# Chemistry of o-Xylidene–Metal Complexes. Part 4.[1] Stereospecific Synthesis of the Early Transition Metal meso-Metallacycles

## [M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] (M = Ti, Zr, Hf, or Nb), their Reversible One-electron Reduction (M = Ti, Zr, Hf, or Nb) and Oxidation (M = Nb) ; and the X-Ray Crystal Structure of the Zirconium Complex *

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The reaction of the organodilithium reagent [{o-C₆H₄(CHSiMe₃)₂}{Li(tmen)}₂] (tmen = Me₂NCH₂CH₂NMe₂) and the appropriate metallocene(ɪv) chloride [M(η-C₅H₅)₂Cl₂] in OEt₂ at ca. 35 °C yields the corresponding crystalline, thermally stable, stereospecifically pure meso-metallaindane

meso-[M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] [M = Ti (2), Zr (3), Hf (4), or Nb (5)] ; by-products in two of these reactions are [{Ti(η-C₅H₅)₂Cl}₂] or the binuclear zirconium compound (6) formulated as meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(μ-σ: η-C₅H₄)₂Zr(η-C₅H₅)₂]. Compounds (2)—(5) are sublimable at ca. 140 °C (10⁻³ Torr), and on pyrolysis afford o-C₆H₄(CH₂SiMe₃)₂; they are reasonably air-stable and inert to CO under ambient conditions. Compound (6) is also accessible from (3) in OEt₂ and successively Li(tmen)Buⁿ in n-C₆H₁₄ and [Zr(η-C₅H₅)₂Cl₂]. Assignment of the meso (rather than rac) diastereoisomeric configuration for complexes (2)—(4) rests on their n.m.r. spectra and for (3) on X-ray data. E.s.r. data on complex (5), or the Na(C₁₀H₈)–tetrahydrofuran reduction products of each of (2)—(4), are consistent with each being a $d^1$ complex. The electrochemical reduction [$-E_{\frac{1}{2}}^{red}$ = 1.46 (Ti), 2.02 (Zr), or 2.26 V (Hf)] of each of the complexes (2)—(4) is pseudo-reversible, but the anions

[M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂]⁻ tend to lose C₅H₅⁻. The niobium complex (5) undergoes reversible one-electron oxidation ($E_{\frac{1}{2}}^{ox}$ = −0.47 V) or reduction ($-E_{\frac{1}{2}}^{red}$ = 1.63 V). The X-ray structure of the title metallaindane (3) shows pseudo-tetrahedral co-ordination of Zr with a centroid–Zr–centroid' angle of 125.1° and bite angle Cᵅ–Zr–Cᵅ' of 80.2(2)°, with ⟨Zr–Cᵅ, Cᵅ'⟩ 2.305(4) and ⟨Zr · · · Cᵝ,Cᵝ'⟩ 2.71(1) Å; hence the o-C₆H₄{CH(SiMe₃)}₂–metal bonding is best described as intermediate between that appropriate for metalla(ɪv)cyclic and an η⁴-5,6-dimethylenecyclohexa-1,3-diene–metal(ɪɪ) structure; consistent also is the fold angle, Φ, of 66.7° (Φ being the dihedral angle between the ZrCᵅCᵅ' plane and and the C₈ extension of the aromatic plane).

Parts 1—3 of the present series dealt with aspects of the complex chemistry of the o-xylenediyl ligand o-C₆H₄(CH₂⁻)₂.[1-3] All the crystalline complexes there reported (of Mg¹¹,[2] Ti¹ᵛ,[3] Zr¹ᵛ,[3] Hf¹ᵛ,[3] Nb¹ᵛ,[3] Wᵛ,[1] Wᵛ¹,[1] and Pt¹¹ [2]) were prepared from the di-Grignard reagent obtained from o-bis(chloromethyl)-benzene, o-C₆H₄(CH₂MgCl)₂, or its chloride-free derivatives [{Mg(μ-CH₂C₆H₄CH₂-o)(thf)ₙ}ₘ] (n = 2 with m = 3, or n = 1 with m unknown; thf = tetrahydrofuran);[2] the corresponding dilithium reagent proved to be inaccessible.

Apart from the dilithium complex [{o-C₆H₄(CHSiMe₃)₂}{Li(tmen)}₂] (1) (tmen = Me₂NCH₂CH₂NMe₂), as will be described in Part 5,[4] this paper is the first in the series to be concerned with [α,α'-bis(trimethylsilyl)-o-xylenediyl]metal complexes. We report the d⁰(Ti, Zr, or Hf) and d¹ (Nb) meso-1,3-bis(trimethylsilyl)-2-metalla(ɪv)indanes (2)—(5) (Scheme), and specifically: (i) their preparation; (ii) their electrochemical

behaviour, studied in conjunction with chemical reduction and e.s.r. experiments; (iii) the conversion of the acidic Zr complex (3) into a binuclear derivative (6); and (iv) molecular structural data based on solution n.m.r. [complexes (2)—(4) and (6)] and e.s.r. spectroscopy, and single-crystal X-ray diffraction analysis for complex (3). Aspects of (i) and (ii) [but not for the Nb complex (5)] have already been briefly communicated.[5] {As mentioned in earlier parts, we use the umbrella form ' o-xylidenemetal complex ' to describe, without prejudice as to bonding, all o-C₆H₄(CHR)₂–metal complexes in which the organic ligand binds in (a) a bridging or (b) a chelating mode; as for (b), this may be (i) in a bis(sigma) fashion [e.g., complexes (8), derived from the o-xylenediyl ligand (7)], (ii) in an η⁴ manner [as in (9)], or (iii) in some intermediate manner.}

The only other studies of [α,α'-bis(trimethylsilyl)-o-xylenediyl]metal complexes of which we are aware concern the complexes [{Snᴵᴵ[meso-CH(SiMe₃)C₆H₄CHSiMe₃-o]}₄]

(ref. 6), [Snᴵᵛ{meso-CH(SiMe₃)C₆H₄CHSiMe₃-o}₂] (ref. 6),

[Ti{meso-CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)Cl] (ref. 7),

and trans-[PtCl₂{meso-P(Ph)CH(SiMe₃)C₆H₄CHSiMe₃-o}₂],[8a] for each of which single-crystal X-ray structural characterisation is available.

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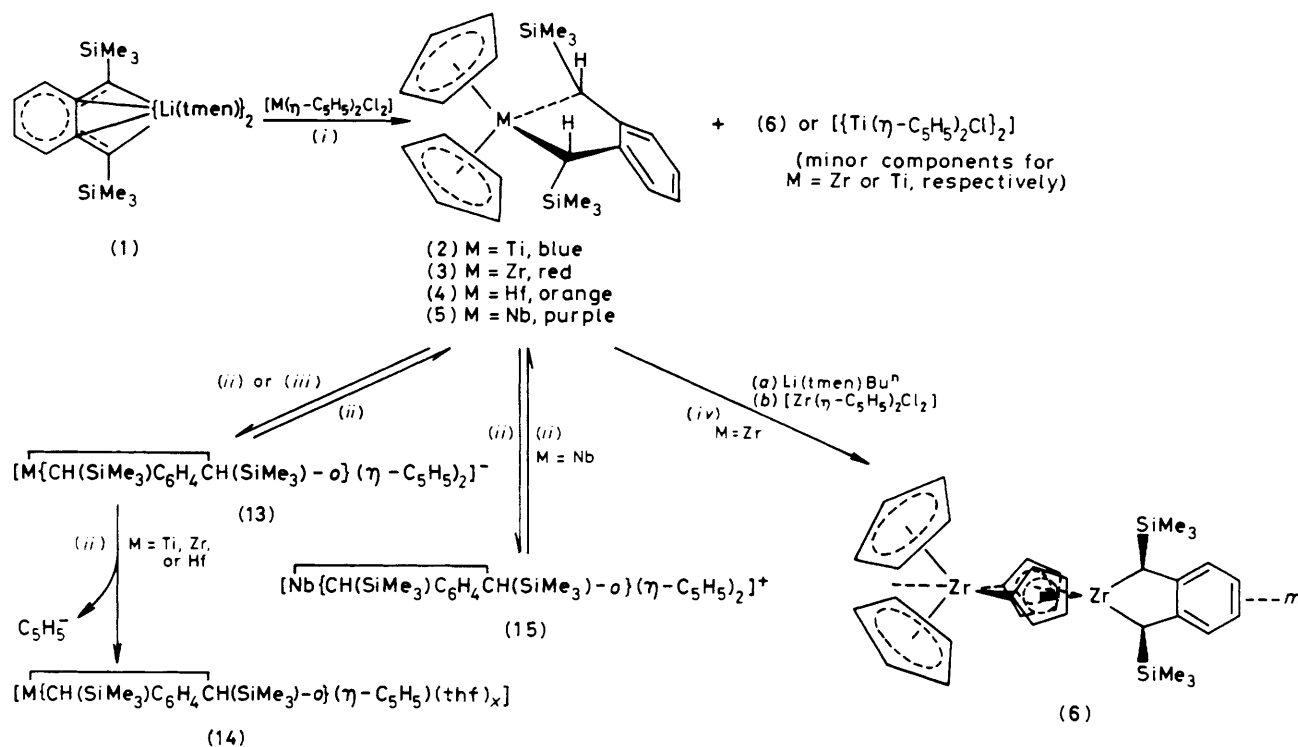
**Scheme.** Synthesis of the *meso*-1,3-bis(trimethylsilyl)-2-metalla(iv)indanes [M{CH(SiMe₃)C₆H₄CHSiMe₃-*o*}(η-C₅H₅)₂] (2)—(5), and some of their properties. Reaction conditions: (*i*) OEt₂, 30 °C, and subsequent removal of solvent and crystallisation from n-C₅H₁₂ at −40 °C; (*ii*) cyclic voltammetry in [NBuⁿ₄][BF₄] (0.2 mol dm⁻³) in thf at a Pt electrode; (*iii*) Na(C₁₀H₈) (1 mol equiv.) in thf, 20 °C; (*iv*) first OEt₂, 0 °C, LiBuⁿ (2 mol equiv.) in n-C₆H₁₄, then tmen (2 mol equiv.), and finally [Zr(η-C₅H₅)₂Cl₂]

