Axially Asymmetric Metal Alkyls. Part 3.† Chemical, Electrochemical, and Structural Studies of Group 5A $d^{0,1,2}$ Metallepines $[M\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]^z$ (M = Nb or Ta; z = 1 −, 0, or 1 +); Synthesis of $[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}X(\eta\text{-}C_5H_5)_2]$ (X = Cl or CO) and $[\{(\eta\text{-}C_5H_5)_2ClV\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$, and Electrochemistry of $[M(CH_2Ph)_{2-n}Cl_n(\eta\text{-}C_5H_5)_2]$ (n = 0, M = Nb, or Ta; n =1, M = V)‡

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Reaction of $[MCl_2(\eta\text{-}C_5H_5)_2]$ with the di-Grignard reagent $\{o\text{-}[(thf)_nClMgCH_2]C_6H_4\}_2$ in tetrahydrofuran (thf) yields either the bimetallic complex $[\{(\eta\text{-}C_5H_5)_2ClV\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (**2**) or the thermally stable metallepines, $[M\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ [M = Nb (**3a**) or Ta (**3b**)]. E.s.r. data on these and the compounds $[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}Cl(\eta\text{-}C_5H_5)_2]$ (**7**) and $[M(CH_2Ph)_{2-n}Cl_n(\eta\text{-}C_5H_5)_2]$ [n = 1, M = V (**8**); n = 0, M = Nb (**9a**) or Ta (**9b**)], prepared by similar methods, are consistent with each being a d^1 complex. Electrochemical reduction and oxidation of (**3a**) is reversible; the cationic d^0 and anionic d^2 species have been generated chemically (using $AgBF_4$ and $Na[C_{10}H_8]$) in thf and isolated as salts of $[BF_4]^-$, (**4a**), and $[Na(18\text{-crown-}6)(thf)_2]^+$, (**5**), respectively (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane). Electrochemical studies on the other d^1 compounds are also reported. Reductive carbonylation of (**7**) or treating (**5**) with CF_3CH_2OH under CO yields $[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}(CO)(\eta\text{-}C_5H_5)_2]$ (**6**). *X*-Ray structures of the $d^{0,1,2}$ niobepines (**4a**), (**3a**), and (**5**) show a large change in $CH_2\text{–}Nb\text{–}CH_2$ angle [106.3(1), $83._0$, 80(1)°] in accordance with molecular orbital predictions, and in the $Nb\text{–}CH_2\text{–}C$ angles [$102._9$, $118._7$, and 123(2)°] and the torsion along the biphenyl axis ($78._4$, $62._4$, and $59._6$°).

Part 1[1] of the present series dealt with the synthesis and structure of the dilithium complexes $[\{Li(tmen)\}_2\{(2\text{-}CHRC_6H_4)_2\}]$ (R = H or $SiMe_3$; tmen = *NNN′N′*-tetramethylethylenediamine), while in another paper[2] silicon and tin 'metallacycles', $[Si\{(2\text{-}CH_2C_6H_4)_2\}Me_2]$ and $[Sn\{(2\text{-}CHRC_6H_4)_2\}Ph_2]$ [R = H or $SiMe_3$ (δ-*SS* and λ-*RR* isomers)], derived from these complexes and a di-Grignard reagent of 2,2′-bis(chloromethyl)biphenyl, (**1**), were described. The potential of the dilithium complex (R = H) and the di-Grignard reagent for metallacycle (metallepine) formation is further explored in this paper. We report the synthesis of the d^1 6,6-bis(η-cyclopentadienyl)-6,7-dihydro-5*H*-dibenzo[*c,e*]metallepines of Nb and Ta, $[M\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**3a**) and (**3b**) (Scheme 1), and a study of their electrochemical behaviour, to ascertain the stability of their single-electron transfer oxidized and reduced species, particularly for the latter since d^2 Group 5 metallocene dialkyl anionic species are ill defined. Only the niobium d^2 species $[Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]^-$ could be isolated, as a $[Na(18\text{-crown-}6)(thf)_2]^+$ salt, (**5**) (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane, thf = tetrahydrofuran). We have investigated the electrochemistry of $[M(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$ [M = Nb (**9a**) or Ta (**9b**)]. These compounds are unidentate analogues of the metallacycles (**3a**) and (**3b**) and a comparison of the electrochemical properties of the two classes of metal alkyls may give insight into the effects, if any, on the stability of the generated species and the ease of their formation, for the presence of a chelate ring.

Other aspects of this work are (*i*) the preparation of d^0 metallacycles for Nb and Ta, $[M\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]^+$ (**4a**) and (**4b**); (*ii*) the interconversion of niobium $d^{0,1,2}$ metallacycles (Scheme 1); (*iii*) formation of a niobocene alkyl carbonyl compound, $[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}(CO)(\eta\text{-}C_5H_5)_2]$ (**6**), from the d^2 metallacycle (**5**), or $[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}Cl(\eta\text{-}C_5H_5)_2]$ (**7**) (Scheme 2); (*iv*) preparation of $[\{(\eta\text{-}C_5H_5)_2ClV\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (**2**), and $[V(CH_2Ph)Cl(\eta\text{-}C_5H_5)_2]$ (**8**); (*v*) single-crystal *X*-ray structure determinations for the d^0, d^1, and d^2 compounds of niobium, being the first trio of mononuclear transition-metal complexes related by a sequential addition of a *d* electron to be structurally authenticated. The synthesis of (**3a**) and (**5**) and items (*i*) [not for the Ta complex, (**4b**)] and (*ii*) have been briefly communicated.[3] Some related Group 4 transition metal chemistry has been reported elsewhere.[3,4]

An important feature of the group $(2\text{-}CH_2C_6H_4)_2^{\,2-}$ is its flexible 'bite', a consequence of unrestricted torsion along the biphenyl axis. It is possible, therefore, for it acting as a bidentate ligand, type (**I**), to accommodate a wide variation in metal size. This has been established by the metallacycles of type (**I**) of Si and Sn;[2] Ti, Zr, and Hf;[4] and Nb.[3] The ligand is also capable of stabilizing unusual oxidation states for metal alkyls, for example compound (**5**),[3] and unusual bonding configurations. In the related *o*-xylenediyl system, departure from metallacyclic bonding is towards a metal–η^4 interaction,[5] of the type shown in (**II**). In the present system each half of the ligand can be thought of as being a benzyl group and it is likely that they can function as η^3-allyl moieties, (**III**), as in complexes of the benzyl ligand itself;[6] in the 'contact-ion-pair' compound $[\{Li(tmen)\}_2\{(2\text{-}Me_3Si\bar{C}HC_6H_4)_2\}]$ the metal–hydrocarbyl interactions are η^3 and to the carbon centres indicated in (**III**).[2]

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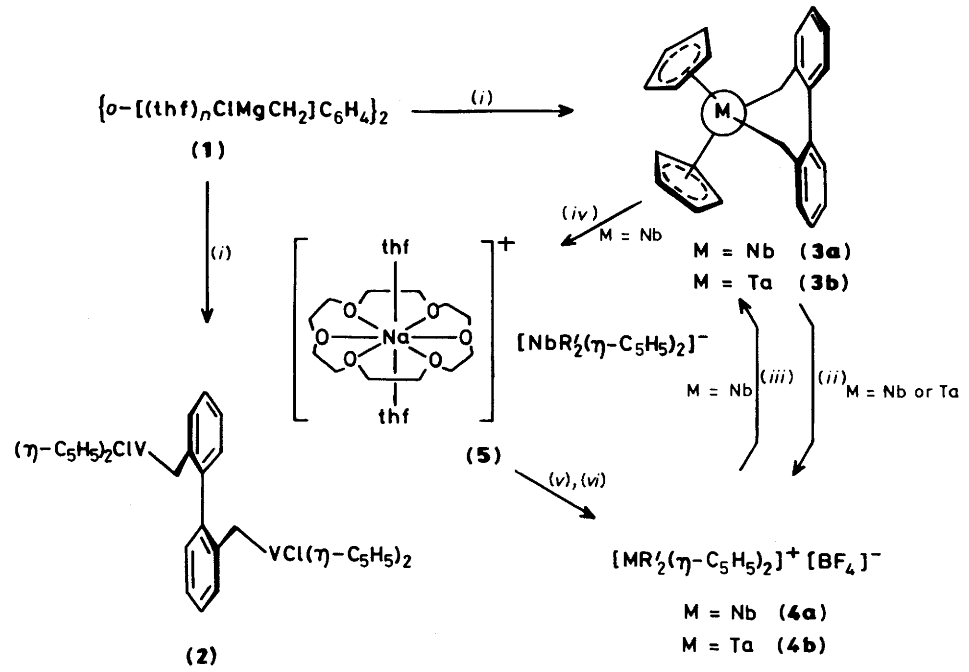
† Part 2 is ref. 2.

‡ *Supplementary data available* (No. SUP 56242, 25 pp.): H-atom coordinates, thermal parameters, ligand geometries and planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: mmHg = 133 Pa, G = 10^{-4} T, atm = 101 325 Pa.



