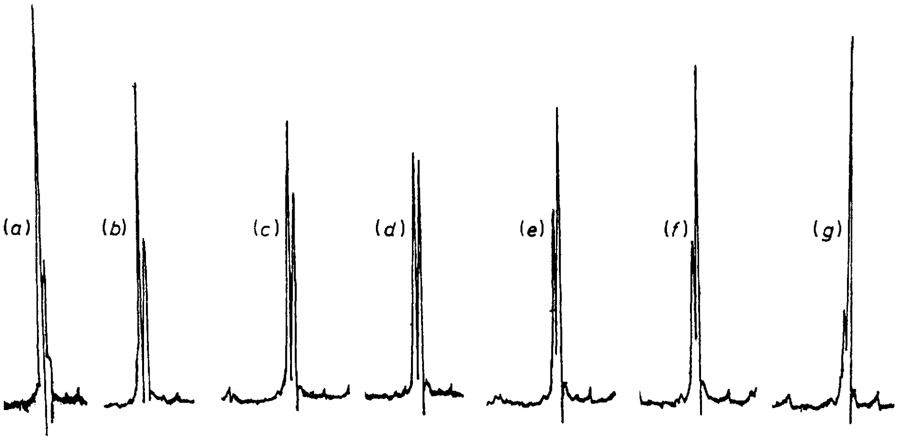
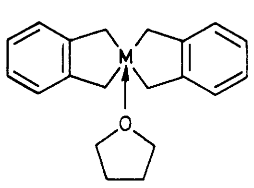


Figure 3. The ^1H n.m.r. spectra, in the $SiMe_3$ region, of the two conformers (12a) and (12b) of formula $[Hf\{C(O)CH_2C_6H_4CH_2CO\text{-}o\}\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$, at various time intervals (min) after dissolving solid (12a) in $CDCl_3$ at 35 °C: (*a*) 7, (*b*) 10, (*c*) 14, (*d*) 17, (*e*) 26, (*f*) 33, and (*g*) 165 min



(13)

We therefore attempted to remove the thf from complex (10) by heating it under vacuum. However, the compound slowly decomposed above 125 °C releasing thf and *o*-xylene, which were collected and identified by their ^1H n.m.r. spectra.

Molecular Structures of the Complexes $[M(\eta\text{-}C_5H_4R)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [R = H, M = Ti (6b), Zr (7), *or* Hf (8); R = $SiMe_3$, M = Nb (5)].—The molecular structures and atom-numbering scheme for the isostructural Ti, Zr, and Hf complexes $[M(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (6b)—(8) are presented in Figure 4. The molecules possess no crystallographically imposed symmetry. Several worthwhile comparisons between the titanium (6b) and zirconium (7) derivatives and related compounds in the literature can be made because of the accuracy of the determinations. The Ti–C(sp^3) bond length in (6b) [2.203(6) Å] is near the value of 2.21(2) Å found in the indenyl complex $[Ti(\eta\text{-}C_9H_7)_2Me_2]$,[50] and also agrees well with the Ti–C(sp^2) length, 2.156(22) Å, in $[Ti(\eta\text{-}C_5H_5)_2(C_4Ph_4)]$,[51] after a correction of 0.03 Å for the change in carbon atom hybridisation.[52] The Ti–C(η) average distance of 2.382(18) Å in (6b) is typical for a titanocene(IV) complex $[Ti(\eta\text{-}C_5H_5)_2XY]$, *e.g.*, 2.306(22) Å in $[Ti(\eta\text{-}C_5H_5)_2(C_4Ph_4)]$.[51] Thus, the *o*-xylidene ligand is seen to present no obvious steric problems.

Complexes (5)—(8) are to be viewed as derived from $o\text{-}{}^-CH_2C_6H_4CH_2{}^-$ rather than $o\text{-}C_6H_4(=CH_2)_2$, or an intermediate, because the M–C^α bond lengths (Tables 6 and 8) are appropriate to an M^{IV}–C(sp^3) σ bond and M–C^β is considerably longer [$\langle M\text{–}C^\beta \rangle$ (Å): 2.913(6) Ti, 2.857(8) Zr, 2.91(1) Hf, and 3.070(6) and 3.088(6) Nb for the two independent molecules of (5)].

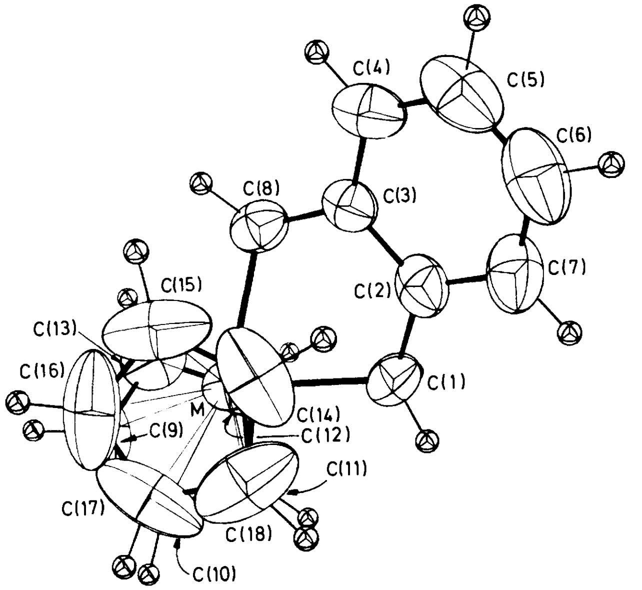


Figure 4. ORTEP diagram of the molecular structures of the isostructural complexes $[M(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [M = Ti (6b), Zr (7), or Hf (8)], showing the numbering system

Table 6. Intramolecular distances (Å) for the complexes $[M(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [M = Ti (6b), Zr (7), or Hf (8)], with estimated standard deviations in parentheses