## Results and Discussion

In attempting to prepare metallacycles (8) using the organo-dilithium reagent (1) and an appropriate dichlorometal complex [MCl₂Lₙ] (Lₙ represents the sum of ligands other than 2Cl⁻ surrounding the metal, M), the choice of reaction solvent and temperature may be critical in order to attenuate reduction of [MCl₂Lₙ]. The potential of the organolithium compound (1) to function as a reducing agent, possibly via formation of a substituted 5,6-dimethylenecyclohexa-1,3-diene

In the context of the structural chemistry of metal complexes derived from the ligand (7) similar versatility as to bonding modes must be considered as for the parent un-substituted *o*-xylenediyl *o*-C₆H₄(CH₂⁻)₂ which may function as a chelating or a bridging ligand;²,³ and within the former category, as a dicarbanion [as in (8)], the neutral 5,6-di-methylenecyclohexa-1,3-diene [as in (9)], or in some intermediate fashion. Add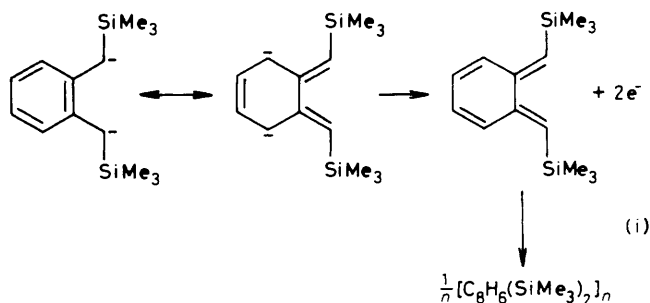itionally, however, the presence of chiral α- and α'-carbon atoms introduces the prospect of alternative (*meso* or *rac*) diastereoisomers being in principle available for a metal complex containing one such ligand; and hence offers a probe for determining the stereoselectivity of appropriate reactions.

Other features of the ligand (7) which we considered might be of interest included the likelihood that its metal complexes compared with unsubstituted *o*-xylidene analogues might have enhanced (*i*) kinetic stability by virtue of the greater shielding afforded by the SiMe₃ groups of the metal centre and (*ii*) hydrocarbon solubility. Complexes derived from the rather bulky ligand (7) probably will have a relatively modest upper limit for metal co-ordination number or oxidation state, and a preference for *endo* SiMe₃ groups [see (2)—(5) or (9)].

[equation (i)], was demonstrated in Part 1.² Thus, [Pt{P(Ph)₂CH₂CH₂P(Ph)₂}₂] was isolated in modest yield from a reaction of (1) and [PtCl₂{P(Ph)₂CH₂CH₂P(Ph)₂}] in thf at −78 °C. Another example relates to the reduction of tin(iv) chloride to a tin(ii) product during the reaction of (1) with SnCl₄ in OEt₂ at −78 °C, but in that case the reduced species

**Table 1.** Yields, analytical and some other physical characteristics of the metallaindanes (2)—(6)

| Compound | Colour | Analysis (%) | | M.p.[b] (°C) | Yield (%) |
| | | C | H | | |
| --- | --- | --- | --- | --- | --- |
| (2) meso-[Ti{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | Blue | 67.4 (67.5) | 7.8 (8.0) | 128—129 | 55 |
| (3) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | Red | 61.1 (61.3) | 7.4 (7.3) | 141—142 | 48 |
| (4) meso-[Hf{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | Orange | 51.8 (51.7) | 5.7 (6.2) | 144—146 | 60 |
| (5) meso-[Nb{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | Purple | 60.0 (61.0) | 7.3 (7.3) | 166—167 | 30 |
| (6) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(μ-σ:η-C₅H₄)₂Zr(η-C₅H₅)₂] | Crimson | 58.8 (59.2) | 6.4 (6.2) | Dec. 160 | 22 |

[a] Calculated values are given in parentheses. [b] Argon atmosphere in sealed capillaries and uncorrected.

[{Sn$^{II}$[meso-CH(SiMe₃)C₆H₄CHSiMe₃-o]₄}], was only a minor product; [6] for the same reaction at 30 °C the exclusive product was [Sn$^{IV}${meso-CH(SiMe₃)C₆H₄CHSiMe₃-o}₂], a spirocyclic complex.

Optimum conditions for the formation of the metallaindanes (2)—(5) [step (i) in Scheme] included the use of diethyl ether as solvent, and a reaction temperature close to 35 °C. In each case a quantitative precipitation of lithium chloride was observed. [For reactions involving various organolithium-tmen complexes in OEt₂, we note that precipitation of LiCl occurs only above 20 °C.] During the synthesis of the blue titanium complex (2), reduction was not fully suppressed, as demonstrated by formation of [{Ti(η-C₅H₅)₂Cl}₂].

The magnesium reagents which we have previously used as sources of the o-xylenediyl ligand, namely o-C₆H₄(CH₂-MgCl)₂ or [{Mg(μ-CH₂C₆H₄CH₂-o)(thf)$_n$}$_m$],[2] are less reducing than the dilithium reagent (1), with reduction detected only in a single reaction, in the alkylation of WOCl₄. There reduction precedes alkylation with initial formation of chloro-oxotungstate(v) complexes and 5,6-dimethylenecyclohexa-1,3-diene polymers [cf. equation (i)].[1]

Using the dilithium reagent (1) in thf at 20 °C we have observed reduction of HgCl₂ (to mercury metal). Reaction of (1) with [Zr(η-C₅H₅)₂Cl₂] in thf at −78 °C for 3 h gave a green, thf-insoluble, pyrophoric powder, which is presumed to contain a reduced hydrocarbylzirconium complex. The same reactants in OEt₂ at −78 °C did not give a green precipitate, but the monomeric metallacycle (3) was not isolated; the only identified product was a binuclear complex (in ca. 20% yield), formulated as (6) (Scheme).

By far the most difficult, and least successful, synthesis was that of the niobium complex (5). Yields were much lower than for the isoleptic * Group 4A compounds, and the isolation of the analytically pure purple complex (5) free from a white impurity proved difficult. A previously noted preference for alkylations of [Nb(η-C₅H₅)₂Cl₂] with an alkyl-lithium was the use of a non-co-ordinating solvent.[8b] However, given that the strong donor tmen is inevitably present during our synthesis [step (i) in Scheme, M = Nb] of complex (5), the low yield (Table 1) is perhaps not unexpected. In contrast, the use of a Grignard reagent is often less sensitive to environment, as demonstrated by the high-yield preparation of the related

complexes [Nb(CH₂C₆H₄CH₂-o)(η-C₅H₄R)₂] (R = H or SiMe₃), using the di-Grignard reagent.[3]

Stereospecificity in metallacycle formation [complexes (3)—(5)] was invariably observed. The meso isomer is the expected kinetically controlled product, on the basis of the planar structure of the o-C₆H₄C₂ moiety in [{o-C₆H₄(CH-SiMe₃)₂}{Li(tmen)}₂] (1).[4] For derived metallocenes [(8), L$_n$ = (η-C₅H₅)₂], formation of a rac isomer may in any case be thermodynamically disfavoured by virtue of the likely powerful non-bonding interactions between the cyclopentadienyl ligands and the bulky SiMe₃ groups. Assignment of meso configuration (see Scheme) to the d⁰ Group 4A metal complexes (2)—(4) is based on n.m.r. data. Both ¹H and ¹³C spectra show the magnetic equivalence of the Si(CH₃)₃ and C$^α$H and C$^{α'}$H groups, but non-equivalence of the cyclopentadienyl ligands, consistent with the C$^α$H and C$^{α'}$H protons being directed towards one η-C₅H₅⁻ and the ligand aromatic plane folded towards the other; for data, see Tables 2 and 3.