Scheme 1. R′ = ½{(2-$CH_2C_6H_4$)$_2$}. (*i*) [MCl_2(η-C_5H_5)$_2$], thf, −78 °C; (*ii*) $AgBF_4$, thf; (*iii*) $NaBH_4$ or K[$BHBu^s{}_3$], thf; (*iv*) Na[$C_{10}H_8$] or Na/Hg, 18-crown-6, thf; (*v*) HBF_4·OMe_2 (2 mol equiv.), thf; (*vi*) [CPh_3][BF_4] (2 equiv.), thf

Results and Discussion

d^1 *Metallocenes.*—All the d^1 metal alkyls in Schemes 1 and 2, and [Ta(CH_2Ph)$_2$(η-C_5H_5)$_2$] (**9b**) and [V(CH_2Ph)Cl(η-C_5H_5)$_2$] (**8**), were prepared from Grignard reagents and the appropriate metallocene dichloride. The procedure for the synthesis of (**9b**) was the same as that for the niobium analogue, (**9a**).[7] For the synthesis of the metallacycles (**3a**) and (**3b**) and the binuclear vanadium complex (**2**), use of the organodilithium complex [{Li(tmen)}$_2${(2-$CH_2C_6H_4$)$_2$}], under the reaction conditions studied, gave intractable mixtures of compounds. The success of the Grignard reagents (**1**) over the lithium alkyl may be related to the greater reducing properties of lithium alkyls than Grignard reagents. A source of reduction using [{Li(tmen)}$_2${(2-$CH_2C_6H_4$)$_2$}] may be intramolecular cyclization of the carbanion forming 9,10-dihydrophenanthrene, as has been demonstrated for a reaction giving reduction of Sn^{IV} to Sn^{II} using [{Li(tmen)}$_2${(2-$Me_3SiCHC_6H_4$)$_2$}] although there the product was a substituted 9,10-dihydrophenanthrene.[1]

A difficulty in the synthesis of vanadocene(IV) alkyl compounds from alkylation of [VCl_2(η-C_5H_5)$_2$] is the ease of reduction of V^{IV} to V^{III}.[8] This is not a problem for the milder reducing Grignard reagents, (**1**) and (thf)$_n$ClMgCH_2Ph. They yield respectively a binuclear complex [{(η-C_5H_5)$_2$ClV}$_2${(2-$CH_2C_6H_4$)$_2$}] (**2**) and [V(CH_2Ph)Cl(η-C_5H_5)$_2$] (**8**), which have been characterized by elemental analysis and e.s.r. spectroscopy. The same reagents with [$NbCl_2$(η-C_5H_5)$_2$] and [$TaCl_2$(η-C_5H_5)$_2$] gave the metallacycles (**3a**) and (**3b**), and [Ta(CH_2Ph)$_2$(η-C_5H_5)$_2$] (**9b**), which were similarly characterized. It is noteworthy that the metallacycles related to (**3a**) and (**3b**), [Nb{*o*-(CH_2)$_2C_6H_4$}(η-C_5H_4R)$_2$] (R = H or $SiMe_3$),[5] were also prepared from a di-Grignard reagent, in high yield, and the reaction of a lithium reagent, [{Li(tmen)}$_2${*o*-(Me_3SiCH)$_2C_6H_4$}], with [$NbCl_2$(η-C_5H_5)$_2$] gave a very low yield of the metallacycle. These results further highlight the greater utility of Grignard reagents over lithium alkyls, although differences in steric hindrance of the two reagents may have some effect.

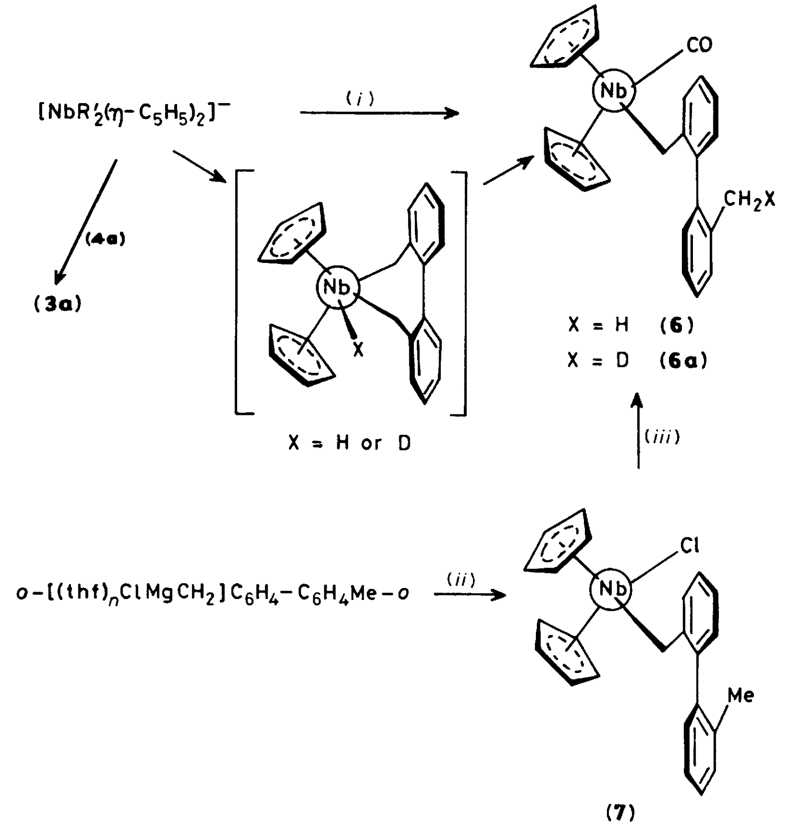
Of the few tantalocene dialkyl syntheses reported there is no evidence for the synthetic difficulties prevalent for V and Nb analogues. For synthesis of the isoleptic Group 4 analogues of (**3a**) and (**3b**), either the di-Grignard or organodilithium reagents were equally effective,[4] although there, with the exception of Ti, the potential for reduction as a competing reaction to alkylation is significantly less.[9]

The ability to prepare metallacycles of Nb and Ta from (**1**), but not of V, it yielding a binuclear complex (**2**), may be related to the smaller size of V. For vanadium to accommodate the chelate there may be unfavourable ring strain at the methylene carbon atoms. The titanium compound in which the metal atom is of similar size is, however, accessible but there the d^0 configuration would permit a larger CH_2–M–CH_2 angle which would have less strain than a vanadium d^1 analogue. Resistance of (**2**) to further alkylation may be due to steric hindrance of the alkyl ligand. Compound (**2**) is the first example of the ligand (2-$CH_2C_6H_4$)$_2{}^{2-}$ bridging two metal centres, further illustrating its potentially rich chemistry.

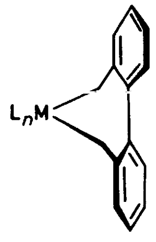
The metallacycles (**3a**) and (**3b**) are thermally robust, being sublimable *in vacuo* at 140 °C (10^{-3} mmHg) with minimal decomposition. This contrasts with, for example, [$NbMe_2$(η-C_5H_5)$_2$] which detonates above 130 °C.[10] Similar differences have been established for the isoleptic Group 4 analogues of (**3a**) and (**3b**) and metallocene dialkyl compounds.[4] Such an enhancement in stability of chelating alkyls *versus* unidentate ones for early transition metals has also been demonstrated for *o*-xylenediyl metallacycles.[5]

Compounds (**3a**) and (**3b**) are unusual in being paramagnetic d^1 metallacycles: the other examples reported are of types (**IV**)[11] and (**V**),[12,13] and also [NbL(η-C_5H_4R)$_2$] (R = H or $SiMe_3$) and [{Mg(thf)$_4$}(OWL$_2$)$_2$] [L = *o*-(CH_2)$_2C_6H_4{}^{2-}$],[5] and *meso*-[Nb{*o*-(Me_3SiCH)$_2C_6H_4$}(η-C_5H_5)$_2$].[7]

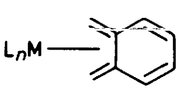
E.s.r. spectra of all the d^1 compounds were recorded in thf solutions at room temperature. Each comprised a multi-line spectrum consistent with hyperfine coupling to the metal (^{51}V, $I = \frac{7}{2}$; ^{93}Nb, $I = \frac{9}{2}$; ^{181}Ta, $I = \frac{7}{2}$); linewidths of the signals were typically 15 G and there was no fine structure associated with coupling to the methylene hydrogen atoms. Values of the



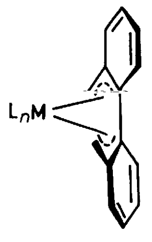
Scheme 2. R' = ½{(2-$CH_2C_6H_4)_2$}. (*i*) CO, thf, CF_3CH_2OH (X = H) or CF_3CH_2OD (X = D); (*ii*) [$NbCl_2(\eta-C_5H_5)_2$], thf, −78 °C; (*iii*) Na/Hg, CO, thf



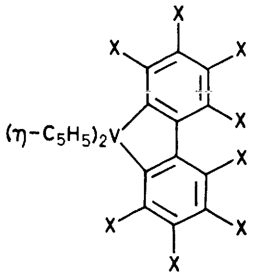
(I)



(II)

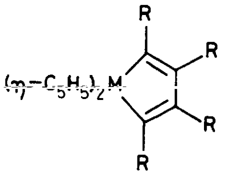


(III)



(IV)