	Ti (6b)	Zr (7)	Hf (8)
M–C(1)	2.204(4)	2.301(6)	2.28(1)
M–C(8)	2.202(5)	2.298(6)	2.28(1)
M–C(9)	2.377(5)	2.511(6)	2.51(1)
M–C(10)	2.378(5)	2.510(6)	2.50(1)
M–C(11)	2.386(5)	2.521(5)	2.49(1)
M–C(12)	2.413(5)	2.541(6)	2.53(1)
M–C(13)	2.398(5)	2.528(6)	2.52(1)
M–C(14)	2.407(5)	2.544(6)	2.53(1)
M–C(15)	2.377(5)	2.532(6)	2.50(1)
M–C(16)	2.365(6)	2.505(6)	2.50(1)
M–C(17)	2.355(6)	2.496(6)	2.51(1)
M–C(18)	2.369(6)	2.511(6)	2.50(1)
M–C(η) (mean)	2.382(18)	2.520(15)	2.51(1)
C(1)–C(2)	1.493(7)	1.488(8)	1.50(2)
C(2)–C(3)	1.399(6)	1.423(9)	1.41(2)
C(2)–C(7)	1.392(7)	1.39(1)	1.40(2)
C(3)–C(4)	1.400(6)	1.395(8)	1.39(1)
C(3)–C(8)	1.466(6)	1.464(8)	1.50(2)
C(4)–C(5)	1.364(7)	1.366(9)	1.36(2)
C(5)–C(6)	1.348(9)	1.36(1)	1.36(2)
C(6)–C(7)	1.380(8)	1.374(9)	1.37(2)
C(9)–C(10)	1.392(7)	1.394(9)	1.40(2)
C(9)–C(13)	1.411(7)	1.407(9)	1.42(2)
C(10)–C(11)	1.412(7)	1.395(8)	1.41(2)
C(11)–C(12)	1.400(7)	1.399(9)	1.39(2)
C(12)–C(13)	1.377(7)	1.394(9)	1.39(2)
C(14)–C(15)	1.357(9)	1.389(9)	1.35(2)
C(14)–C(18)	1.347(9)	1.36(1)	1.33(2)
C(15)–C(16)	1.38(1)	1.40(1)	1.42(2)
C(16)–C(17)	1.32(1)	1.36(1)	1.36(2)
C(17)–C(18)	1.29(1)	1.357(9)	1.35(2)

Table 7. Intramolecular bond angles (°) for the complexes $[M(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ [M = Ti (6b), Zr (7), or Hf (8)], with estimated standard deviations in parentheses

	Ti (6b)	Zr (7)	Hf (8)
C(1)–M–C(8)	76.7(2)	77.3(2)	77.2(4)
M–C(1)–C(2)	102.4(3)	95.5(4)	98.5(7)
C(1)–C(2)–C(3)	116.3(4)	119.2(7)	118(1)
C(1)–C(2)–C(7)	124.5(5)	122.6(7)	123(1)
C(3)–C(2)–C(7)	119.1(4)	118.0(5)	118(1)
C(2)–C(3)–C(4)	117.9(5)	117.8(7)	118(1)
C(2)–C(3)–C(8)	117.3(4)	119.6(5)	118.5(9)
C(4)–C(3)–C(8)	124.6(5)	122.3(6)	123(1)
C(3)–C(4)–C(5)	121.9(5)	122.6(7)	122(1)
C(4)–C(5)–C(6)	119.8(5)	119.3(6)	120(1)
C(5)–C(6)–C(7)	120.8(6)	120.7(8)	121(1)
C(2)–C(7)–C(6)	120.5(6)	121.6(8)	121(2)
M–C(8)–C(3)	103.2(3)	96.3(3)	98.7(7)
C(10)–C(9)–C(13)	107.9(5)	108.3(6)	107(1)
C(9)–C(10)–C(11)	107.0(5)	107.8(6)	107(1)
C(10)–C(11)–C(12)	108.7(5)	108.3(6)	109(1)
C(11)–C(12)–C(13)	107.4(5)	108.1(6)	108(1)
C(9)–C(13)–C(12)	108.9(5)	107.5(6)	109(1)
C(15)–C(14)–C(18)	106.5(6)	108.2(6)	111(2)
C(14)–C(15)–C(16)	107.1(6)	106.8(6)	105(1)
C(15)–C(16)–C(17)	106.2(7)	107.1(7)	107(1)
C(16)–C(17)–C(18)	111.1(8)	109.2(6)	108(1)
C(14)–C(18)–C(17)	109.0(7)	108.7(7)	109(2)
Fold angle	41	53	53

Since Ti^{4+} is 0.07 Å smaller than Zr^{4+} or Hf^{4+},[53] normal bond lengths in the zirconium and hafnium derivatives are to be anticipated. Indeed, this is borne out with regard to both the complexes (7) and (8). The Zr–C(sp^3) length is best typified by the value of 2.283(6) Å in $[Zr(\eta\text{-}C_5H_5)_2Me_2]$ and 2.280(2) Å in $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$. These values are only 0.02 Å less than the 2.300(8) Å found in the title derivative (7). The Zr–C(η) separation [2.520(15) Å] may be compared with 2.52(1) and 2.52(2) Å in $[Zr(\eta\text{-}C_5H_5)_2Me_2]$[54] and $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$,[32] respectively.

Unfortunately, a truly significant evaluation of the hafnium–carbon *versus* the zirconium–carbon parameters cannot be made because of the relative inaccuracy of the determination of the structure of the hafnium analogue, (8). However, the Hf–C(sp^3) length, 2.28(1) Å, is 0.02 Å shorter than the Zr–C(sp^3) distance. Contrary to early reports, it has recently been shown that the Hf–C(sp^3) bond distance is 0.04 Å *shorter* than the Zr–C(sp^3) length in $[M(\eta\text{-}C_5H_5)_2Me_2]$.[54] The presently determined structures of the *o*-xylidene complexes (7) and (8) are thus consistent with that observation.