Further evidence for the meso isomer comes from an X-ray structure determination of the red zirconium complex (3) (see below); and i.r. spectra show that bands attributable to η-C₅H₅⁻ ligands, at 3 100, 1 430, 1 005, and 820 cm⁻¹,[1,10] each appear as doublets. Designation of the meso configuration for the niobium(IV) complex (5) rests solely on i.r. data, but is considered to be reasonable, partly by analogy with available results on complexes of P$^{III}$, Ti$^{IV}$, Zr$^{IV}$, Hf$^{IV}$, Sn$^{II}$, and Sn$^{IV}$, and also for geometrical considerations.

The presence of bulky SiMe₃ groups at C$^α$ and C$^{α'}$ in the o-C₆H₄{CH(SiMe₃)}₂ moiety of complexes (2)—(5) has a pronounced effect on their stability, reactivity, and structure. The complexes are remarkably thermally stable, being sublimable in vacuo at 140 °C (10⁻³ Torr), with minimal decomposition, and this offers a useful further purification procedure. Under similar conditions the unsubstituted analogues [M(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂] undergo substantial decomposition, to release o-xylene.[3] In the present compounds (2)—(5), pyrolysis to yield o-bis(trimethylsilylmethyl)benzene occurs only at temperatures in excess of 180 °C. That the SiMe₃ groups offer enhanced kinetic protection to the metal centre is evident also by (i) their relative air-insensitivity (several minutes) compared to the simple parent Group 4A or Nb metallaindanes (seconds), and (ii) the lack of CO insertion for the Group 4A metal complexes (2)—(4) at ambient temperature and pressure in benzene or hexane. As for (ii), this contrasts with the rapid reactions of [M(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂] (M = Ti, Zr, or Hf) under

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* This term refers to two or more metal complexes which have the same type of molecular formula; e.g., the complexes [M(η-C₅H₅)₂Cl₂] (M = Ti, Zr, Hf, Nb, or Mo) are isoleptic (these particular complexes may each also be described as 'heteroleptic,' i.e., of mixed-ligand type).[9]

**Table 2.** Hydrogen-1 n.m.r. chemical shift data [a] for the metallaindanes (2)—(4) and (6), measured in $C_6D_6$

| Compound | $Si(CH_3)_3$ | $C^\alpha H, C^{\alpha'} H$ | $C_6H_4$ | $\eta\text{-}C_5H_5$ | $\sigma:\eta\text{-}C_5H_4$ |
|---|---|---|---|---|---|
| (2) meso-[Ti{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 9.80 (s) | 8.50 (s) | 2.9 (m) | 5.23 (s), 4.46 (s) | |
| (3) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 9.72 (s) | 10.34 (s) | 2.9 (m) | 5.35 (s), 4.36 (s) | |
| (4) meso-[Hf{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 9.73 (s) | 10.22 (s) | 2.9 (m) | 5.26 (s), 4.44 (s) | |
| (6) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(μ-σ:η-C₅H₄)₂Zr(η-C₅H₅)₂] | 9.70 (s) | 10.06 (s) | 3.0 (m) | 4.36 (s) | 4.13 (4 H,[b] m), 4.72 (2 H,[b] m), 5.26 (2 H,[b] m) |

[a] Values (τ) quoted relative to external $SiMe_4 = 10$. [b] These represent integrals.

**Table 3.** Carbon-13 n.m.r. chemical shift data [*] for the metallaindanes (2)—(4) and (6), measured in $C_6D_6$

| Compound | Si-$(CH_3)_3$ | $C^\alpha H,$ $C^{\alpha'} H$ | $C_6H_4$ | $\eta\text{-}C_5H_5$ | $\sigma:\eta\text{-}C_5H_4$ |
|---|---|---|---|---|---|
| (2) meso-[Ti{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 3.1 | 76.6 | 145.7, 124.8, 125.9 | 108.8, 110.6 | |
| (3) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 2.7 | 60.7 | 136.8, 125.0, 129.3 | 107.6, 112.6 | |
| (4) meso-[Hf{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 2.9 | 56.3 | 139.3, 124.5, 127.6 | 106.7, 107.9 | |
| (6) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(μ-σ:η-C₅H₄)₂Zr(η-C₅H₅)₂] | 2.8 | 60.0 | 128.3, 124.2, 127.8 | 110.0 | 111.4, 111.6, 114.6, 115.6, 115.8, 117.4 |

[*] Values (δ/p.p.m.) relative to $SiMe_4 = 0$, calculated from solvent resonances: $C_6D_6 = 128.0$.

similar conditions; *e.g.*, the Hf complex gave two conformers of the bis(σ-acyl) complex [Hf{C(O)CH₂C₆H₄CH₂CO-o}(η-C₅H₅)₂].[3]

In addition to the i.r. bands assigned to the η-cyclopentadienyl ligands, complexes (2)—(5) show others characteristic of the $C_6H_4$ unit of a co-ordinated o-xylenediyl ligand (as described in Part 2 [3]) or of $SiMe_3$ (1 243—1 246 cm⁻¹ and 838—842 cm⁻¹).

Mass spectra of complexes (2)—(5) invariably showed a parent molecular ion with its expected metal isotope pattern; the main peaks were ascribed to $[P - C_8H_6(SiMe_3)_2]^+$ for the Ti (2) and Nb (5) complexes, or $[P - C_8H_8(SiMe_3)_2]^+$ for the Zr (3) and Hf (4) analogues, with the corresponding organic fragment peaks at $[C_8H_6(SiMe_3)_2]^+$ or $[C_8H_8(SiMe_3)_2]^+$, respectively. This difference in fragmentation behaviour may reflect the readier availability of lower oxidation states for Ti and Nb thus allowing for reductive elimination. On the other hand, complexes (3) and (4) may fragment by a pathway involving release of the o-xylenediyl ligand as a result of hydrogen abstraction from the C₅H₅ groups. Against this differentiation, we note, however, that all four of the complexes undergo thermal decomposition with formation of the o-xylene derivative, $C_8H_8(SiMe_3)_2$.

We now turn to the question of the nature of the minor product (6), from the reaction of [Zr(η-C₅H₅)₂Cl₂] and the organodilithium reagent (1) [reaction (i) of Scheme]. [It is interesting that in the synthesis of the Group 4A metallaindanes (2)—(4), only for the hafnium complex is there evidently no side-reaction; for the titanium case, formation of chlorobis(η-cyclopentadienyl)titanium(III) appears to be unavoidable, whereas for Zr the by-product is complex (6).] N.m.r. data (Tables 2 and 3) are suggestive of a bimetallic structure of overall symmetry *m*, consistent with the proposed formulation of (6). ¹H N.m.r. spectra show (i) equivalence of $SiMe_3$ groups and $C^\alpha H$ and $C^{\alpha'} H$ protons, (ii) the presence of

σ:η-C₅H₄⁻ ligands,[11] (iii) symmetrically bound η-cyclopentadienyl ligands of one type, and (iv) integration consistent with structure (6). The ¹³C n.m.r. spectrum is more definitive for a meso-metallacycle showing terminal equivalent η-C₅H₅ groups. Six peaks are expected for the bridging ligand carbon atoms of two non-equivalent ligands but with each half of one ligand related to the other half by a mirror plane [see (6), Scheme].

The reaction pathway leading to the bimetallic complex (6) may involve a metalladicarbanion intermediate, (11), as depicted in equation (ii). For synthesis of the zirconacycle (3)



(11)
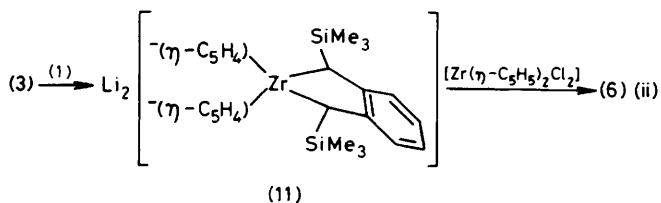
the optimum conditions dictate that there be an excess of the alkylating agent (1) in solution during the course of the reaction, [Zr(η-C₅H₅)₂Cl₂] being only sparingly soluble in $OEt_2$. The proposed sequence of equation (ii) is supported by an alternative synthesis of complex (6), albeit in modest yield (*ca.* 30%) and without isolation of the pure solid. This involved the metallation of complex (3), using Li(tmen)Buⁿ, followed by addition of [Zr(η-C₅H₅)₂Cl₂] [reaction (iv) of Scheme].