X = H or F



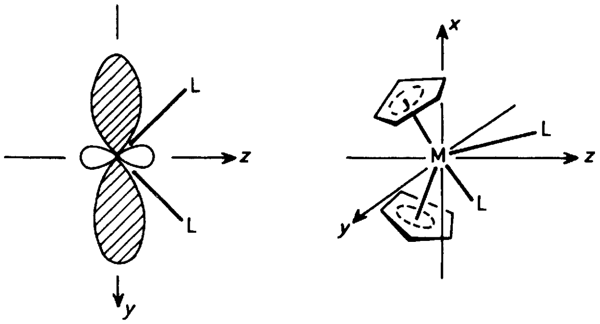
(V)

M	R
V	Ph
Nb	CF_3
Nb	Ph

metal hyperfine coupling constants, *a*(M), were calculated from the second-order spectrum using the Breit–Rabi equations.[14] The hyperfine coupling in d^1 compounds of the type $[MX_2(\eta-C_5H_5)_2]^{x\pm}$ is a sensitive measure of their steric and electronic variations;[15,16] low *a*(M) values are associated with greater metal character of the highest occupied molecular orbital $1a_1$ (VI), and a low value of the X–M–X angle. Values of $g_{av.}$ and *a*(M) for compounds (**3a**), (**3b**), and (**9a**) and all other Nb and Ta metallocene dialkyl (or aryl) compounds,[7,9,10,17–20] *viz.* all compounds with M–C σ-bonds for type X ligands, are presented in Table 1. For the three structurally characterized niobocene compounds containing benzylic type ligands there is the expected trend of angular variation *versus* $a(^{93}Nb)$. Surprisingly the H_2C–Nb–CH_2 angle in (**3a**) (83°) is enlarged relative to that of the open-chain analogue, [$Nb(CH_2Ph)_2(\eta-C_5H_5)_2$] (79°),[7] but the change in $a(^{93}Nb)$ is consistent with these results. The only other structure type in Table 1 is (V, M = Nb, R = CF_3) for which the C–M–C angle of 75°[12] is greater than in the *o*-xylenediyl compound, 72.4°.[5] The $a(^{93}Nb)$ value is, however, exceptionally low and it is likely that the Nb–C(sp^2) bonding as opposed to Nb–C(sp^3) bonding facilitates extra spin density delocalization onto the bidentate ligand in (V).

In considering all the Nb compounds in Table 1, those possessing the most sterically hindered σ-hydrocarbyl ligands, CH_2XMe_3 (X = C or Si) have high $a(^{93}Nb)$ values in accordance with ligand repulsions dictating a more open C–M–C angle. The *a*(M) value for (**3a**) is also high and therefore it would be expected to possess a high C–M–C angle. A similar argument is proposed for tantalum compounds. Furthermore the similar size of Nb^{4+} and Ta^{4+} implies that the C–M–C angles in (**3a**) and (**3b**) are likely to be similar, at 83°. The ligand 'bite' in (3) is unlike that of the other metallacycles in being flexible but it is controlled by the d^1 electron populating the $1a_1$ metallocene orbital (VI).

E.s.r. data for (**7**), $g_{av.}$ = 1.996, $a(^{93}Nb)$ = 106.6 G, are within



(VI)

the range of related compounds; the $a(^{93}Nb)$ value is identical to that of $[Nb(CH_2SiMe_3)Cl(\eta\text{-}C_5H_5)_2]$[7] and if the steric constraints imposed by the alkyl ligand control the C–M–Cl angle which is related to the a(M) value then the new alkyl ligand of (**7**) may have a similar steric requirement to that of the group CH_2SiMe_3. The complex related to (**7**), $[Nb(CH_2Ph)Cl(\eta\text{-}C_5H_5)_2]$,[18] cannot be isolated as it redistributes to $[Nb(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$ and $[NbCl_2(\eta\text{-}C_5H_5)_2]$. This problem is not evident for (**7**) and in the light of the above discussion the alkyl ligand of (**7**), $2\text{-}CH_2(C_6H_4)_2Me\text{-}2'$, is more sterically hindered than CH_2Ph and possibly similar to CH_2SiMe_3.

The vanadium d^1 compounds, (**2**) and (**8**), have similar e.s.r. data, *viz.* $g_{av.}$ 2.001, a(M) = 67.1 G and $g_{av.}$ = 1.9983, a(M) = 64.57 G respectively. These are similar to other vanadocene alkyl chloride compounds, *viz.* $[V(Me)Cl(\eta\text{-}C_5H_5)_2]$ [$g_{av.}$ = 1.990, a(M) = 69.2 G] and $[V(CH_2SiMe_3)Cl(\eta\text{-}C_5H_5)_2]$ [$g_{av.}$ = 1.990, a(M) = 70.0 G].[21] No redistribution was evident for $[V(CH_2Ph)Cl(\eta\text{-}C_5H_5)_2]$ in contrast to the niobium analogue, which is possibly a consequence of the smaller size of V^{4+} compared with Nb^{4+}. Moreover, the complex does not react further to yield $[V(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$.

$d^{0,2}$ *Metallocenes.*—Oxidation of (**3a**) and (**3b**) with $AgBF_4$ in thf gave d^0 metallocene metallacycle cations, isolated as tetrafluoroborates, (**4a**) and (**4b**) respectively (Scheme 1), which were characterized by ^1H and ^{13}C n.m.r. spectroscopy and a structure determination for (**4a**) only. In the ^1H n.m.r. spectrum of both, recorded in $[^2H_3]$nitromethane, the methylene protons which are anisochronous exhibit a characteristic AB pattern.

Reduction of (**3**) using either sodium amalgam or sodium dihydronaphthylide in thf and 18-crown-6 gave a crystalline d^2 compound, only for the niobium substrate. It is extremely air sensitive and has been characterized by a structure determination which showed it to be the one-electron reduction product with $[Na(18\text{-crown-}6)(thf)_2]^+$ as the counter ion, (**5**). Electrochemical studies however show the d^2 anion to be of limited stability in solution ($t_{\frac{1}{2}} \approx$ 10 s) and thus in the electrochemical experiments it may be reacting with the supporting electrolyte. Although it is expected to be diamagnetic, traces of the d^1 compound precluded the likelihood of obtaining n.m.r. data on it. The inability to isolate an analogous d^2 Ta compound is consistent with instability of the anion, established by electrochemical studies (see below).

The compounds (**4a**) and (**4b**) are unusual in that they are stable cationic metal alkyl species. Early transition metal species of this type can be unstable with respect to loss of a carbonium ion and/or proton abstraction.[21] Several species related to (**4**) have been reported: $[MoMe_2(\eta\text{-}C_5H_5)_2]^+$ (d^1),[20] $[W(H)Ph(\eta\text{-}C_5H_5)_2]^+$ (d^1),[22] $[TaMe_2(\eta\text{-}C_5H_5)_2]^+$ (d^0),[23] $[Ta(Me)X(\eta\text{-}C_5H_4R)_2]^+$ (d^0; X = Br[24] or Cl[25]), $[M(CH_2SiMe_3)_2(\eta\text{-}C_5H_5)_2]^+$ (d^0, M = Nb or Ta),[20] $[Nb(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]^+$ (d^0; not isolated),[18] $[Nb\{o\text{-}(Me_3SiCH)_2C_6H_4\}(\eta\text{-}C_5H_5)_2]^+$ (d^0; not isolated).[5]

Table 1. E.s.r. and some structural data for the d^1 metallocene complexes $[MR'_2(\eta\text{-}C_5H_4R'')_2]$ (M = Nb or Ta)[a]

R'	$g_{av.}$	a(M)/G	C–$\hat{M}$–C/°	Ref.
M = Nb				
CH_2SiMe_3	1.9961	95.0		7
	1.9948	94.2		7
CH_2SiMe_3[b]	1.998	91.4	83.0	*c*
$\frac{1}{2}\{(2\text{-}CH_2C_6H_4)_2\}$[(**3a**)]	1.9913	90.5		7
CH_2SiMe_3[d]	1.9984	88.8		10
Me	1.9982	88.8		17
Ph	1.9989	88.3		17
CD_3	1.9956	87.6	79.0	7
CH_2Ph	2.0001	87.1		7
CH_2CMe_3[d]	1.9912	86.1		18
CH_2Ph[d]				
Me[b]	1.9981	85.8		19
Me[e]	1.9992	85.6		7
Me[f]	1.9981	85.4		19
$CH_2(o\text{-}C_6H_4OMe)$	2.01	84		18
Me[g]	2.0006	80.8		19
Me[h]	1.996	80.4		19
$\frac{1}{2}\{o\text{-}(Me_3SiCH)_2C_6H_4\}$	1.999	77.5		9
$\frac{1}{2}\{o\text{-}(CH_2)_2C_6H_4$[d]$\}$	1.999	77.2	72.4	5
$\frac{1}{2}\{o\text{-}(CH_2)_2C_6H_4\}$	1.996	76.3		5
$\frac{1}{2}C_4(CF_3)_4$	1.994	68	75(3)	12
M = Ta				
$\frac{1}{2}\{(2\text{-}CH_2C_6H_4)_2\}$[(**3b**)]	1.964	102.1		*c*
CH_2SiMe_3	2.021	98		20
Ph	1.988	93.6		17
Me	1.993	93		10
Me[b]	1.993	93		17
CH_2Ph	2.0001	87.3		*c*

[a] R'' = H unless stated otherwise. [b] R'' = Me. [c] This work. [d] R'' = $SiMe_3$. [e] R'' = CH_2Ph. [f] R'' = $CHMe_2$. [g] R'' = CMe_2Ph. [h] R'' = CMe_3.