The molecular structure and atom-numbering scheme for $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (5) is given in Figure 5. The Nb–C(sp^3) average length, 2.286(9) Å, may be compared to 2.340(3) Å in $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$,[36] 2.28(1) Å in $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2(CH_2SiMe_3)Cl]$,[55] and 2.316(8) Å in $[Nb(\eta\text{-}C_5H_5)_2Et(\eta\text{-}C_2H_4)]$.[56] An important feature of the structure of the metallacycle (5) is the reduction in the bite angle, C(sp^3)–M–C(sp^3), from 77.3(2)° with M = Zr [in complex (7)] to 72.4(7)° for M = Nb [in (5)], apparently due to the presence of the single *d* electron in the latter.

Another interesting comparison lies in the fold angle, Φ, {defined as that made by the normal to the plane of $MC^{\alpha}C^{\alpha'}$ [*i.e.*, MC(1)C(8)] and the normal to the plane of the four carbon atoms of the metallacyclopentene ring [*i.e.*, C(1)C(2)-C(3)C(8)]} for the four complexes (5)—(8), as illustrated in Figure 6. The angle Φ is clearly influenced by both steric and electronic factors: values of 41, 44, 53, and 53° are found for the Ti (6b), Nb (5), Zr (7), and Hf (8) structures, respectively.

The C_6 rings are planar to better than 0.01 Å, while the carbon atoms of the α-CH_2 units lie 0.07, 0.10, 0.12, and 0.12 Å out of the plane for the Nb, Ti, Zr, and Hf structures, respectively. The σ-bonded carbon atoms also reside on the same side of the C_6 plane as the metal atoms.

Table 8. Intramolecular bond lengths (Å) and angles (°) for [Nb{η-$C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}$] (5) (two independent molecules in the unit cell)

	A	B
Nb(1)–C(1)	2.275(5)	2.279(5)
Nb(1)–C(8)	2.295(4)	2.296(5)
Nb(1)–C(9)	2.430(5)	2.406(4)
Nb(1)–C(10)	2.407(5)	2.433(4)
Nb(1)–C(11)	2.424(5)	2.458(4)
Nb(1)–C(12)	2.437(5)	2.421(5)
Nb(1)–C(13)	2.435(5)	2.392(4)
Nb(1)–C(17)	2.425(4)	2.430(4)
Nb(1)–C(18)	2.408(4)	2.410(5)
Nb(1)–C(19)	2.427(5)	2.428(5)
Nb(1)–C(20)	2.443(5)	2.450(5)
Nb(1)–C(21)	2.428(4)	2.432(4)
Si(1)–C(9)	1.856(5)	1.870(5)
Si(1)–C(14)	1.867(7)	1.863(7)
Si(1)–C(15)	1.860(6)	1.853(6)
Si(1)–C(16)	1.864(7)	1.826(7)
Si(2)–C(17)	1.873(5)	1.863(5)
Si(2)–C(22)	1.865(6)	1.849(6)
Si(2)–C(23)	1.865(7)	1.878(7)
Si(2)–C(24)	1.855(6)	1.871(7)
C(1)–C(2)	1.491(7)	1.513(7)
C(2)–C(3)	1.385(7)	1.392(7)
C(2)–C(7)	1.401(7)	1.405(7)
C(3)–C(4)	1.394(9)	1.398(9)
C(4)–C(5)	1.35(1)	1.37(1)
C(5)–C(6)	1.405(9)	1.394(9)
C(6)–C(7)	1.400(7)	1.400(7)
C(7)–C(8)	1.488(7)	1.501(7)
C(9)–C(10)	1.437(7)	1.428(6)
C(9)–C(13)	1.425(7)	1.430(6)
C(10)–C(11)	1.411(7)	1.409(6)
C(11)–C(12)	1.402(8)	1.399(7)
C(12)–C(13)	1.416(7)	1.408(6)
C(17)–C(18)	1.404(6)	1.427(6)
C(17)–C(21)	1.428(6)	1.436(6)
C(18)–C(19)	1.409(7)	1.410(7)
C(19)–C(20)	1.394(7)	1.396(7)
C(20)–C(21)	1.402(7)	1.406(7)
C(1)–Nb(1)–C(8)	71.9(2)	72.9(2)
C(9)–Si(1)–C(14)	105.8(3)	106.0(2)
C(9)–Si(1)–C(15)	112.8(2)	114 0(2)
C(14)–Si(1)–C(15)	108.0(3)	106.8(3)
C(9)–Si(1)–C(16)	109.5(3)	109.7(3)
C(14)–Si(1)–C(16)	109.5(4)	110.6(4)
C(15)–Si(1)–C(16)	111.1(3)	109.6(4)
C(17)–Si(2)–C(22)	110.9(2)	111.6(2)
C(17)–Si(2)–C(23)	106.7(3)	110.2(2)
C(22)–Si(2)–C(23)	108.9(3)	110.5(3)
C(17)–Si(2)–C(24)	110.8(2)	106.3(3)
C(22)–Si(2)–C(24)	110.2(3)	109.4(3)
C(23)–Si(2)–C(24)	109.3(3)	108.8(4)
Nb(1)–C(1)–C(2)	107.2(3)	107.2(3)
C(1)–C(2)–C(3)	125.4(5)	123.8(5)
C(1)–C(2)–C(7)	115.5(4)	115.5(4)
C(3)–C(2)–C(7)	119.0(5)	120.7(5)
C(2)–C(3)–C(4)	120.9(6)	119.3(6)
C(3)–C(4)–C(5)	120.0(6)	120.7(6)
C(4)–C(5)–C(6)	121.2(6)	120.3(6)
C(5)–C(6)–C(7)	118.9(6)	120.5(6)
C(2)–C(7)–C(6)	120.0(5)	118.5(5)
C(2)–C(7)–C(8)	115.5(4)	116.2(4)
C(6)–C(7)–C(8)	124.4(5)	125.2(5)
Nb(1)–C(8)–C(7)	106.7(3)	107.0(3)
Si(1)–C(9)–C(10)	124.5(4)	126.0(3)
Si(1)–C(9)–C(13)	128.6(4)	128.3(3)
C(10)–C(9)–C(13)	105.9(4)	105.0(4)
C(9)–C(10)–C(11)	109.1(5)	109.5(4)
C(10)–C(11)–C(12)	107.8(5)	108.1(4)
C(11)–C(12)–C(13)	108.5(5)	107.7(4)
C(9)–C(13)–C(12)	108.8(5)	109.7(4)
Si(2)–C(17)–C(18)	127.4(4)	124.8(4)
Si(2)–C(17)–C(21)	126.0(4)	129.2(4)
C(18)–C(17)–C(21)	105.8(4)	105.2(4)
C(17)–C(18)–C(19)	109.7(4)	108.9(4)
C(18)–C(19)–C(20)	107.4(4)	108.7(4)
C(19)–C(20)–C(21)	108.4(4)	107.7(4)
C(17)–C(21)–C(20)	108.7(4)	109.5(4)