While metallation of the co-ordinated cyclopentadienyl ligand, using an organolithium–tertiary amine reagent, is well known, particularly in the case of ferrocene,[12] the formation of the presently proposed dianion intermediate (11) would represent a new class of reaction for a bent sandwich

**Table 4.** E.s.r. [for the $d^1$ Nb complex (5) and the Na($C_{10}H_8$) reduction products of complexes (2)—(4)] and electrochemical data, measured in thf at 20 °C, for the metallaindanes (2)—(5)

| Compound | $g_{av.}$ [a] | $a(M)/G$ [a,b] | $-E_{\frac{1}{2}}$ [c] Reduction | $-E_{\frac{1}{2}}$ [c] Oxidation |
|---|---|---|---|---|
| (2) meso-[Ti{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 1.982 | 10.0 | 1.46 | — |
| (3) meso-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 1.979 | 18.6 | 2.02 | — |
| (4) meso-[Hf{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 1.943 | d | 2.26 | — |
| (5) meso-[Nb{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] | 1.999 [e] | 77.5 [e] | 1.63 | 0.47 |

[a] These refer to complexes (5) or [M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂]⁻ (13) obtained from complexes (2)—(4) (M = Ti, Zr, or Hf). [b] The spin-active metal nuclei (with their spin and natural abundance) are: ⁴⁷Ti, $I = \frac{5}{2}$, 7.3%; ⁴⁹Ti, $I = \frac{7}{2}$, 5.5%; ⁹¹Zr, $I = \frac{5}{2}$, 11.2%; ¹⁷⁹Hf, $I = \frac{9}{2}$, 13.7%; ⁹³Nb, $I = \frac{9}{2}$, 100%. [c] $E_{\frac{1}{2}}$ versus s.c.e., measured in thf, using [NBuⁿ₄][BF₄] (0.2 mol dm⁻³) as a supporting electrolyte at a Pt electrode. [d] Not observed. [e] In toluene.

substrate. For the $d^0$ complex ions [Nb(η-C₅H₅)₂R₂]⁺ the acidities of the CᵅH and Cᵅ′H protons are evidently greater than those of the cyclopentadienyl ligands, as demonstrated by the reaction with Li[N(SiMe₃)₂] to yield ylide–metal complexes, such as [Nb{CH(SiMe₃)}(CH₂SiMe₃)(η-C₅H₅)₂] for the case of R = CH₂SiMe₃.[13] Proton abstraction from co-ordinated η-C₅H₅⁻ ligands in the present case may be a consequence of steric shielding of the CᵅH or Cᵅ′H protons, geometrical constraints (the alternative ylide product would be [Zr{C(SiMe₃)(C₆H₄CH(SiMe₃)-o}(C₅H₅)₂]), and/or the nature of the metal o-xylenediyl interaction.

E.s.r. data for the $d^1$ species are presented in Table 4. Complexes formulated as Group 4A metallates(III) were derived from the $d^0$ metallacycles (2)—(4) by reduction using 1 mol equiv. of sodium dihydronaphthylide, Na(C₁₀H₈), in thf [reaction (iii) in Scheme]. For none of these products, nor for the niobacycle (5), was hydrogen hyperfine coupling observed, but, except for the hafnium compound, characteristic metal hyperfine couplings were found (⁴⁷Ti, $I = \frac{5}{2}$, 7.3%; ⁴⁹Ti, $I = \frac{7}{2}$, 5.5%; ⁹¹Zr, $I = \frac{5}{2}$, 11.2%; ⁹³Nb, $I = \frac{9}{2}$, 100%). The absence of ¹H coupling is normal for $d^1$ niobocene(IV) and hafnocene(III) alkyl complexes,[9,14] but unexpected for titanium(III) and zirconium(III) analogues.[14,15]

The $g_{av.}$ and $a(^{93}Nb)$ values for complex (5) of 1.999 and 77.5 G, respectively, are similar to those of the unsubstituted o-xylenediyl-niobacycles: [Nb(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂], $g = 1.996$ and $a = 76.3$ G, and [Nb(CH₂C₆H₄CH₂-o)(η-C₅H₄SiMe₃)₂], $g = 1.999$ and $a = 77.2$ G.[3] The isotropic coupling constant was calculated from the second-order spectrum using the Breit–Rabi equations.[14,16]

It has been proposed[17] that the magnitude of $g_{av.}$ and $a(M)$ is related to the size of the X–M–X angle for $d^1$ complexes of the type [MX₂(η-C₅H₅)₂]; higher $g_{av.}$ and lower $a$ values correlate with greater metal character of the h.o.m.o. $a_1$ orbital, and a lower X–M–X angle.[3,9] In [Nb(CH₂C₆H₄CH₂-o)(η-C₅H₄SiMe₃)₂], this angle is 72.5°.[3] In view of the similar e.s.r. data for this complex and its bis(η-cyclopentadienyl) analogue, as well as for complex (5), and the likelihood of a fixed o-xylenediyl bite angle in Nbᴵⱽ complexes, Cᵅ–Nb–Cᵅ′ is expected to be similar in these niobium metallacycles, but the SiMe₃ substituents may perturb the o-xylenediyl–metal interaction :as is the case when comparing (see below) the zirconium complex (3) and its silyl-free analogue, complex [Zr(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂] (10)}. In the closely related [Nb(CH₂C₆H₅)₂(η-C₅H₅)₂], although the $g$ value is similar at

1.996, the $a$ value is higher at 87.6 G, correlating with the larger value of CH₂–Nb–CH₂, 79.0(4)°.[9]

Reduction of the Group 4A metallaindanes (2)—(4) by Na(C₁₀H₈) at ambient temperature in thf shows the presence of a $d^1$ species in each case, stable for several minutes (Ti), indefinitely (Zr), or days (Hf), respectively. All attempts to isolate a $d^1$ complex for the most stable of these species, that of reduced (3), were unsuccessful. For example, reduction in thf followed by removal of solvent in vacuo, subsequent hexane washing to remove naphthalene, and redissolving of the purple microcrystalline residue in degassed thf, gave, in addition to the e.s.r. parameters ascribed to the complex [Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂]⁻ (13; M = Zr) (Table 4), a singlet ($g_{av.}$ = 1.992) flanked by isotopic zirconium hyperfine coupling peaks with $a(^{91}Zr) = 12.5$ G.

The chemistry of zirconocene(III) compounds is still not well defined and, apart from the results of this investigation, analogous hafnium chemistry is barely chartered,[18] being restricted to a complex formulated as (12; M = Hf).[3] In an attempt to clarify the nature of the $d^1$ complexes obtained from complexes (2)—(4), their electrochemical reduction was examined. Each of the Group 4A metallaindanes (2)—(4) is reversibly reduced, with $-E_{\frac{1}{2}}^{red}$ values of 1.46, 2.02, and 2.26 V versus a saturated calomel electrode (s.c.e.), respectively. The ease of Mᴵⱽ ⟶ Mᴵᴵᴵ reduction is thus Ti ⪢ Zr > Hf, and for Ti and Zr parallels the trend observed for the reversible reductions [M(η-C₅H₅)₂Cl₂] ⇌ [M(η-C₅H₅)₂Cl₂]⁻ ($E_{\frac{1}{2}}^{red}$: M = Ti, −0.75; M = Zr, −1.70 V).[14] However, the present results are the first not only for metallocene(IV) hydrocarbyls but also for a complete isoleptic series of Group 4A metal complexes.

In the cyclic voltammograms, the ratios $i_p^{ox} : i_p^{red}$ of the anodic to cathodic peaks were close to unity and hence indicative of a relatively stable generated anion [M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂]⁻ (13), with $t_{\frac{1}{2}}$ > 10 s, whereas the peak current functions $i_p^{red}/v^{\frac{1}{2}}$ suggest their lifetimes might be shorter than this. Also the experiments cannot be considered as providing evidence for a rigorously reversible one-electron process, because the separation of the peaks was greater than theoretical (59 mV), with magnitude dependent upon the scan rate, v. In every case there was a peak in the reverse scan corresponding to oxidation of the free cyclopentadienyl anion,[19] which suggests that the reduced species are unstable with respect to loss of C₅H₅⁻ and that the e.s.r.-detected species may be not of the metallate(III) anion (13) but of the neutral complex [M{CH(SiMe₃)C₆H₄CHSiMe₃-

$$\left[(\eta\text{-}C_5H_5)_n M(thf)_x \overbrace{\phantom{xxxx}}^{\phantom{x}}\middle|\underset{Na^+\ \bar{C}H_2}{\phantom{xx}}\right]^{(2-n)+}$$
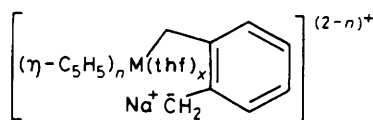
(12) ( n = 1 or 2 )

o}(η-C$_5$H$_5$)(thf)$_x$] (14) (see Scheme). (The o-xylenediyl ligand could in principle change to an η$^4$ mode, into the neutral 5,6-dimethylenecyclohexa-1,3-diene, for such a transformation.) It is unlikely that the supporting electrolyte [NBu$^n$$_4$][BF$_4$] is implicated in the decomposition, because in the case of Ti (2) or Zr (3) metallaindanes, the e.s.r. spectral features were unperturbed by the presence of the tetrafluoroborate when the chemical reduction at −78 °C was followed by immediate recording of the spectrum; a similar experiment involving the Hf complex (4) failed to provide an e.s.r. signal. Addition of PPh$_3$ to a solution of the reduced species from (2) or (3) had no effect, [31]P hyperfine coupling not being detected and the e.s.r. spectrum being unchanged. {Zr[III] intermediates of the type [Zr(η-C$_5$H$_5$)$_2$(PPh$_2$Me)X] (X = Cl or alkyl), showing Zr-P coupling in the e.s.r. spectra, have recently been reported.[20,21]} This may indicate that the radical anion (13) is a stable species and the detection of free C$_5$H$_5$$^-$ is a consequence of the electrochemical reaction conditions.