To our knowledge, the anion of (**5**) is the first example of a mononuclear anionic d^2 Group 5A species to be isolated in the solid. Prior to this work only electrochemically generated species of this type had been reported, *viz.* short-lived $[NbCl_2(\eta\text{-}C_5H_5)_2]^-$,[25] which undergoes chloride elimination, $[Nb\{o\text{-}Me_3SiCH)_2C_6H_4\}(\eta\text{-}C_5H_5)_2]^-$,[9] and $[Nb(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]^-$.[18] In contrast to the stability of the anion of (**5**), its tantalum analogue is a transient species (see below). It is noteworthy that the electron-reduced niobocene[25–27] and tantalocene[28] dihalides, and $[Nb(CH_2SiMe_3)Cl(\eta\text{-}C_5H_4Me)_2]$,[29] are unstable with respect to metal–halogen bond rupture. We find this also occurs on reduction of the metallocene alkylchloride, (**7**); it is irreversibly reduced and on chemical reduction under an atmosphere of carbon monoxide the corresponding carbonyl compound, (**6**), is formed. Similar reactions are found in the literature for $[Nb(Ph)Cl(\eta\text{-}C_5H_5)_2]$,[18] $[NbX_2(\eta\text{-}C_5H_5)_2]$ (X = Br[26] or Cl[30]), and $[NbCl_2(\eta\text{-}C_5H_4Me)_2]$.[27]

Compound (**6**) was identified by n.m.r. and i.r. spectroscopy. The ν_{CO} band at 1 888 cm^{-1} is comparable to that of related niobium carbonyl complexes of the type $[NbX(CO)(\eta\text{-}C_5H_5)_2]$: *viz.* 1 930 cm^{-1}, X = Br;[26] 1 900 cm^{-1}, X = Cl,[30] X = H[31] and $Pr^nHC{=}CPr^n$,[32] 1 890 cm^{-1}, X = Me.[30]

Reactions of $d^{0,1,2}$ *Niobepines.*—Interconversion of the $d^{0,1,2}$ niobepines, (**4a**), (**3a**), and (**5**) respectively, is possible by chemical (Scheme 1) and electrochemical (see below) methods. $NaBH_4$ or $K[BHBu^s_3]$ in thf were effective reductants for d^0 (**4a**) $\longrightarrow$ d^1 (**3a**) and the oxidation step d^2 (**5**) $\longrightarrow$ d^0 (**4a**) by two equivalents of either $[CPh_3][BF_4]$ or $HBF_4{\cdot}OMe_2$ in thf.

Table 2. Electrochemical data*

Compound	$E_{\frac{1}{2}}^{ox}$/V	$E_{\frac{1}{2}}^{red}$/V	$t_{\frac{1}{2}}^{red}$/s
(**8**)	−0.38 (irr)	—	—
(**9a**)	-0.81_6	-2.21_3	$>10^3$
(**9b**)	−0.83 (irr)	−2.32	7
(**2**)	−0.22 (irr)	−2.14	4
(**3a**)	-0.83_5	-2.32_5	10
(**3b**)	−1.070	−2.43	2
(**6**)	−0.44 (irr)	—	—

* $E_{\frac{1}{2}}^{ox}$ = half-wave potential for oxidation; anodic peak potential is given for irreversible (irr) processes. $E_{\frac{1}{2}}^{red}$ = half-wave potential for reduction. $t_{\frac{1}{2}}^{red}$ = half-life of reduced species.

Compound (**5**) undergoes a one-electron transfer reaction with (**4a**) to afford (**3a**), a reaction which is electrochemically favoured.

Protonation of (**5**) at high dilution with CF_3CH_2OH under a CO atmosphere gave (**6**), the same product as reductive carbonylation of (**7**) (Scheme 2). This type of reaction was originally reported by Threlkel and Bercaw[18] for the synthesis of [Nb(CH_2Ph)(CO)(η-C_5H_5)$_2$] from [Nb(CH_2Ph)$_2$(η-C_5H_5)$_2$]; the mechanism proposed involves formation of a Nb^V hydride intermediate (*cf.* Scheme 2) which reductively eliminates CH_3Ph. We carried out a deuterium labelling experiment using CF_3CH_2OD and found that *ca.* 80% of the deuterium was incorporated in the methyl group, supporting this mechanism. The residual deuterium is associated with the cyclopentadienyl rings and possibly originates from electrophilic attack of a cyclopentadienyl group followed by hydride migration to the metal, as proposed for various metallocenes of Mo and W.[33]

Electrochemistry.—Selected data for the series of compounds (**9a**), (**9b**), (**3a**), and (**3b**) and several other compounds are collected in Table 2, where the potentials are reported *versus* the ferrocenium/ferrocene redox couple, [Fe(η-C_5H_5)$_2$]$^{+/0}$. A discussion of the results for these and other compounds follows.

[{(η-C_5H_5)$_2$ClV}$_2${(2-$CH_2C_6H_4$)$_2$}] (**2**). Cyclic voltammetric scans, sweeping initially in the anodic direction from the rest potential, show a completely irreversible oxidation E_p^a = −0.22 V. Sweeping initially in the cathodic direction (0.020 V s^{-1}), reduction occurs at $E_p^c = -2.23$ V. A smaller anodic peak, showing greater sweep-rate dependence, and indicating a considerable rate of decomposition of the reduced species ($t_{\frac{1}{2}} \approx$ 4 s), is subsequently observed at $E_p^a = -2.05$ V. As the reference redox systems [Fe(η-C_5H_5)$_2$] and bis(biphenyl)chromium(I) tetraphenylborate, added later, showed ΔE_p values of *ca.* 70—80 mV at 0.100 V s^{-1}, it is clear that the large observed peak separation ($\Delta E_p = E_p^a - E_p^c$ = 180 mV) is due to a slow redox reaction in which the slow step is presumably a structural or solvation change accompanying the charge transfer.[34]

[Nb{(2-$CH_2C_6H_4$)$_2$}(η-C_5H_5)$_2$] (**3a**). The cyclic voltammogram (c.v.) shows a reversible one-electron oxidation (ΔE_p = 65 mV at 0.100 V s^{-1}), to produce the Nb^V species, at $E_{\frac{1}{2}} = -0.835$ V, and a fairly reversible one-electron reduction (ΔE_p = 70 mV at 0.020 V s^{-1}) giving the Nb^{III} species at $E_{\frac{1}{2}} = -2.325$ V. A c.v. of (**3a**) is shown in Figure 1. The Nb^V species is completely stable on the c.v. time-scale ($t_{\frac{1}{2}} > 10^3$ s). The reversibility of the $Nb^{V/IV}$ couple was further demonstrated by the linearity of peak current *versus* (sweep rate)$^{\frac{1}{2}}$ plots. Moreover, plots of current *versus* (time)$^{-\frac{1}{2}}$ were linear for potential-step chronoamperometry, and double potential-step chronoamperometric current ratios were as expected for a reversible system. Studies with different sweep rates from 0.5 to 0.005 V s^{-1} indicated that the reduced Nb^{III} species decomposes substantially during the time span of a c.v. scan, with $t_{\frac{1}{2}}$ = 10 s. Some c.v.s of (**3a**), at different sweep rates, showing the comparison between the $Nb^{IV/III}$ reduction leading to decomposition, and the $Nb^{IV/V}$ oxidation yielding stable products, are given in Figure 2.

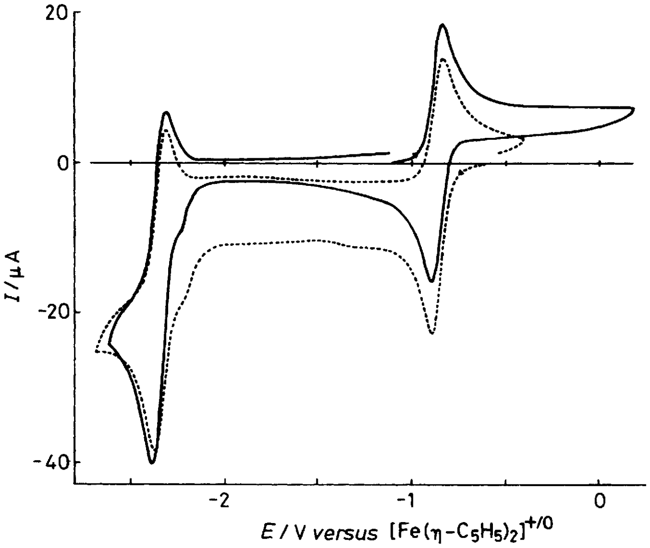


Figure 1. Cyclic voltammograms of 10^{-3} mol dm^{-3} (**3a**) (———) and 10^{-3} mol dm^{-3} (**4a**) (- - -): 0.2 mol dm^{-3} [NBu_4][BF_4] in thf, at a Pt electrode. Sweep rate = 0.100 V s^{-1}