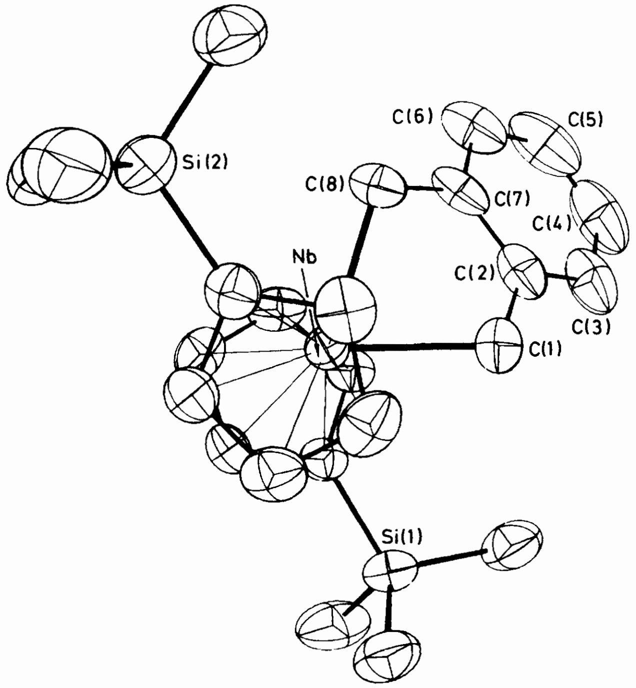


Figure 5. ORTEP diagram of the molecular structure of [Nb{η-$C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}$] (5) showing the numbering system

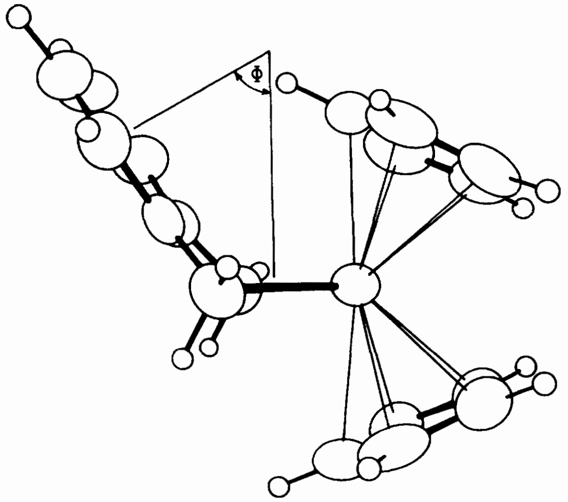


Figure 6. View of the structure of [Zr(η-$C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}$] (7) illustrating the defining vectors for the angle of fold, Φ

Table 9. Crystal data[a] and refinement parameters for $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ [M = Ti (6b), Zr (7), or Hf (8)] and $[\mathrm{Nb}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ (5)

Complex	(6b)	(7)	(8)	(5)[b]
M	282.3	325.6	412.9	471.6
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
a/Å	8.158(4)	8.276(4)	8.251(5)	12.371(8)
b/Å	10.992(5)	11.075(5)	11.070(7)	14.249(9)
c/Å	15.713(7)	15.721(7)	15.748(8)	14.514(9)
U/Å^3	1 409.0	1 440.9	1 438.4	2 403.1
D_c/g cm^{-3}	1.33	1.50	1.91	1.30
F(000)	592	664	792	988
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
μ(Mo-K_α)/cm^{-1}	6.14	7.35	76.24	4.93
2θ limits/°	$\geqslant 50$	$\geqslant 50$	$\geqslant 50$	$\geqslant 35$
Reflections used in refinements [$I > 3\sigma(I)$]	963	970	1 189	4 667
R	0.026	0.019	0.024	0.027
R'	0.027	0.021	0.027	0.034

[a] For all complexes D_m not measured, $Z = 4$, and λ(Mo-K_α) = 0.710 69 Å. [b] α = 78.51(3), β = 89.47(3), and γ = 73.67(3)°.

Table 10. Fractional atomic co-ordinates for $[\mathrm{Ti}(\eta\text{-}\mathrm{C_5H_5})_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ (6b), with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Ti	0.258 7(1)	0.106 48(7)	0.707 02(4)
C(1)	0.224 7(7)	−0.010 3(4)	0.594 4(3)
C(2)	0.393 7(6)	−0.016 0(5)	0.558 0(3)
C(3)	0.488 8(5)	0.089 4(4)	0.565 9(2)
C(4)	0.651 4(6)	0.084 9(5)	0.537 6(3)
C(5)	0.717 0(7)	−0.017 7(7)	0.502 6(3)
C(6)	0.624 0(8)	−0.118 4(7)	0.494 6(4)
C(7)	0.463 1(7)	−0.119 4(6)	0.521 8(3)
C(8)	0.414 9(6)	0.193 2(4)	0.610 1(3)
C(9)	0.106 5(7)	0.254 2(5)	0.784 1(4)
C(10)	0.009 7(7)	0.150 1(5)	0.779 6(4)
C(11)	−0.030 4(6)	0.132 7(5)	0.693 0(4)
C(12)	0.041 2(6)	0.226 1(5)	0.645 2(3)
C(13)	0.124 6(6)	0.300 4(4)	0.700 9(4)
C(14)	0.471(1)	−0.038 0(8)	0.740 4(4)
C(15)	0.515 3(7)	0.070 7(9)	0.774 1(6)
C(16)	0.404(1)	0.097 7(8)	0.837 1(6)
C(17)	0.298(1)	0.007(1)	0.838 2(5)
C(18)	0.334(1)	−0.072 7(6)	0.781 3(7)