The present results leading to complexes (13) and (14) (M = Ti, Zr, or Hf) show a difference from the observations on the reaction of [M(CH$_2$C$_6$H$_4$CH$_2$-o)(η-C$_5$H$_5$)$_2$] (M = Ti, Zr, or Hf) with Na(C$_{10}$H$_8$)-thf;[3] the products showed e.s.r. coupling to two α-hydrogen atoms (excluding M = Hf) and hence the assignment of structures (12). The absence of hydrogen hyperfine coupling in the present series may be a consequence of η$^4$-bonding to M, since coupling to hydrogen atoms of polyhapto-ligands is not usually observed.

The lighter Group 4A metallocene(IV) alkyls, [M(η-C$_5$H$_5$)$_2$R$_2$] (M = Ti or Zr), have been observed to undergo irreversible one-electron reduction, followed by loss of C$_5$H$_5$$^-$.[14,19] The metallacycles of titanium (2) and zirconium (3) may be behaving in a similar manner but with an extended lifetime of the radical anion (13) prior to loss of C$_5$H$_5$$^-$. The only other zirconocene(IV) alkyl complex which approaches a reversible electrochemical reduction at a platinum electrode is [Zr{CH(SiMe$_3$)C$_6$H$_4$Me-o}(η-C$_5$H$_5$)$_2$Cl].[22] Other complexes of the type [Zr(η-C$_5$H$_5$)$_2$Cl(R)] are irreversibly reduced.[14] Radical anions, [Ti(η-C$_5$H$_5$)$_2$R$_2$]$^-$ (R = CH$_2$SiMe$_3$ or R$_2$ = CH$_2$SiMe$_2$XSiMe$_2$CH$_2$, X = O or CH$_2$; these are clearly metallacycles), have similar half-lives to that of the reduced Ti complex (2), but differ in that hydrogen-hyperfine coupling to C$^α$H or C$^{α'}$H was observed.[15]

Although the $d^1$ complexes [Nb(η-C$_5$H$_5$)$_2$R$_2$] are well known,[9] only a few examples of related niobocene(IV) metallacycles have been reported:[23] [Nb(CH$_2$C$_6$H$_4$CH$_2$-o)(η-C$_5$H$_4$R)$_2$] (R = H or SiMe$_3$),[3] and [Nb{CR=C(R)C(R)=CR}(η-C$_5$H$_5$)$_2$] (R = Ph[24] or CF$_3$[25]).

Electrochemical studies on the niobaindane (5) show reversible one-electron processes both for oxidation, $E_{\frac{1}{2}}$$^{ox.}$ = −0.47 V versus s.c.e., and reduction, $E_{\frac{1}{2}}$$^{red.}$ = −1.63 V versus s.c.e., as illustrated in Figure 1. Features of the cyclic voltammograms were the same as those noted above for the reduction of the isoleptic Group 4A metallacycles (2)—(4), except that no peak was detected corresponding to the oxidation of free C$_5$H$_5$$^-$. The only previously reported electrochemical study of a niobocene(IV) alkyl was that for [Nb(CH$_2$Ph)$_2$(η-C$_5$H$_5$)$_2$], where a similar reversible behaviour was observed ($E_{\frac{1}{2}}$ = −0.62 and −2.08 V versus Ag/Ag$^+$).[26] In



Figure 1. Cyclic voltammogram of [Nb{CH(SiMe$_3$)C$_6$H$_4$CHSiMe$_3$-o}(η-C$_5$H$_5$)$_2$] (5) at a Pt electrode in 0.2 mol dm$^{-3}$ [NBu$^n$$_4$][BF$_4$]-thf as supporting electrolyte; scan rate v = 0.2 V s$^{-1}$; $E_{\frac{1}{2}}$ = −0.47 and −1.63 V versus s.c.e.
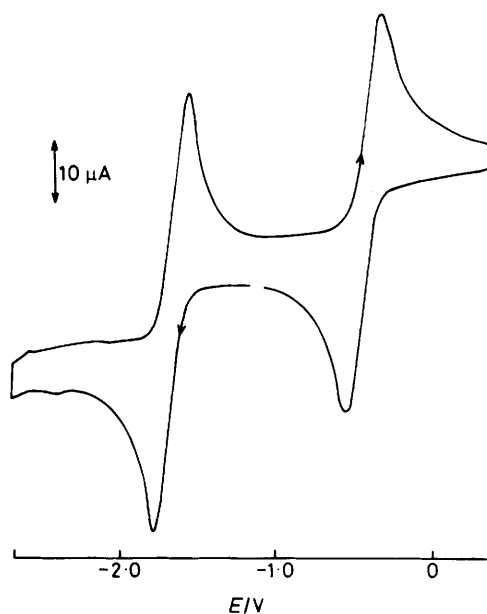
the case of the generation of stable $d^0$ species, further credence as to the stability of [Nb{CH(SiMe$_3$)C$_6$H$_4$CHSiMe$_3$-o}(η-C$_5$H$_5$)$_2$]$^+$ (15) derives from the isolation[9] of crystalline salts, such as [Nb(CH$_2$Ph)$_2$(η-C$_5$H$_5$)$_2$][BF$_4$].

Molecular Structure of meso-[Zr{CH(SiMe$_3$)C$_6$H$_4$CHSiMe$_3$-o}(η-C$_5$H$_5$)$_2$] (3).—A structure determination was undertaken on a benzene solvate of the title zirconium complex (3), prepared by slow cooling of a saturated solution; the specimen crystal was seated in a capillary under an argon atmosphere. Unsolvated crystals, crystallised from hexane, were found to be unsatisfactory. The unit cell (Figure 2) comprises discrete molecules of (3) lying on a mirror plane, plus a benzene molecule, also of m symmetry, the mirror plane passing through the midpoints of two C–C bonds, together with a disordered benzene molecule centred about the origin; the overall stoicheiometry is [Zr{CH(SiMe$_3$)C$_6$H$_4$CHSiMe$_3$-o}-(η-C$_5$H$_5$)$_2$]·1.33C$_6$H$_6$. There are no significant intermolecular contacts.

The mirror plane of complex (3) bisects each cyclopentadienyl ligand and the metallacyclic framework (Figure 3); the cyclopentadienyl ligands are staggered with the unique carbon atoms in an anti conformation. Staggered, eclipsed, and intermediate conformations have been reported for a wide variety of 'bent' zirconium complexes and it has been proposed that crystal-packing forces play a role in determining conformations.[17] Bonding within the metallocene moiety is the usual bis-η$^5$ arrangement, the Zr–C distances being in the range 2.490(5)—2.535(5) Å, mean 2.51 Å. The centroid–Zr–centroid angle (125.0°) is unexceptional,[27] and very similar to that found in the unsubstituted analogue of complex (3); thus, in [Zr(CH$_2$C$_6$H$_4$CH$_2$-o)(η-C$_5$H$_5$)$_2$] (10), the Zr–C(cyclopentadienyl) distances are 2.496(6)—2.544(6) Å, mean 2.52 Å.[3]