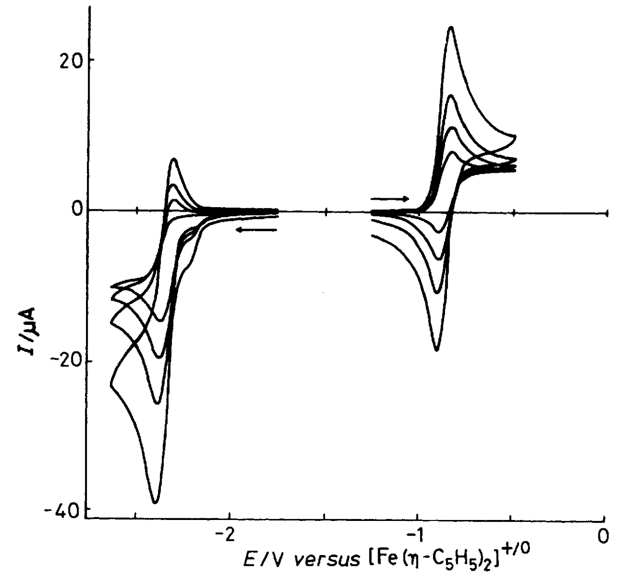


Figure 2. Cyclic voltammograms of 10^{-3} mol dm^{-3} (**3a**): 0.2 mol dm^{-3} [NBu_4][BF_4] in thf at a Pt electrode. The Nb^V/Nb^{IV} and Nb^{IV}/Nb^{III} reactions are shown separately at −0.83 and −2.32 V respectively. Sweep rates (in order of decreasing current) = 0.100, 0.050, 0.020, 0.010 V s^{-1}

[Ta{(2-$CH_2C_6H_4$)$_2$}(η-C_5H_5)$_2$] (**3b**). The c.v. shows a reversible one-electron anodic wave (ΔE_p = 65 mV at 0.100 V s^{-1}) at $E_{\frac{1}{2}} = -1.070$ V and a fairly reversible one electron reduction (ΔE_p = 80 mV at 0.100 V s^{-1}) at $E_{\frac{1}{2}} = -2.43$ V. Sweep-rate dependence shows that the Ta^V species formed by oxidation is completely stable on the c.v. time-scale, whereas the Ta^{III} species formed by reduction decomposes quite rapidly, $t_{\frac{1}{2}} \approx 2$ s. Chronoamperometric data for the $Ta^{V/IV}$ couple also satisfied the same criteria for reversibility as for compound (**3a**).

$[Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ **(4a)**. A c.v. of this compound is shown in Figure 1, showing complete agreement with the c.v. of **(3a)**. The only difference is that the Nb centre is clearly in the +5 oxidation state. The reduction potentials $Nb^{V/IV} = -0.832$ V and $Nb^{IV/III} = -2.320$ V are in excellent agreement with those obtained using the Nb^{IV} species **(3a)**. The sweep-rate dependence of the c.v., and chronoamperometric measurements, confirm the observations made on **(3a)** that the $Nb^{V/IV}$ couple is fully reversible, and that the Nb^{III} species is unstable in solution and undergoes a fairly rapid decomposition ($t_{\frac{1}{2}} \approx 9$ s).

$[Ta\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ **(4b)**. By analogy with **(3a)** and **(4a)** the c.v. and chronoamperometry of this compound was in complete agreement with that of **(3b)**, indicating likewise that the Ta^{III} species is unstable and decomposes quite rapidly ($t_{\frac{1}{2}} \approx 2$ s). The potentials $Ta^{V/IV} = 1.065$ V and $Ta^{IV/III} = -2.41$ V are in good agreement with those obtained from the corresponding Ta^{IV} compound, **(3b)**.

$[Na(18\text{-crown-6})(thf)_2][Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ **(5)**. The c.v.s and equilibrium potential measurements of this species revealed that it was not present in solution, at the time of the electrochemical experiments, in the anionic Nb^{III} oxidation state, but rather as the neutral Nb^{IV} species. The work previously described for **(3a)** and **(4a)** has already indicated that the Nb^{III} species is quite unstable.[18] The c.v. shows that the $Nb^{IV/III}$ electrode reaction occurs superimposed on the fringe of the thf decomposition (background discharge). Thus, while other modes of decomposition may also occur, it is thermodynamically possible that at least some of the solid Nb^{III} compound, upon dissolution in thf, reduces the thf in some unspecified manner, and is itself oxidised to the Nb^{IV} species observed electrochemically. The potentials for $Nb^{V/IV} = -0.845$ V and $Nb^{IV/III} = -2.325$ V are, again, in excellent agreement with those of **(3a)** and **(4a)**.

$[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}(CO)(\eta\text{-}C_5H_5)_2]$ **(6)**. A well-defined, but completely irreversible oxidation is observed in the c.v. at $E_p{}^a = -0.44$ V. Further, smaller, irreversible oxidation peaks were presumably due to decomposition products of the first reaction. Cathodic scans showed no evidence of any reduction prior to background discharge.

$[Nb\{2\text{-}CH_2(C_6H_4)_2Me\text{-}2'\}Cl(\eta\text{-}C_5H_5)_2]$ **(7)**. The c.v. shows an irreversible oxidation at $E_p{}^a = -0.45$ V and an irreversible reduction peak at $E_p{}^c = -2.48$ V, in addition to the quasi-reversible couple at $E_{\frac{1}{2}} = -0.17$ V and associated irreversible reduction around −1.75 V expected[25,35] for $[NbCl_2(\eta\text{-}C_5H_5)_2]$. The comparison of the half-life of the couple at −0.17 V with that for $[NbCl_2(\eta\text{-}C_5H_5)_2]$ confirms the origin of these peaks. These observations can be explained by a redistribution of the type shown below (R′ = alkyl). The irreversible oxidation and reduction peaks may then be presumed to be due to the other products, presumably the dialkyl $[NbR'_2(\eta\text{-}C_5H_5)_2]$, or possibly products of the further decomposition of this material.

$$[Nb(R')Cl(\eta\text{-}C_5H_5)_2] \longrightarrow [NbCl_2(\eta\text{-}C_5H_5)_2] + [NbR'_2(\eta\text{-}C_5H_5)_2]$$

$[V(CH_2Ph)Cl(\eta\text{-}C_5H_5)_2]$ **(8)**. Irreversible oxidation occurs at $E_p{}^a = -0.38$ V, but no evidence of reduction can be seen in the c.v. down to the limits of background decomposition.

$[Nb(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$ **(9a)**. The c.v. of this compound showed a one-electron reversible oxidation ($\Delta E_p = 60$ mV at 0.100 V s^{-1}) at $E_{\frac{1}{2}} = -0.816$ V and a fairly reversible one-electron reduction ($\Delta E_p = 75$ mV at 0.100 V s^{-1}) at $E_{\frac{1}{2}} = -2.213$ V. Over the time-span of c.v. experiments both the Nb^V and the Nb^{III} species are completely stable to decomposition, in contrast with the ready decomposition of the Nb^{III} analogue **(5)**. Despite the fact that the electrochemistry indicated that the Nb^V and Nb^{III} species are quite stable, attempts to prepare these compounds by methods analogous to the preparation of **(4a)** and **(5)** from **(3a)** have so far been unsuccessful. The $E_{\frac{1}{2}}$ values obtained in this work are quite close to those reported previously by Threlkel and Bercaw[18] for the c.v. of **(9a)** in 1 mol dm^{-3} $[NBu^n{}_4][BF_4]$ in thf at a platinum electrode, but must be considered more reliable since although these workers claim $\Delta E_p \approx 90$ mV, ΔE_p can be estimated to be ≈ 300 mV from the c.v. in their Figure 1, *i.e.* far less electrochemically reversible than our results. Their use of a reference electrode containing MeCN (and hence, liquid junctions) casts uncertainty on their potential scale. Nevertheless, although not employing $[Fe(\eta\text{-}C_5H_5)_2]$ as an internal reference, they do quote an $E_{\frac{1}{2}}$ value for $[Fe(\eta\text{-}C_5H_5)_2]$ (but not to sufficient accuracy for reliable referencing) which enables an approximate conversion of their figures to give $E_{\frac{1}{2}}$ values of *ca.* −0.82 and −2.28 V.

$[Ta(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$. **(9b)**. The c.v.s were of rather poor quality. Cathodic scans showed a shoulder at $E_p{}^c = 2.13$ V on a quasi-reversible couple at $E_{\frac{1}{2}} = -2.32$ V. This wave is presumably due to the formation of the Ta^{III} species, $t_{\frac{1}{2}} \approx 7$ s. On an anodic scan, a shoulder at $E_p{}^a = -0.98$ V occurred on an irreversible peak $E_p{}^a = -0.83$ V followed by a broad irreversible peak $E_p{}^a = -0.4$ V: no corresponding reductions were seen.