Table 11. Fractional atomic co-ordinates for $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ (7), with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Zr	0.257 33(7)	0.110 06(4)	0.701 87(3)
C(1)	0.204 4(7)	−0.004 0(6)	0.582 8(4)
C(2)	0.375 3(7)	−0.010 5(7)	0.553 7(4)
C(3)	0.475 4(6)	0.093 3(6)	0.561 5(3)
C(4)	0.638 6(7)	0.081 2(7)	0.540 9(4)
C(5)	0.703 5(7)	−0.025 0(8)	0.512 6(4)
C(6)	0.607 0(9)	−0.123 4(8)	0.504 6(4)
C(7)	0.445 9(8)	−0.117 4(7)	0.525 3(4)
C(8)	0.409 6(7)	0.203 8(5)	0.599 1(4)
C(9)	0.104 7(8)	0.264 5(7)	0.786 8(5)
C(10)	0.006 3(8)	0.162 5(7)	0.783 5(4)
C(11)	−0.063 2(6)	0.147 2(5)	0.699 4(5)
C(12)	0.023 9(7)	0.240 1(7)	0.650 6(4)
C(13)	0.116 5(7)	0.312 6(5)	0.704 2(5)
C(14)	0.486 2(9)	−0.035 2(7)	0.736 6(4)
C(15)	0.519 4(3)	0.070 9(7)	0.780 3(5)
C(16)	0.398(1)	0.084 3(7)	0.841 8(4)
C(17)	0.296 8(8)	−0.012 0(9)	0.833 7(5)
C(18)	0.349(1)	−0.083 6(6)	0.769 3(5)

Experimental

Physical Measurements.—Cyclic voltammetry was carried out as described previously.[27,57] Hydrogen-1 n.m.r. spectra were obtained on a Perkin-Elmer R32 or a Varian T60 instrument and carbon-13 n.m.r. data were collected using a JEOL PFT 100 spectrometer. E.s.r. spectra were recorded on a Varian E4 spectrometer, g_{av} values being measured relative to polycrystalline 2,2-diphenylpicrylhydrazyl. Elemental analyses were carried out in the microanalytical laboratory of the University of Sussex. I.r. spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 597 spectrophotometer.

General Procedures.—All reactions and manipulations were carried out under an atmosphere of dinitrogen or argon, unless otherwise stated, using Schlenk-type glassware. All solvents were dried and distilled from Na (diethyl ether, thf, n-hexane), K (toluene, benzene), $\mathrm{CaH_2}$ (n-pentane), or $\mathrm{P_2O_5}$ ($\mathrm{CH_2Cl_2}$), under an atmosphere of dinitrogen and freeze-degassed prior to use.

Materials.—The metallocene chlorides $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$ were purchased from Ventron (M = Ti) or Aldrich (M = Zr). Analogues, $[\mathrm{Hf}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$ and $[\mathrm{M}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\mathrm{Cl_2}]$ (M = Ti, Zr, Hf, or Nb), were prepared as in the literature.[27,36] The di-Grignard, '$o\text{-}\mathrm{C_6H_4}(\mathrm{CH_2MgCl})_2$' (1) was prepared as described previously.[1]

Preparations.—$[\mathrm{Ti}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ (2). To a stirred, cooled (−78 °C) solution of $[\mathrm{Ti}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\mathrm{Cl_2}]$ (0.74 g, 1.89 mmol) in thf (10 cm^3) in the dark was added the di-Grignard reagent (1) (22.5 cm^3, 0.084 mol dm^{-3}, 1.89 mmol) dropwise over 0.5 h. On completion of the addition the mixture was allowed to warm to room temperature and stirred for a further 12 h. The solvent was removed from the resultant blue-black solution *in vacuo* and the residue extracted with diethyl ether (40 cm^3). The combined extract was cooled (−40 °C), filtered cold, evaporated, and extracted into n-hexane (20 cm^3). Cooling of this solution (−78 °C) afforded dark blue microcrystals of *complex* (2) (0.35 g, 43%).

$[\mathrm{Zr}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\{o\text{-}(\mathrm{CH_2})_2\mathrm{C_6H_4}\}]$ (3). Reaction between $[\mathrm{Zr}\{\eta\text{-}\mathrm{C_5H_4}(\mathrm{SiMe_3})\}_2\mathrm{Cl_2}]$ (1.60 g, 3.67 mmol) and the di-Grignard reagent (1) (40 cm^3, 0.09 mol dm^{-3}, 3.60 mmol) in a similar fashion to that above, but without the exclusion of light, gave a deep red solution. The thf was removed *in vacuo* and the residue extracted with diethyl ether (60 cm^3). The

Table 12. Fractional atomic co-ordinates for $[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (8), with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Hf	0.258 03(5)	0.110 77(4)	0.703 24(2)
C(1)	0.213(1)	−0.006(1)	0.586 0(7)
C(2)	0.383(1)	−0.013(1)	0.554 2(7)
C(3)	0.483(1)	0.090(1)	0.561 8(6)
C(4)	0.646(1)	0.079(1)	0.539 5(7)
C(5)	0.709(1)	−0.025(2)	0.508 8(8)
C(6)	0.613(2)	−0.124(2)	0.501 0(8)
C(7)	0.453(2)	−0.120(1)	0.524 2(8)
C(8)	0.414(1)	0.201(1)	0.602 5(8)
C(9)	0.104(2)	0.268(1)	0.786(1)
C(10)	0.006(2)	0.165(2)	0.782 1(9)
C(11)	−0.040(1)	0.148(1)	0.696 5(9)
C(12)	0.028(2)	0.240(1)	0.647 7(8)
C(13)	0.118(1)	0.313(1)	0.701(1)
C(14)	0.483(2)	−0.035(2)	0.741 1(9)
C(15)	0.519(2)	0.071(2)	0.779(1)
C(16)	0.399(2)	0.086(2)	0.842 9(9)
C(17)	0.295(2)	−0.009(2)	0.837(1)
C(18)	0.347(2)	−0.081(1)	0.773(1)

extract was cooled (−20 °C), filtered cold, and re-cooled (−40 °C) to afford red crystals of *complex* (3) (0.45 g). From the mother-liquors in n-pentane (50 cm^3) a second crop of crystals of (3) was obtained (combined yield 1.09 g, 63%).