We now turn to the o-xylenediyl–metal interactions. The Zr–C$^α$ distance, 2.305(4) Å, is very similar to that in the parent
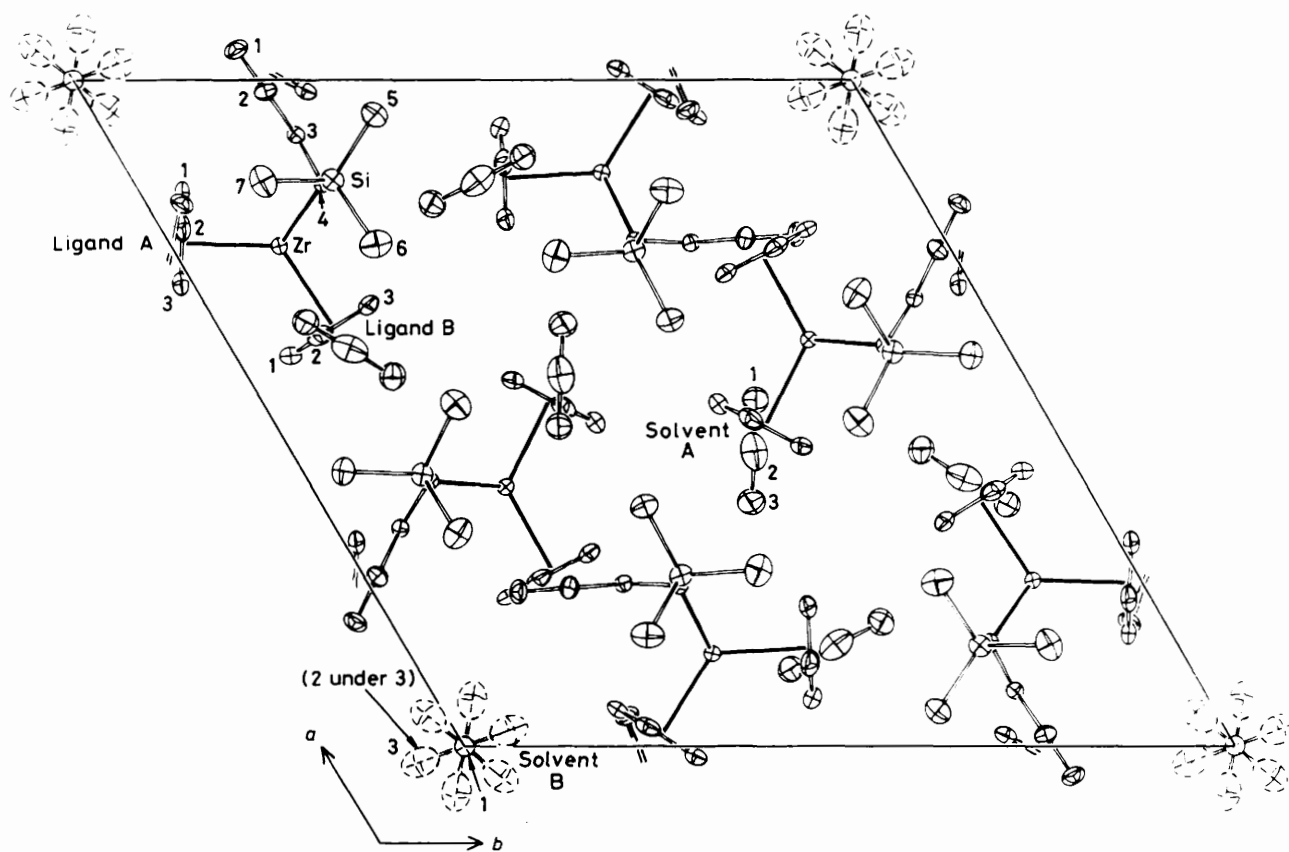
**Figure 2.** Unit-cell contents of *meso*-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-*o*}(η-C₅H₅)₂] (3), projected down *c*, showing non-hydrogen atoms with 20% probability ellipsoids; broken ellipsoids represent electron density regions for a disordered benzene molecule
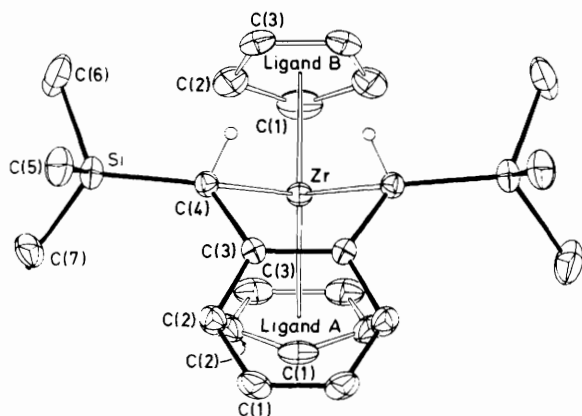


**Figure 3.** Projection of *meso*-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-*o*}(η-C₅H₅)₂] (3), along the centroid–Zr–centroid bisector showing the atom labelling; the only hydrogen atoms included are for C(4) with an arbitrary radius of 0.1 Å

*o*-xylenediyl zirconocene(IV) complex (10),[3] 2.301(6) and 2.298(6) Å. Other Zr–C($sp^3$) distances in the literature range from 2.280(2) Å in [Zr(CH₂SiMe₃)₂(η-C₅H₅)₂] [28] to 2.327(3) Å in the sterically crowded molecule [Zr{CH(SiMe₃)₂}(η-C₅H₄SiMe₃)₂Cl].[29] The presence of trimethylsilyl substituents at C$^\alpha$ in a *meso* disposition produces considerable distortion of the *o*-xylenediyl–metal interaction relative to the unsubstituted complex, (10).[3] The most pronounced effect is the

increase in the *o*-xylenediyl fold angle, Φ. The latter is defined as the dihedral angle between ZrC$^\alpha$C$^{\alpha'}$ and the extension of the aromatic plane, and is 66.7° in the title complex (3), compared with 53.1° in (10).[3] This difference possibly originates from a minimisation of non-bonding interactions in (3) between η-C₅H₅⁻ ligands and the bulky SiMe₃ groups; Figure 3 clearly shows the latter to be equally disposed with respect to the cyclopentadienyl ligands. {A remarkably similar situation occurs in [Zr(CH₂SiMe₃)₂(η-C₅H₅)₂],[28] the unidentate counterpart of (3).} Because SiMe₃ groups are constrained into pseudo-equatorial positions, this may dictate, on geometrical considerations, a greater fold angle, Φ.

In Part 2,[3] it was proposed that the fold angle in metallaindanes is dependent both on electronic and steric factors, and these are difficult to separate out. Fold angles for such complexes [M(CH₂C₆H₄CH₂-*o*)(η-C₅H₄R)₂] are 41° (M = Nb, R = SiMe₃), 53° [M = Zr (10) or Hf, R = H], and 44° (M = Ti, R = H). The small value for the Ti complex is expected because of the geometrical consequence of incorporating a smaller atom into a five-membered ring. Extended folding in the title complex (3) may arise either from the above-mentioned steric effects and/or electronic factors. Increase in the fold angle effectively allows interactions between the formally electron-deficient zirconium centre and the π-system of the electron-rich *o*-xylenediyl ligand. A Zr–C$^\beta$ distance of 2.71(1) Å [*cf.* 2.857(8) Å in (10)[3]] suggests that such an interaction may be in operation. In the *cis*-buta-1,3-diene derived complexes [Zr{*cis*-η-CH₂C(R)=C(R)CH₂}(η-C₅H₅)₂] there is a similar effect, with Zr–C$^\beta$ at 2.597(3) Å

**Table 5.** Ligand geometries (non-hydrogen atoms) in complex (3)

(a) α,α′-Bis(trimethylsilyl)-o-xylenediyl ligand

(i) Distances (Å)

| | |
|---|---|
| C(1)–C(1) | 1.399(8) |
| C(1)–C(2) | 1.352(10) |
| C(2)–C(3) | 1.408(9) |
| C(3)–C(3) | 1.446(7) |
| C(3)–C(4) | 1.482(8) |
| C(4)–Si | 1.864(5) |
| Si–C(5) | 1.875(6) |
| Si–C(6) | 1.874(10) |
| Si–C(7) | 1.870(9) |

(ii) Angles (°)

| | |
|---|---|
| C(1)–C(1)–C(2) | 119.8(7) |
| C(1)–C(2)–C(3) | 122.7(5) |
| C(2)–C(3)–C(3) | 117.5(5) |
| C(2)–C(3)–C(4) | 121.3(5) |
| C(3)–C(3)–C(4) | 121.0(5) |
| Zr–C(4)–Si | 135.8(2) |
| Zr–C(4)–C(3) | 88.4(3) |
| C(3)–C(4)–Si | 122.0(4) |
| C(4)–Si–C(5) | 111.9(2) |
| C(4)–Si–C(6) | 109.6(3) |
| C(4)–Si–C(7) | 114.3(3) |
| C(5)–Si–C(6) | 106.7(4) |
| C(5)–Si–C(7) | 107.8(3) |
| C(6)–Si–C(7) | 106.1(4) |

(b) Cyclopentadienyl ligands A and B

(i) Distances (Å)

| | |
|---|---|
| C(1)–C(2) | 1.388(9), 1.379(9) |
| C(2)–C(3) | 1.363(9), 1.388(9) |
| C(3)–C(3) | 1.454(9), 1.379(9) |

(ii) Angles (°)

| | |
|---|---|
| C(2)–C(1)–C(2) | 108.3(7), 107.4(7) |
| C(1)–C(2)–C(3) | 108.9(6), 108.6(6) |
| C(2)–C(3)–C(3) | 107.0(5), 107.7(5) |

**Table 6.** Zirconium atom environments in complex (3). The first column in the matrix relates to the zirconium–ligand bond lengths, $r$(Zr–L) (Å); other entries are the angles subtended at the metal by the relevant ligand atoms. Italicised atoms are generated by the intramolecular mirror plane

| | $r$(Zr–L) | C(0A) | C(0B) | $C$(4) |
|---|---|---|---|---|
| C(4) | 2.305(4) | 114.3(—) | 107.0(—) | 80.2(2) |
| C(0A) * | 2.253(1) | | 125.0(—) | 114.3(—) |
| C(0B) * | 2.254(1) | | | 107.0(—) |

* Cyclopentadienyl ring centroid.