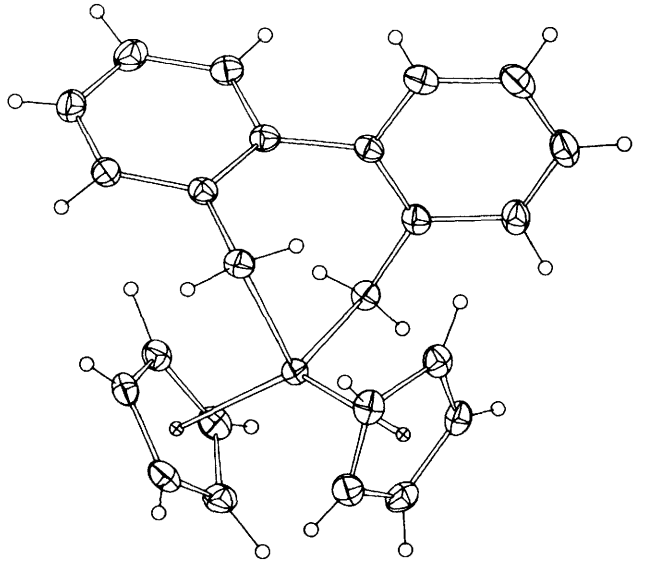


Figure 3. The cation of **(4a)**; 20% probability thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å

Structures.—Single-crystal *X*-ray structure determinations of **(3a)**, **(4a)**, and **(5)** are consistent with the above assignments of stoicheiometry and connectivity. In **(3a)**, the asymmetric unit of the structure comprises a single molecule with no crystallographically imposed symmetry and half of each of a pair of molecules, each disposed with the metal atom located on a crystallographic two-fold axis. In **(4a)**, a cation/anion pair devoid of crystallographic symmetry comprises the asymmetric unit, while in **(5)** one half of each of two independent cations, each located with the metal atom at a crystallographic inversion centre, together with an anion devoid of crystallographically imposed symmetry, comprise the asymmetric unit. The niobium-containing species in all three cases is $[Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ as neutral molecule, monocation, and monoanion respectively; the basic connectivity and disposition of the component fragments is the same in all three species and is depicted for **(4a)** in Figure 3. Consideration of the sequence **(4a)**, **(3a)**, **(5)** offers an opportunity for the comparison of

Table 3. Niobium atom environments in (**3a**), (**4a**), and (**5**); selected bond lengths and angles*

Compound (**3a**)

Molecule 1

Atom	*r*(M–L)	C(1a)	C(1b)
C(1a)	2.33(1)	—	82.9(5)
C(1b)	2.31(1)	82.9(5)	—
C(a1)	2.40(2)	114.0(6)	78.8(6)
C(a2)	2.41(2)	136.0(6)	106.8(6)
C(a3)	2.41(2)	111.5(6)	133.9(6)
C(a4)	2.44(2)	82.5(5)	118.8(5)
C(a5)	2.38(2)	84.5(6)	85.3(5)
C(a0)	2.11(–)	106.8(–)	105.9(–)
C(b1)	2.37(2)	83.2(6)	87.4(6)
C(b2)	2.45(2)	114.2(6)	80.5(6)
C(b3)	2.39(2)	135.8(6)	106.8(6)
C(b4)	2.39(2)	112.4(6)	135.3(6)
C(b5)	2.41(2)	81.2(6)	119.7(6)
C(b0)	2.10(–)	106.5(–)	107.1(–)

C(a0)–M–*C(b0)* 135.2(–)°

Molecule 2

Atom	*r*(M–L)	C(1a)	C(1a′)
C(1a)	2.29(1)	—	84.5(5)
C(1a′)	2.29(1)	84.5(5)	—
C(a1)	2.42(1)	82.4(6)	86.3(6)
C(a2)	2.45(2)	114.5(6)	80.7(6)
C(a3)	2.43(2)	135.0(6)	108.4(6)
C(a4)	2.40(2)	109.2(6)	135.9(6)
C(a5)	2.44(2)	78.3(6)	119.2(6)
C(a0)	2.10(–)	104.0(–)	108.2(–)

C(a0)–M–*C(a0′)* 136.0°

Molecule 3

Atom	*r*(M–L)	C(1a)	C(1a′)
C(1a)	2.25(1)	—	81.5(5)
C(1a′)	2.25(1)	81.5(5)	—
C(a1)	2.40(2)	79.9(6)	119.2(6)
C(a2)	2.42(2)	108.3(6)	138.8(6)
C(a3)	2.40(2)	134.7(6)	109.9(6)
C(a4)	2.39(2)	114.1(6)	81.3(6)
C(a5)	2.37(2)	83.9(6)	86.9(6)
C(a0)	2.08(–)	105.3(–)	108.6(–)

C(a0)–M–*C(a0′)* 134.8(–)°

Compound (**4a**)

Cation

Atom	*r*(M–L)	C(1a)	C(1b)
C(1a)	2.249(3)	—	106.3(1)
C(1b)	2.251(4)	106.3(1)	—
C(a1)	2.430(4)	77.2(1)	117.9(1)
C(a2)	2.394(4)	100.9(1)	131.9(2)
C(a3)	2.400(4)	132.6(1)	102.5(1)
C(a4)	2.428(4)	124.4(1)	75.6(1)
C(a5)	2.440(5)	90.4(1)	84.5(1)
C(a0)	2.103(–)	106.1(–)	103.3(–)
C(b1)	2.441(4)	83.0(1)	90.8(1)
C(b2)	2.436(4)	115.9(1)	76.8(1)
C(b3)	2.396(4)	131.5(1)	99.3(1)
C(b4)	2.396(5)	103.2(1)	131.9(1)
C(b5)	2.418(5)	75.4(1)	124.3(1)
C(b0)	2.102(–)	102.6(–)	105.6(–)

C(a0)–M–*C(b0)* 131.0(–)°

Compound (**5**)

Anion

Atom	*r*(M–L)	C(1a)	C(1b)
C(1a)	2.30(3)	—	80.1(11)
C(1b)	2.35(3)	80.1(11)	—
C(a1)	2.32(4)	134.9(14)	116.5(15)
C(a2)	2.39(6)	100.8(15)	133.5(9)
C(a3)	2.44(5)	79.0(14)	107.1(12)
C(a4)	2.50(6)	86.7(15)	81.3(18)
C(a5)	2.42(5)	123.5(19)	82.5(18)
C(a0)	2.10(–)	105.6(–)	104.9(–)
C(b1)	2.34(6)	103.2(23)	133.3(32)
C(b2)	2.32(5)	132.2(23)	117.9(27)
C(b3)	2.33(7)	131.8(26)	88.3(27)
C(b4)	2.34(9)	97.4(21)	76.7(20)
C(b5)	2.36(7)	82.2(17)	104.7(31)
C(b0)	2.05(–)	110.7(–)	105.2(–)

C(a0)–M–*C(b0)* 136.0(–)°

* Cyclopentadienyl atoms are italicized. The first column in the matrix is the bond length (Å); other entries are the angles subtended by the relevant atoms at the head of the row and column. In the case of (**3a**), primed atoms are generated by the intramolecular two-fold rotor. C(0) represents the centroid of the C_5H_5 ring.

perturbations arising from the sequential addition of single *d* electrons to the d^0 configuration; for this purpose Table 3 provides data enabling a comparison of the geometry of the metal atom environment, albeit rather imprecisely for (**5**). In the sequence (**4a**), (**3a**), (**5**), there is an increase in the niobium–carbon distances of the chelating ligand, from 2.249(3) and 2.251(4) (mean 2.25_0) to 2.25(1)—2.33(1) (mean 2.29_7) to 2.30(3) and 2.35(3) (mean 2.32_5 Å); the associated chelate angle diminishes from 106.3(1) to 81.5(5)—84.5(5) (mean $83._0$) to 80(1)°. Clearly the most pronounced change is found on passing from the d^0 to d^1 configuration, and that most notably in respect of the chelate angle. While diminution in the angle follows naturally as a consequence of increased metal–ligand distance, the magnitude of the change in this instance supports the possibility of some additional effect, probably electronic in nature, in accordance with theoretical predictions[36] that populating the d^0 lowest unoccupied molecular orbital (**VI**) reduces the angle subtended by the σ-bound ligands.

In keeping with this large change, parallel variations are observed in respect of the angles subtended at the chelating atoms [103.1(2) and 102.7(2) (mean $102._9$) to 117.0(9)—121.6(9) (mean $118._7$) to 123(2)° (two)] and also in respect of the Nb···C(2) distances [2.959(4) and 2.960(4) Å to 3.26(1)—3.29(1) Å to 3.35(3) and 3.39(3) Å] respectively for (**4a**), (**3a**), and (**5**). The effect of chelation may be assessed, at least in regard

Table 4. Independent cation geometries for (**5**)*

Cation 1

Atom	*r*(M–L)	O(2)	O(5)	O(8)
O	2.28(2)	82.5(9)	95.2(9)	91.5(8)
O(2)	2.77(3)		61.4(7)	119.5(7)
O(5)	2.80(3)			59.4(7)
O(8)	2.68(2)			

Cation 2

Atom	*r*(M–L)	O(2)	O(5)	O(8)
O	2.32(4)	84.4(11)	85.1(10)	91.4(9)
O(2)	2.79(3)		59.0(6)	119.1(7)
O(5)	2.73(2)			61.1(6)
O(8)	2.77(2)			

* The first column in the matrix is the metal–ligand distance (Å). Other entries are the angles subtended at the metal by the relevant atoms at the head of the row and column. Italicized atoms belong to the thf ligands.