$[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (4). Reaction between $[Hf\{\eta\text{-}C_5H_4(SiMe_3)\}_2Cl_2]$ (1.90 g, 3.63 mmol) and the di-Grignard reagent (1) (40 cm^3, 0.92 mol dm^{-3}, 3.68 mmol), and a work-up procedure identical to that for (3) above, gave *complex* (4) (0.89 g, 43%) as yellow crystals.

$[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (5). To a stirred suspension of $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2Cl_2]$ (1.53 g, 3.5 mmol) in thf (10 cm^3) at −40 °C was added the di-Grignard reagent (1) (50 cm^3, 0.07 mol dm^{-3}, 3.5 mmol) over 10 min. As the mixture was warmed to room temperature the solution darkened to purple. After 18 h at room temperature the mixture was evaporated to dryness, extracted with n-pentane (50 cm^3), and filtered. Successive cooling (−40 °C) and concentration of the filtrate gave two crops of dark purple cubes of *complex* (5) (0.74 g, 45%).

$[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (6b). The di-Grignard reagent (1) (80 cm^3, 0.07 mol dm^{-3}, 5.6 mmol) was added dropwise to a stirred and cooled (−78 °C) suspension of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ (1.39 g, 5.6 mmol) in thf (10 cm^3) in the dark. An immediate reaction ensued; the addition was completed in 0.5 h. The mixture was allowed to warm to room temperature and stirred for a further 12 h. The violet-black solution was evaporated to dryness, extracted with toluene–diethyl ether (50 cm^3, 1 : 1), and filtered. Solvent was removed from the filtrate to yield a solid. Crystallisation of the solid from diethyl ether gave two crops of violet microcrystals of $[Ti(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]\cdot 0.5OEt_2$, (6a), (1.05 g, 59%). Addition of n-hexane (10 cm^3) to a solution of *complex* (6a) in toluene (10 cm^3) and cooling to −30 °C gave blue-black crystals of *complex* (6b) suitable for *X*-ray crystallographic analysis.

$[Zr(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (7). The reaction between $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ (2.0 g, 6.84 mmol) and the di-Grignard reagent (1) (99 cm^3, 0.07 mol dm^{-3}, 6.93 mmol) in thf at −78 °C gave a deep red solution. After warming and stirring at room temperature for 8 h, the product was extracted from the evaporated reaction mixture with toluene–diethyl ether (50 cm^3, 1 : 1). Flitration, addition of diethyl ether (20 cm^3) to the filtrate, and cooling (−40 °C) gave red crystals of *complex* (7) (1.56 g, 70%).

Table 13. Fractional atomic co-ordinates for $[Nb\{\eta\text{-}C_5H_4(SiMe_3)\}_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (5), with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Nb(1)	0.994 81(3)	0.244 10(3)	0.568 48(3)
Nb(2)	0.664 30(3)	0.246 80(3)	0.068 30(3)
Si(1)	1.298 4(1)	0.202 0(1)	0.479 1(1)
Si(2)	0.712 5(1)	0.182 0(1)	0.619 4(1)
Si(3)	0.987 5(1)	0.167 0(1)	0.099 97(9)
Si(4)	0.382 8(1)	0.221 6(1)	−0.022 7(1)
C(1A)	0.866 7(4)	0.396 2(3)	0.559 0(3)
C(2A)	0.883 3(5)	0.431 8(3)	0.646 4(4)
C(3A)	0.797 5(5)	0.483 9(4)	0.695 4(5)
C(4A)	0.821 5(7)	0.508 9(5)	0.779 5(5)
C(5A)	0.929 6(8)	0.483 3(5)	0.813 6(5)
C(6A)	1.019 2(6)	0.429 1(4)	0.767 1(4)
C(7A)	0.995 3(5)	0.403 8(4)	0.682 7(4)
C(8A)	1.081 2(4)	0.343 3(4)	0.628 6(3)
C(9A)	1.144 0(4)	0.224 9(4)	0.457 0(3)
C(10A)	1.089 9(4)	0.148 3(4)	0.456 6(3)
C(11A)	0.976 9(5)	0.192 6(4)	0.421 3(3)
C(12A)	0.958 8(5)	0.295 8(4)	0.399 1(3)
C(13A)	1.060 4(5)	0.316 4(4)	0.420 7(3)
C(14A)	1.364 7(6)	0.182 8(6)	0.365 5(5)
C(15A)	1.333 2(5)	0.309 5(5)	0.512 9(4)
C(16A)	1.354 0(6)	0.086 9(5)	0.570 2(6)
C(17A)	0.864 7(4)	0.163 7(3)	0.653 1(3)
C(18A)	0.959 5(4)	0.088 6(3)	0.635 2(3)
C(19A)	1.056 0(4)	0.091 1(4)	0.684 8(4)
C(20A)	1.021 4(5)	0.167 4(4)	0.735 1(3)
C(21A)	0.905 0(4)	0.213 0(3)	0.716 1(3)
C(22A)	0.694 8(5)	0.180 1(5)	0.492 6(4)
C(23A)	0.670 9(6)	0.076 0(6)	0.691 0(5)
C(24A)	0.621 2(5)	0.300 4(5)	0.646 1(4)
C(1B)	0.518 0(4)	0.339 5(4)	0.139 1(3)
C(2B)	0.568 1(4)	0.392 9(4)	0.200 1(4)
C(3B)	0.528 5(5)	0.409 9(4)	0.237 2(4)
C(4B)	0.583 8(7)	0.456 4(5)	0.339 8(5)
C(5B)	0.676 2(7)	0.484 6(5)	0.306 8(5)
C(6B)	0.717 2(5)	0.466 8(4)	0.220 1(4)
C(7B)	0.663 3(5)	0.421 1(4)	0.165 3(4)
C(8B)	0.703 2(4)	0.393 3(3)	0.073 6(3)
C(9B)	0.847 6(4)	0.153 1(3)	0.141 0(3)
C(10B)	0.784 0(4)	0.198 6(3)	0.211 6(3)
C(11B)	0.692 1(4)	0.159 3(4)	0.233 0(3)
C(12B)	0.695 5(4)	0.089 5(4)	0.176 7(4)
C(13B)	0.791 0(4)	0.084 0(3)	0.121 7(3)
C(14B)	1.084 6(5)	0.038 4(5)	0.112 9(5)
C(15B)	0.984 5(5)	0.226 6(6)	−0.025 3(4)
C(16B)	1.039 8(7)	0.237 3(7)	0.172 7(5)
C(17B)	0.523 7(4)	0.243 0(3)	−0.045 9(3)
C(18B)	0.625 6(4)	0.167 3(4)	−0.054 4(3)
C(19B)	0.710 3(4)	0.212 5(4)	−0.087 0(3)
C(20B)	0.664 5(5)	0.315 5(4)	−0.099 5(3)
C(21B)	0.550 9(4)	0.335 1(3)	−0.074 6(3)
C(22B)	0.277 2(4)	0.334 3(4)	0.001 1(4)
C(23B)	0.396 4(5)	0.114 2(5)	0.077 8(6)
C(24B)	0.336 3(6)	0.188 8(6)	−0.131 4(6)