(R = Me) and 2.71₄ Å (R = Ph), and Zr–Cᵅ at 2.300(3) and 2.28₉ Å, respectively.[30] [In the corresponding trans-η-1,3-diene complexes, the Zr–Cᵝ distances, 2.38 Å (R = Ph)[31] and 2.33₁ Å (R = H),[32] are shorter than Zr–Cᵅ, 2.50 and 2.47₇ Å, respectively.] Distortions of a similar magnitude have been noted for unidentate benzyl ligand-containing complexes, as in [Zr(CH₂Ph)₄] with Zr–Cᵝ 2.74 Å.[33]

A second fundamental structural change associated with Cᵅ,Cᵅ′-disubstitution is a significant contribution from the 5,6-dimethylenecyclohexa-1,3-diene resonance form, (9). This is clearly indicated by noting the variations in C–C distances within the o-xylidene C₈ skeleton (Table 5). A similar observation was made for [W̄(CH₂C₆H₄CH₂-o)₃],[1] in which the W–Cᵝ distance is 2.48 Å. Overall, the o-xylidene–zirconium interaction in complex (3) is intermediate between that expected for a metallacyclic structure (8) and the η⁴-bound 5,6-dimethylenecyclohexa-1,3-diene–metal complex structure (9). Although several complexes have been reported as typically η⁴-bonding, as in (9), notably some carbonyl-iron [34,35] and phosphine–ruthenium [36,37] compounds, only two such complexes have been structurally characterised, namely [Fe(η⁴-C₈H₈)(CO)₂(PPh₃)] [38] and [Ru(η⁴-C₈H₈)(PPh-Me₂)₃].[39] There the disparity between M–Cᵅ and M–Cᵝ distances is diminished and hence the 5,6-dimethylenecyclo-hexa-1,3-diene resonance contributions are more pronounced [Fe–Cᵅ 2.073(5) and 2.097(4) Å and Fe–Cᵝ 2.115(4) and

2.137(4) Å; Ru–Cᵅ 2.168(4) and 2.179(5) Å, and Ru–Cᵝ 2.290(4) and 2.305(4) Å].

Another feature of interest concerns the bite angle (Cᵅ–Zr–Cᵅ′) in the five-membered ring of the title complex (3). It is more open, at 80.2(2)°, than in the unsubstituted complex [Zr(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂] (10), 77.3(2)°,[3] but is still well below the usual range of 90—96° associated with dialkyl-zirconocene(iv) complexes [Zr(η-C₅H₅)₂R₂].[27]

With the similar size of M⁴⁺ radii of zirconium and hafnium, the latter only 0.01—0.02 Å smaller,[40] it is not unreasonable to predict that the structure of the hafnium complex (4) will prove to be similar to that of (3). The smaller size of Ti⁴⁺ and Nb⁴⁺ may on steric hindrance grounds and the geometrical constraint of incorporating a smaller heteroatom in the metallacycle, result in a further departure from η⁴-bonding. The similarity in e.s.r. data for the niobium(iv) complex (5) and [Nb(CH₂C₆H₄CH₂-o)₂(η-C₅H₅)₂] [3] supports this view, as does careful analysis of the ¹H n.m.r. data (Table 2 and ref. 3) for the titanium(iv) analogues. The CᵅH (= Cᵅ′H) resonances in the zirconium (3) and hafnium (4) complexes are similar in position to that of the assigned H_{exo} protons of the CH₂ groups in [W(CH₂C₆H₄CH₂-o)₃] [1] at τ 10.39, but differ considerably from the τ 7.51 proposed for the H_{endo} protons. However, the CᵅH (= Cᵅ′H) resonance for the titanium analogue (2) is intermediate, at τ 8.50, possibly indicative of a more predominantly metallacyclic structure (8).

As for the structures in solution and possible dynamic behaviour, the ¹H and ¹³C n.m.r. spectra of the d⁰ Group 4A metal(iv) complexes [M{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] are invariant with temperature in the range −60 to −80 °C, which suggests that a ring inversion phenomenon is not observed. By contrast, in the corresponding unsubstituted complexes [M(CH₂C₆H₄CH₂-o)(η-C₅H₅)₂], the inversion process is too rapid to be observed on the n.m.r. time-scale, the methylene protons being equivalent (fast pair of H_{endo}/H_{exo} exchanges) and lying in the range τ 7.72—8.57.[3] The difference is attributed to the steric effects of the trimethyl-silyl groups causing a high activation barrier to inversion.

## Experimental

General procedures have been described in Part 1.[2]

*Physical and Analytical Measurements.*—Cyclic voltammetry was carried out as outlined in Part 3.[1] The g_{av} values from e.s.r. data were measured relative to polycrystalline diphenylpicrylhydrazyl, using a Varian E3 spectrometer. Hydrogen-1 n.m.r. spectra were obtained on a Perkin-Elmer R32 or Varian T60 instrument and carbon-13 n.m.r. data on a JEOL PFT 100. Elemental analyses were carried out in the microanalytical laboratory of the University of Sussex.

*Materials.*—The metallocene(iv) chlorides [M(η-C₅H₅)₂Cl₂] (M = Ti, Zr, Hf, or Nb) were purchased (Ti, Zr) or prepared as described in Part 2.[3] The compound [{o-C₆H₄(CHSiMe₃)₂}-{Li(tmen)}₂] (1) will be described in Part 5.[4]

*Synthesis of meso-*[Ti{CH(SiMe₃)C₆H₄CH(SiMe₃)-o}(η-C₅H₅)₂] (2).—To a mixture of [Ti(η-C₅H₅)₂Cl₂] (1.26 g, 5.06 mmol) and the organodilithium reagent (1) (2.50 g, 5.06 mmol) was added diethyl ether (40 cm³) preheated to *ca.* 35 °C, and the reaction mixture was maintained at this temperature for *ca.* 1 h with stirring. The solvent was removed from the resultant blue-black solution *in vacuo*, the residue extracted with hot hexane (50 cm³, at *ca.* 60 °C), and the extract was filtered and concentrated to *ca.* 10 cm³. Cooling of this solution for 2 days at −40 °C afforded violet-brown crystals of [{Ti(η-C₅H₅)₂Cl}₂] (0.35 g, 32%) (Found: C, 56.5; H, 5.25. Calc. for C₁₀H₁₀ClTi: C, 56.2; H, 4.7%), $g_{av.}$ = 1.978 with no hyperfine coupling (*cf.* ref. 41, $g_{av.}$ = 1.978); mass spectrum, *m/e* 424 (*P*)⁺, 212 (*P*)²⁺, with the expected isotope pattern. Further concentration of the filtrate (to *ca.* 3 cm³) and cooling (−40 °C) furnished dark blue microcrystals of *complex* (2), which were filtered off and washed with cold pentane (3 × 1 cm³, −40 °C). The mass spectrum showed the following peaks (*m/e*), with assignments in parentheses: 426 (*P*)⁺, 411 (*P* − CH₃)⁺, 361 (*P* − C₅H₅)⁺, 248 [C₈H₆(SiMe₃)₂]⁺, and 178 [*P* − C₈H₆(SiMe₃)₂]⁺. The i.r. spectrum (Nujol, KBr plates) showed features associated with η-C₅H₅ groups: 3 110w, 3 070w, 1 435 (sh), 1 021m, 1 015 (sh), and 813br cm⁻¹; and other strong bands at 1 256, 1 243, 895, 858, 839, 760, 742, 668, 614, 434, and 414 cm⁻¹.

*Synthesis of meso-*[Zr{CH(SiMe₃)C₆H₄CH(SiMe₃)-o}(η-C₅H₅)₂] (3), *and of a Bimetallic Complex* (6).—The same procedure was followed as that for synthesis of complex (2). The minor product (6) was isolated in the same fashion from the initial red solution as the titanocene(iii) chloride in the preceding experiment. The mass spectra (*m/e*) were as follows: 468 (*P*)⁺, 453 (*P* − CH₃)⁺, 250 [C₈H₈(SiMe₃)₂]⁺, 220 [*P* − C₈H₈(SiMe₃)₂]⁻: complex (6), 468 (*P* − ZrC₁₀H₈)⁺, 250 [C₈H₈(SiMe₃)₂]⁺, 220 [*P* − Zr(C₁₀H₈){C₈H₈(SiMe₃)₂}]⁺. The i.r. spectra (Nujol, KBr plates) showed the following bands: complex (3), 3 105w, 3 088w, 1 450 (sh), 1 430m, 1 021s, 1 011s, 814m, and 807m cm⁻¹ for η-C₅H₅, and other strong bands at 1 258, 1 246, 892, 853, 838, 770, 742, 672, and 415 cm⁻¹; for complex (6), 3 105w, 3 090w, 1 446 (sh), 1 432m, 1 260s, 1 244 (sh), 1 068m, 1 047m, 1 016br, 892 (sh), 840br, 800br, 735br, 660m, 640s, 582s, and 500w cm⁻¹.