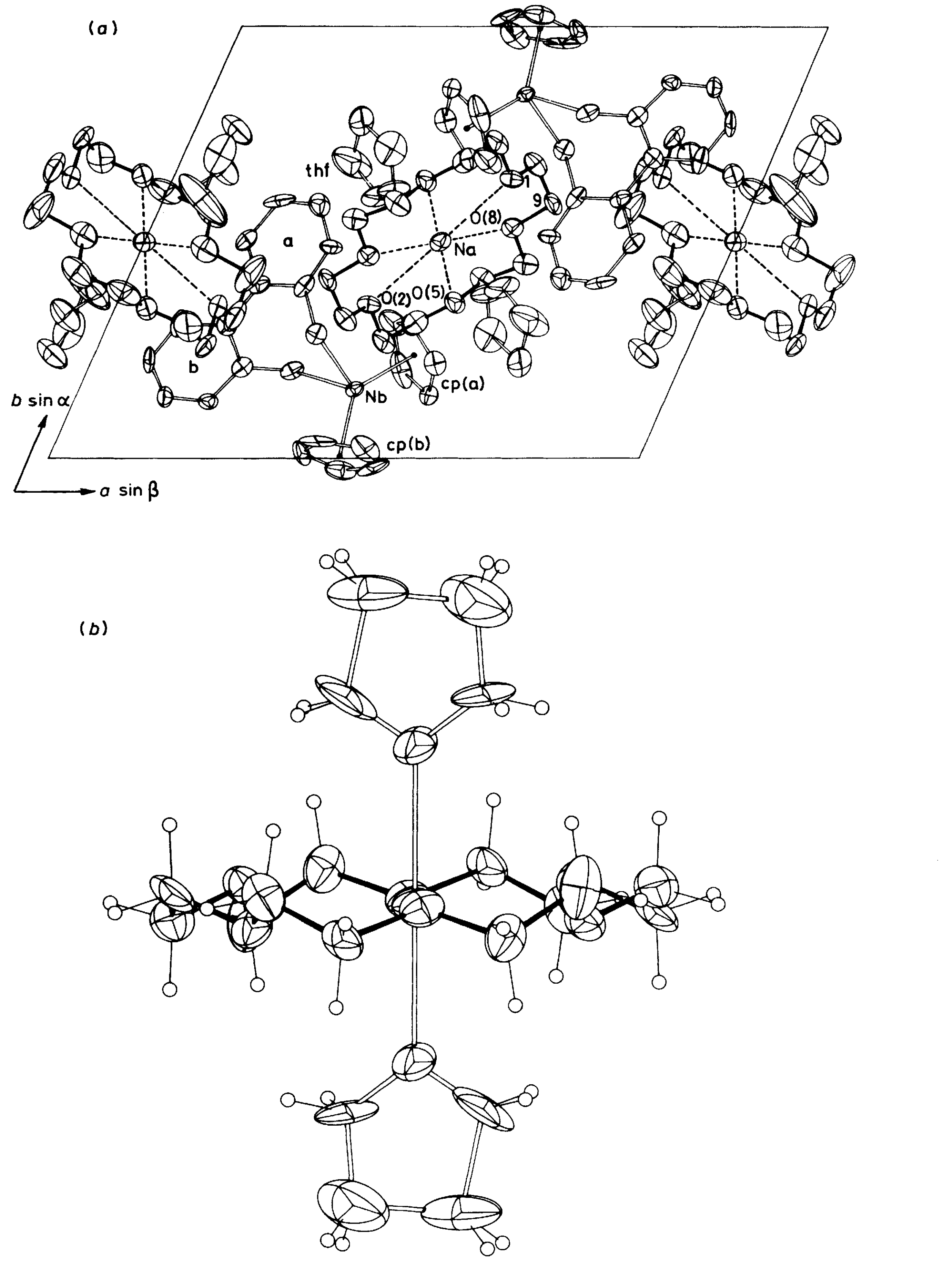


Figure 4. (*a*) Unit-cell contents of (**5**) projected down *c* (cp = cyclopentadienyl); (*b*) the cation of (**5**) projected normal to the Na–O(thf) axis

to (**3a**) [niobium–ligand distance (mean) 2.29$_7$ Å, chelate angle (mean) 83.$_0$°], by comparison with [Nb(CH$_2$Ph)$_2$(η-C$_5$H$_5$)$_2$]^{7} and [Nb(CH$_2$C$_6$H$_4$CH$_2$-*o*)(η-C$_5$H$_4$SiMe$_3$)$_2$]^{37} for which these parameters are 2.304 Å, 79.0° and 2.286 Å, 72.5° respectively; the chelate angle in the present complex is, unusually, larger than the values for related monodentate systems in consequence of the ligand 'bite' which remains large in spite of the flexibility of the ligand. (In the case of the second related compound, however, the comparison is probably not valid because of the unusual bulk associated with the cyclopentadienide ligands, by virtue of the trimethylsilyl substituents.) Also of interest for comparative purposes are the parameters of the 'complex' of the smallest available 'metal', namely the ether, (2-CH$_2$C$_6$H$_4$)$_2$O, in its magnesium bromide complex discussed elsewhere;^{38} here,

Table 5. Non-hydrogen atom co-ordinates for (**3a**)

Atom	*x*	*y*	*z*
Molecule 1			
Nb	0.253 56(4)	0.2021(1)	0
Cyclopentadienyl a			
C(1)	0.3025(6)	0.3361(19)	−0.0308(21)
C(2)	0.2909(5)	0.2926(18)	−0.1522(16)
C(3)	0.2989(6)	0.1676(15)	−0.1515(16)
C(4)	0.3152(5)	0.1342(14)	−0.0386(16)
C(5)	0.3158(5)	0.2429(16)	0.0364(15)
C(0)	0.3047(−)	0.2347(−)	−0.0674(−)
Cyclopentadienyl b			
C(1)	0.1719(5)	0.1503(19)	0.0159(19)
C(2)	0.1715(5)	0.2575(18)	−0.0531(16)
C(3)	0.1929(6)	0.2353(16)	−0.1630(19)
C(4)	0.2032(6)	0.1122(19)	−0.1674(20)
C(5)	0.1894(6)	0.0569(14)	−0.0528(22)
C(0)	0.1858(−)	0.1625(−)	−0.0842(−)
Ligand section a			
C(1)	0.2497(5)	0.0722(11)	0.1753(15)
C(2)	0.2730(4)	0.1156(13)	0.2857(14)
C(3)	0.3129(5)	0.0715(14)	0.3084(14)
C(4)	0.3365(5)	0.1098(17)	0.4113(20)
C(5)	0.3189(5)	0.1876(17)	0.5000(18)
C(6)	0.2787(5)	0.2260(17)	0.4807(15)
C(7)	0.2562(5)	0.1956(16)	0.3744(14)
Ligand section b			
C(1)	0.2316(5)	0.3492(12)	0.1544(14)
C(2)	0.2006(5)	0.3186(12)	0.2576(15)
C(3)	0.1610(5)	0.3652(15)	0.2568(16)
C(4)	0.1325(7)	0.3413(19)	0.3476(18)
C(5)	0.1411(6)	0.2657(19)	0.4445(20)
C(6)	0.1827(5)	0.2183(15)	0.4519(14)
C(7)	0.2111(4)	0.2437(14)	0.3588(16)
Molecule 2			
Nb	$\frac{1}{2}$	0	0.1852(2)
Cyclopentadienyl			
C(1)	0.5749(5)	0.0055(19)	0.1549(12)
C(2)	0.5669(6)	−0.1016(17)	0.2249(17)
C(3)	0.5496(6)	−0.0686(16)	0.3447(21)
C(4)	0.5489(6)	0.0602(20)	0.3466(13)
C(5)	0.5647(5)	0.1100(15)	0.2297(17)
C(0)	0.5609(−)	0.0054(−)	0.2601(−)
Ligand			
C(1)	0.5012(5)	0.1415(13)	0.0243(11)
C(2)	0.4713(4)	0.1220(12)	−0.0840(12)
C(3)	0.4348(5)	0.1914(15)	−0.0974(16)
C(4)	0.4094(5)	0.1833(18)	−0.2029(21)
C(5)	0.4206(5)	0.1030(17)	−0.2975(15)
C(6)	0.4549(4)	0.0370(11)	−0.2915(11)
C(7)	0.4810(4)	0.0397(10)	−0.1831(11)
Molecule 3			
Nb	0	0	0.1269(2)
Cyclopentadienyl			
C(1)	0.0419(6)	0.1770(14)	0.1739(20)
C(2)	0.0322(6)	0.1248(17)	0.2888(18)
C(3)	0.0545(7)	0.0033(20)	0.2842(15)
C(4)	0.0736(6)	−0.0076(20)	0.1654(19)
C(5)	0.0660(6)	0.0953(21)	0.1032(17)
C(0)	0.0538(−)	0.0787(−)	0.2029(−)
Ligand			
C(1)	−0.0186(5)	0.1238(12)	−0.0354(12)
C(2)	−0.0426(5)	0.0766(13)	−0.1461(16)
C(3)	−0.0854(6)	0.0958(18)	−0.1495(17)
C(4)	−0.1091(6)	0.0590(20)	−0.2544(23)
C(5)	−0.0893(6)	−0.0031(21)	−0.3493(18)
C(6)	−0.0488(6)	−0.0261(15)	−0.3432(14)
C(7)	−0.0228(5)	0.0101(15)	−0.2423(15)

C–O distances are 1.440(9)—1.458(8) Å, with O–C–O 112.1(5)—113.0(5)°. Given the flexibility of the ligand, the effect of changing metal–ligand distance may be observed in the variation of the torsion angle of the biphenyl system. For (**4a**), (**3a**), (**5**), the mean falls from $78._4$ to $62._4$ to $59._6$°; for the ether, the value is $38._5$°.