$[Hf(\eta\text{-}C_5H_5)_2\{o\text{-}(CH_2)_2C_6H_4\}]$ (8). To $[Hf(\eta\text{-}C_5H_5)_2Cl_2]$ (1.0 g, 2.64 mmol) in thf (10 cm^3) was added the di-Grignard reagent (1) (35 cm^3, 0.08 mol dm^{-3}, 2.80 mmol) in thf. After stirring for 1 h and removal of the solvent *in vacuo*, the resulting orange solid was extracted with toluene–diethyl ether (30 cm^3, 1 : 1). The filtrate was concentrated to *ca*. 10 cm^3. Addition of diethyl ether (5 cm^3) and cooling afforded two crops of yellow crystals of *complex* (8) (0.41 g, 38%).

$[\{Ti(CH_2C_6H_4CH_2\text{-}o)_2(thf)\}_n]$ (9). To a cooled (−78 °C) solution of the di-Grignard reagent (1) (100 cm^3, 0.07 mol dm^{-3}, 7.0 mmol) in the dark, was added a solution of $TiCl_4$ (0.39 cm^3, 3.55 mmol) in n-hexane (10 cm^3). An immediate reaction occurred to give a black mixture. On completion of the addition (20 min) the mixture was warmed to 0 °C, stirred for a further 1 h, and filtered. The final residue was then washed with thf and dried *in vacuo* to give *complex* (9) as a dark solid (0.28 g, 24%).

[{$Zr(CH_2C_6H_4CH_2$-*o*$)_2$(thf)}$_n$] (10). To a stirred suspension of finely powdered, freshly sublimed $ZrCl_4$ (0.29 g, 1.23 mmol) in thf (10 cm^3) at −40 °C, was added the di-Grignard reagent (1) (35 cm^3, 0.07 mol dm^{-3}, 2.45 mmol). After 1 h at −40 °C the mixture was stirred at −10 °C for 4 h and then at 0 °C for 2 h. The mixture was filtered and the residue washed repeatedly with thf, and finally dried *in vacuo* to give yellow *complex* (10) (0.16 g, 34%).

[{$Hf(CH_2C_6H_4CH_2$-*o*$)_2$(thf)}$_n$] (11). A solution of the di-Grignard reagent (1) (63 cm^3, 0.073 mol dm^{-3}, 4.6 mmol) was evaporated and dried under high vacuum. The resulting solid was suspended in diethyl ether (50 cm^3) and to the cooled (−20 °C), stirred suspension, finely powdered $HfCl_4$ (0.75 g, 2.3 mmol) was added. After 4 h at −20 °C and then 4 h at 0 °C the mixture was filtered. The filtrate did not afford tractable products, nor did a toluene or dichloromethane extraction of the residue. Washing of the residue with thf left a pale yellow solid, which was dried and identified as *complex* (11) (0.32 g, 30%).

[Hf{η-$C_5H_4(SiMe_3)$}$_2${$(CO)_2(CH_2)_2C_6H_4$}] (12a). An n-pentane solution (15 cm^3) of (4) (0.63 g) was freeze-degassed and then stirred at room temperature under 1 atm of carbon monoxide. The yellow solution became cloudy and colourless microcrystals were slowly precipitated. After 12 h, the crystals were collected by filtration, washed with two portions of n-pentane (5 cm^3), and dried to give *complex* (12a) (0.47 g, 65%).

In a similar manner a sample was prepared using ^{13}C-enriched carbon monoxide. The i.r. spectra of the two compounds were identical, except in the 1 500—1 600 and 1 200—1 280 cm^{-1} regions.

Infrared Spectra (CH *Regions*) *of Complexes* (2)—(12).—I.r. bands assignable to hydrogen out-of-plane deformations of the C_6H_4 fragment of the *o*-xylidene ligand in the expected region,[34] between 740 and 755 cm^{-1}, were observed. Complexes (6)—(8) displayed bands due to the cyclopentadienyl ring [35] at 1 014—1 022 and 805—820 cm^{-1} while complexes (2)—(5) and (12a) had an additional band at 1 402—1 408 cm^{-1} whilst the cyclopentadienyl ring band was shifted to higher wavenumber, 1 040—1 047 cm^{-1}. Complexes (2)—(5) and (12a) also showed CH deformation modes from the trimethylsilyl group at 1 245—1 250 and 830—836 cm^{-1}.

Reaction of [Ti(η-$C_5H_5)_2${*o*-$(CH_2)_2C_6H_4$}]·0.5OEt_2 (6a) *with Carbon Monoxide*.—A toluene solution of complex (6a) was stirred under 1 atm of carbon monoxide at room temperature, and rapidly turned brown. This solution was used to obtain a solution i.r. spectrum of the reaction products.