*Synthesis of meso-*[Hf{CH(SiMe₃)C₆H₄CH(SiMe₃)-o}(η-C₅H₅)₂] (4).—The reaction between [Hf(η-C₅H₅)₂Cl₂] (2.24 g, 5.90 mmol) and the organodilithium reagent (1) (2.90 g, 5.90 mmol) was as described for the Ti and Zr analogues, but no minor product was isolated; the orange hexane extract was concentrated (to *ca.* 40 cm³), and crystals of the *metallacycle* (4) were obtained by cooling to *ca.* −40 °C. The mass spectrum showed the following peaks (*m/e*): 556 (*P*)⁺, 541 (*P* − CH₃)⁺, 321, 306 [*P* − C₈H₈(SiMe₃)₂]⁺, 250 [C₈H₈(SiMe₃)₂]⁺. The i.r. spectrum (Nujol, KBr plates) showed η-C₅H₅ bands at 3 105w, 3 088w, 1 450 (sh), 1 434m, 1 021s, 1 011s, 814m, and 807m cm⁻¹, as well as other strong bands at 1 259, 1 244, 898, 856, 838, 770, 736, 673, and 417 cm⁻¹.

*Synthesis of* [Nb{CH(SiMe₃)C₆H₄CH(SiMe₃)-o}(η-C₅H₅)₂] (5).—To a mixture of [Nb(η-C₅H₅)₂Cl₂] (1.2 g, 4.1 mmol) and the organodilithium reagent (1) (2.0 g, 4.1 mmol) was added warm (35 °C) diethyl ether (50 cm³), and the resultant purple

**Table 7.** Non-hydrogen atomic co-ordinates for the complex *meso*-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] (3)

| Atom | x | y | z |
|---|---|---|---|
| Zr | 0.749 73(4) | 0.140 06(4) | 0.250 00(—) |
| *Trimethylsilyl ligand* | | | |
| C(1) | 1.045 7(4) | 0.233 0(4) | 0.208 7(3) |
| C(2) | 0.983 2(4) | 0.238 9(4) | 0.168 9(3) |
| C(3) | 0.916 5(3) | 0.245 2(3) | 0.207 3(3) |
| C(4) | 0.844 1(3) | 0.242 7(3) | 0.162 2(3) |
| Si | 0.848 8(1) | 0.257 8(1) | 0.053 0(1) |
| C(5) | 0.947 3(4) | 0.360 8(4) | 0.021 9(4) |
| C(6) | 0.752 7(5) | 0.265 1(5) | 0.019 2(4) |
| C(7) | 0.846 7(5) | 0.167 3(5) | −0.004 5(4) |
| *Cyclopentadienyl ligand A* | | | |
| C(0) [a] | 0.753 8(—) | 0.015 9(—) | 0.250 0(—) |
| C(1) | 0.829 6(6) | 0.055 1(5) | 0.250 0(—) |
| C(2) | 0.777 0(5) | 0.028 6(4) | 0.183 5(4) |
| C(3) | 0.692 7(4) | −0.016 4(3) | 0.207 0(4) |
| *Cyclopentadienyl ligand B* | | | |
| C(0) [a] | 0.628 0(—) | 0.148 7(—) | 0.250 0(—) |
| C(1) | 0.585 8(6) | 0.072 3(6) | 0.250 0(—) |
| C(2) | 0.615 9(4) | 0.125 0(5) | 0.184 3(4) |
| C(3) | 0.661 2(4) | 0.210 5(4) | 0.209 3(4) |
| *Benzene solvent A* | | | |
| C(1) | 0.519 8(5) | 0.636 3(5) | 0.210 3(5) |
| C(2) | 0.443 1(8) | 0.595 9(6) | 0.171 9(4) |
| C(3) | 0.367 8(5) | 0.555 1(5) | 0.211 2(5) |
| *Benzene solvent B* | | | |
| C(1) [b] | 0.000(—) | 0.000(—) | 0.090 0(—) |
| C(2) [b] | −0.024 0(—) | −0.069 0(—) | −0.041 0(—) |
| C(3) [b] | −0.024 0(—) | −0.069 0(—) | −0.041 0(—) |

[a] Ring centroid. [b] Population: 0.33(—).

solution was maintained at this temperature for 1 h. Removal of the solvent *in vacuo*, followed by extraction with hexane (50 cm³) at *ca.* 60 °C and filtration resulted in a purple solution and a brown residue. Concentration of the filtrate to *ca.* 10 cm³ and cooling for 1 day at *ca.* −40 °C afforded a mixture of white and purple crystals. Filtration and concentration of the filtrate, upon further cooling at *ca.* −40 °C for 1 day gave purple needles of *complex* (5) (0.58 g). Further purification was achieved by sublimation at 160 °C (10⁻³ Torr). The mass spectrum showed the following peaks (*m/e*): 471 (*P*)⁺, 248 [C₈H₆(SiMe₃)₂]⁺, and 223 [*P* − C₈H₆(SiMe₃)₂]⁺. The i.r. spectrum (Nujol, KBr plates) showed η-C₅H₅ bands at 3 106w, 3 070w, 1 434m, 1 020br, 812m, and 807m cm⁻¹, and other strong bands at 1 258, 1 244, 888, 866, 862, 842, 750, 670, and 408 cm⁻¹.

*Synthesis of the Binuclear Complex* (6) *from meso*-[Zr{CH(SiMe₃)C₆H₄CHSiMe₃-o}(η-C₅H₅)₂] (3).—To a cooled (0 °C) solution of complex (3) (0.116 g, 0.25 mmol) in OEt₂ (5 cm³) was added a hexane solution of n-butyl-lithium (0.29 cm³, 0.5 mmol, 1.7 mol dm⁻³) followed by tmen (0.074 cm³, 0.5 mmol). After 8 h at room temperature the reaction mixture was heated to 35 °C and [Zr(η-C₅H₅)₂Cl₂] (0.072 g, 0.25 mmol) was added. Subsequent stirring for 30 min at the same temperature, followed by solvent removal *in vacuo* gave a red-brown solid. The ¹H n.m.r. spectrum (C₆D₆) of an extract showed the presence of *ca.* 30% of complex (6).

*Reduction of the Metallaindanes* (2), (3), and (4).—Drop-wise addition of a thf solution of sodium dihydronaphthylide (slightly less than 1 mol), prepared according to ref. 9, to a thf solution of complex (2), (3), or (4) (1 mol equiv.) generated a purple (2), red-brown (3), or orange (4) solution respectively at ambient temperature. The derived e.s.r. signals differed in their persistence from several minutes (Ti) or days (Hf) to being indefinitely stable (Zr); decay of the Ti$^{III}$ complex was accompanied by formation of a more complicated e.s.r. spectrum. In each case the initial e.s.r. signal was identical to that derived from reduction of the appropriate Ti$^{IV}$, Zr$^{IV}$, or Hf$^{IV}$ complex (2), (3), or (4) in the presence of the supporting electrolyte, [NBu$^n_4$][BF$_4$], used in the electrochemical experiments.

*X-Ray Data Collection, Structure Solution, and Refinement for* meso-[Zr{CH(SiMe$_3$)C$_6$H$_4$CHSiMe$_3$-o}(η-C$_5$H$_5$)$_2$] (3).— *Crystal data.* C$_{32}$H$_{42}$Si$_2$Zr, $M$ = 574.1, Hexagonal, space group $P6_3/m$ ($C^2_{6h}$, no. 176), $a$ = 17.849(8), $c$ = 16.923(8) Å, $U$ = 4 670(3) Å$^3$, $Z$ = 6, $D_c$ = 1.22 g cm$^{-3}$, $F(000)$ = 1 812, mono-chromatic Mo-$K_\alpha$ radiation, λ = 0.710 6$_9$ Å, μ = 4.2 cm$^{-1}$; Specimen size 0.20 × 0.60 × 0.45 mm (capillary), $T$ = 295(1) K.

*Structure determination.* A unique data set was measured within the limit 2θ$_{max.}$ = 50°, using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode; 2 870 inde-pendent reflections were obtained, 1 645 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U)_H$ were constrained at estimated values. One of the solvent molecules was found to be disordered about the unique axis; $(x,y,z)$ for the associated carbon atoms were constrained at estimated values consistent with difference maps and assigned populations of $\frac{1}{2}$. At convergence, $R$ and $R'$ were 0.044 and 0.053, respectively, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion $(f', f'')$.[42] Computation used the X-RAY 76 program system,[43] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. The geometry of the complex is presented in Tables 5 and 6. Final atomic co-ordinates are in Table 7.

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