A solution of complex (6a) in [$^2H_6$]benzene was allowed to react with carbon monoxide in a similar manner to that above and the ^1H n.m.r. spectrum of the resulting solution was obtained. Thereafter the solvent was evaporated and the resulting solid extracted with diethyl ether (10 cm^3). The solution was then filtered, reduced in volume and used for g.l.c. (5 ft column, 5% OV 17 silicone oil, 200 °C).

Reaction of [Ti{η-$C_5H_4(SiMe_3)$}$_2${*o*-$(CH_2)_2C_6H_4$}] (2) *with Carbon Monoxide*.—A solution of complex (2) in n-pentane was stirred under 1 atm of carbon monoxide (30 min) during which time the solution became dark green. The i.r. spectrum of the reaction mixture indicated the presence of indan-2-one and [Ti{η-$C_5H_4(SiMe_3)$}$_2(CO)_2$].

Reaction of [Zr(η-$C_5H_5)_2${*o*-$(CH_2)_2C_6H_4$}] (7) *with Carbon Monoxide*.—A solution of complex (7) in toluene reacted under ambient conditions with carbon monoxide over a period of 0.5 h to give a yellow solution and a slight yellow precipitate. Removal of solvent *in vacuo* followed by repeated careful recrystallisation of the product from dichloromethane yielded two pale yellow products.

E.S.R. Experiments.—The paramagnetic Group 4A metal(III) species were prepared by the dropwise addition of a sodium dihydronaphthylide solution to a freeze-degassed solution of the appropriate metallocene *o*-xylidene precursor in an e.s.r. tube. Addition of the reducing agent was continued until its green colour was not immediately dispersed, whilst it was also ensured that the reactants were thoroughly mixed. Coupling constants were obtained directly from the spectra using field sweep calibration from Frémy's salt, see Table 5.

The e.s.r. spectra of the niobium(IV) metallacycles (5) and [Nb(η-$C_5H_5)_2${*o*-$(CH_2)_2C_6H_4$}] [which was not otherwise characterised but was prepared in a manner similar to that described for complex (5)] were second order, showing an anisotropic hyperfine interaction with the niobium nucleus. Isotropic $a(^{93}Nb)$ and g_{av} values (Table 4) were calculated using the following form [37] of the Breit–Rabi equation,[38] where

$$H_i = -(M_i) + \sqrt{(M_i)^2(A)^2 - 25(A)^2 + (H_0)^2}$$

M_i is the quantum number of the *i*th line, A is the calculated isotropic niobium hyperfine coupling constant, H_i is the transition corresponding to the quantum number M_i, and H_0 is the calculated field for the centre of the spectrum, leading to g_{av}.

X-*Ray Data Collection, Structure Solution, and Refinement*.—The crystal data are summarised in Table 9. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections {2θ ⩾ 50° [(6b), (7), or (8)] or 35° (5)} accurately centred on an Enraf-Nonius CAD-4 diffractometer. Data collection details are illustrated for the zirconium compound (7).

A single crystal of the zirconium compound (7) of dimensions 0.35 × 0.40 × 0.50 mm was sealed in a thin-walled glass capillary under a dinitrogen atmosphere. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation [$\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å]. The diffracted intensities were measured by the ω–2θ scan technique in a manner similar to that described previously.[58] All reflections in one independent octant out to 2θ ⩾ 50° were measured; 970 were considered observed [$I \geqslant 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption (the minimum and maximum transmission factors differed by less than 5%).

Full-matrix least-squares refinement was carried out using the SHELX system of computer programs.* No corrections were made for extinction. Atomic scattering factors for H were taken from ref. 59 while those for all non-hydrogen atoms were taken from Cromer and Waber.[60] The scattering for the metal atom (Ti, Zr, Hf, or Nb) was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[61]

Systematic absences in the zirconium data indicated that the space group was uniquely defined as $P2_12_12_1$. The zirconium atom was located by the inspection of a Patterson map. Subsequent calculation of difference-Fourier maps afforded

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* Other crystallographic programs used on a UNIVAC 1110 include ORTEP (thermal ellipsoid drawings, by C. K. Johnson) and BPL (least-squares planes, by W. E. Hunter).

the location of the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.069$. Conversion to anisotropic thermal parameters and addition of hydrogen atoms at geometry fixed locations led to final values of $R = 0.019$ and $R' = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{\frac{1}{2}} = 0.021$. The largest parameter shift in the final cycle of refinement was 0.03 of its estimated standard deviation. A final difference-Fourier map showed no feature greater than 0.5 e Å^{-3}. The standard deviation of an observation of unit weight was 0.78. Unit weights were used at all stages and unobserved reflections were not included. No systematic variation of $\omega(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Tables 10—13 for the Ti, Zr, Hf, and Nb compounds, respectively.

The Ti (6b) and Hf (8) compounds were found to be isostructural to the Zr compound (7). Data collection for (6b) and (8) was carried out in the manner described for the Zr analogue resulting in 963 observed reflections for the former and 1 189 for the latter. The Hf compound (8) was corrected for absorption using the psi-scan technique described by Churchill and Hollander.[62] The final parameters for the non-hydrogen atoms of the Zr structure were used for the Ti and Hf analogues. Refinement was carried out in the manner described for the Zr compound resulting in final agreement factors of $R = 0.026$ and 0.024, $R' = 0.027$ and 0.027 for Ti and Hf, respectively. The standard deviation of an observation of unit weight was 0.62 and 1.74 for Ti and Hf, respectively.

Acknowledgements

We thank the S.E.R.C. for the award of studentships (to G. S. B. and T. R. M.) and other support, B.P. Chemicals Ltd, Hull and Dr. H. Green for a CASE collaboration (to G. S. B.), and the U.S. National Science Foundation for partial support (of J. L. A.). We also gratefully acknowledge the collaboration of Dr. C. R. C. Milne in preliminary experiments with the Nb^{IV} complexes.

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Received 14*th March* 1983; *Paper* 3/396