By contrast, the metal–cyclopentadienyl geometry is much less sensitive to change in oxidation state; for all three systems, the distance of the niobium to the ring centroids is 2.10 Å, with the exception of one ring in (**5**) (2.05 Å); mean niobium–carbon distances for (**4a**), (**3a**), (**5**) are 2.41_8, 2.4_1, and 2.3_8 Å. Corresponding centroid–niobium–centroid angles are $131._0$, $135._3$, and $136._0$°, the enlargement of angle paralleling the diminution of the chelate angle of the bidentate ligand; these values are similar to a number of values available for bis(η^5-cyclopentadienyl)niobium(IV) complexes.[7] In (**3a**) the relatively short Nb ··· C(2) distances [2.959(4) and 2.960(4) Å] may be indicative of some metal–π-arene interaction, and thus a departure from a metallacycle structure towards that of (**III**).

The two independent sodium environments in (**5**), Figures 4(*a*) and (*b*), both disposed about the metal atom on a crystallographic inversion centre are (puckered) hexagonal bipyramidal with the Na–O(thf), O(crown ether) distances being 2.28(2) and 2.32(4), (mean 2.3_0) and 2.68(2)—2.80(3) (mean 2.7_6 Å) respectively; *cf.* the more precisely determined values of 2.364(7) and 2.712(5)—2.791(4) (mean 2.74_7 Å) observed for the same species, also centrosymmetric, in ref. 39.

Experimental

General Procedures.—These were described in Parts 1[1] and 2.[2]

Materials.—The dichlorobis(η-cyclopentadienyl)metal(IV) complexes $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = V, Nb, or Ta) were purchased (M = V, Sigma) or prepared according to the literature procedures.[40] The Grignard reagents $\{o\text{-}[(thf)_nClMgCH_2]C_6H_4\}_2$ (**1**), and $o\text{-}[(thf)_nClMgCH_2]C_6H_4\text{–}C_6H_4Me\text{-}o$ were obtained by the methods described in Part 2.[2] $K[BHBu^s_3]$ (1 mol dm^{-3}) in thf, $HBF_4{\cdot}OMe_2$, and CF_3CH_2OH were purchased from Aldrich. CF_3CH_2OD was prepared by passing DCl, generated from D_2O and neat PCl_3, through a suspension of $Na[OCH_2CF_3]$ in OEt_2 and purified by distillation (b.p. 66—70 °C).

Physical and Analytical Measurements.—The $g_{av.}$ values from e.s.r. data were measured at 20 °C relative to polycrystalline 2,2-diphenylpicrylhydrazyl, using a Varian or Brüker ER100 spectrometer. Proton and ^{13}C n.m.r. were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz) or Brüker WP-80 spectrometers. I.r. were recorded on a Perkin-Elmer 283 spectrometer. Elemental (C, H, Cl) analyses of the compounds were performed by Canadian Microanalytical Service Ltd., Vancouver.

Preparation of $[Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**3a**).—To a suspension of $[NbCl_2(\eta\text{-}C_5H_5)_2]$ (5.9 g, 20 mmol) in thf (20 cm^3) at −78 °C was added the di-Grignard reagent (**1**) (250 cm^3, 0.08 mol dm^{-3}, 20 mmol). The purple solution was warmed to room temperature and stirred for 2 h whereupon the solvent was removed *in vacuo* and the product extracted with diethyl ether (*ca.* 3 × 200 cm^3). Concentration of the filtrate to *ca.* 50 cm^3 and cooling for 1 day at *ca.* −30 °C afforded purple crystals of the *product* (**3a**) (6.3 g, 78%). M.p. 192 °C (Found: C, 71.1; H, 5.65. Calc. for $C_{24}H_{22}Nb$: C, 71.5; H, 5.5%).

Preparation of [Ta{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$] (**3b**).—The procedure was as described for the Nb analogue. [$TaCl_2$(η-$C_5H_5)_2$] (2.4 g, 6.3 mmol) and (**1**) (90 cm^3, 0.07 mol dm^{-3}, 6.3 mmol) afforded the *product* (**3b**) (2.50 g, 81%) as a dark brown solid. M.p. 185 °C (Found: C, 58.3; H, 4.5. Calc. for $C_{24}H_{22}Ta$: C, 58.6; H, 4.5%).

Preparation of [{(η-$C_5H_5)_2$ClV}$_2${(2-$CH_2C_6H_4)_2$}] (**2**).—The reaction between [VCl_2(η-$C_5H_5)_2$] (1.5 g, 6.0 mmol) and the di-Grignard reagent (100 cm^3, 0.06 mol dm^{-3}, 6.0 mmol) was as described for the Nb analogue. Yield of (**2**) as a dark green solid, 1.4 g (65%); m.p. 142 °C (Found: C, 66.4; H, 5.45; Cl, 11.1. Calc. for $C_{34}H_{32}Cl_2V_2$: C, 66.6; H, 5.3; Cl, 11.6%); *m*/*e* 542 (P − 2Cl)$^+$.

Preparation of [Nb{2-$CH_2(C_6H_4)_2$Me-2′}Cl(η-$C_5H_5)_2$] (**7**).—To a suspension of [$NbCl_2$(η-$C_5H_5)_2$] (1.3 g, 4.4 mmol) in thf (10 cm^3) at −78 °C was added the Grignard reagent of 2-chloromethyl-2′-methylbiphenyl[1] (90 cm^3, 0.05 mol dm^{-3}, 4.5 mmol). On warming to room temperature the mixture was stirred for 15 h whereupon the solvent was removed *in vacuo* and the residue extracted with OEt_2 (100 cm^3). Concentration of the filtrate to *ca.* 20 cm^3 and cooling for 1 d at *ca.* −30 °C afforded the *product*, (**7**), as purple crystals. Yield 1.3 g (67%); m.p. 129 °C.

Preparation of [V(CH_2Ph)Cl(η-$C_5H_5)_2$] (**8**).—To a suspension of [VCl_2(η-$C_5H_5)_2$] (1.0 g, 3.98 mmol) in thf (10 cm^3) at −78 °C was added benzylmagnesium chloride (9.5 cm^3, 0.88 mol dm^{-3}, 8.36 mmol). On warming to room temperature the mixture was stirred for 18 h whereupon the solvent was removed *in vacuo* and the residue extracted with OEt_2 (100 cm^3). Concentration of the filtrate to 50 cm^3 and cooling at −30 °C afforded the *product*, (**8**), as dark green crystals. Yield 0.87 g (60%); m.p. 98 °C (Found: C, 65.1; H, 5.6. Calc. for $C_{17}H_{17}ClV$: C, 66.4; H, 5.6%).

Preparation of [Ta($CH_2Ph)_2$(η-$C_5H_5)_2$] (**9b**).—The reaction between [$TaCl_2$(η-$C_5H_5)_2$] (0.91 g, 1.97 mmol) and benzylmagnesium chloride (5 cm^3, 0.88 mol dm^{-3}, 4.40 mmol) was as described for (**8**), except that the residue was washed with OEt_2 (20 cm^3), extracted with benzene (100 cm^3) and filtered. Concentration of the filtrate to 30 cm^3 and cooling at 10 °C afforded the product, (**9b**), as reddish brown crystals. Yield 0.60 g (62%); m.p. 149 °C (Found: C, 59.0; H, 4.8. Calc. for $C_{24}H_{24}Ta$: C, 58.4; H, 4.9%).

Preparation of [Nb{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$][BF_4] (**4a**).—To a mixture of (**3a**) (1.0 g, 2.5 mmol) and $AgBF_4$ (0.48 g, 2.5 mmol) was added thf (30 cm^3) at room temperature. After 1 h the solvent was removed by filtration and the residue extracted with nitromethane (30 cm^3). Filtration yielded a red solution which on concentration to *ca.* 5 cm^3 and cooling to *ca.* −30 °C afforded deep red prisms of the *product* (**4a**) (0.97 g, 80%). M.p. 238 °C (Found: C, 58.5; H, 4.55. Calc. for $C_{24}H_{22}BF_4Nb$: C, 58.8; H, 4.55%). ^{1}H N.m.r. (60 MHz, CD_3NO_2), δ 3.23 (AB, J_{AB} 11.5 Hz, 4 H), 5.99 (s, 10 H), 7.03, 7.50 (m, 8 H); ^{13}C n.m.r. (^{1}H decoupled, CD_3NO_2), δ 57.2 (CH_2), 111.8 (C_5H_5), 125.7, 130.8, 131.6, 142.8, 144.9 (C_6H_4).

Table 6. Non-hydrogen atom co-ordinates for (**4a**)

Atom	x	y	z
Nb	0.897 19(2)	0.258 41(2)	0.115 61(2)
Cyclopentadienyl a			
C(1)	0.8327(3)	0.4299(3)	0.1353(3)
C(2)	0.9373(3)	0.4388(3)	0.1429(3)
C(3)	0.9995(3)	0.3878(3)	0.2426(3)
C(4)	0.9345(3)	0.3465(3)	0.2951(3)
C(5)	0.8298(3)	0.3720(3)	0.2289(3)
C(0)	0.9068(−)	0.3950(−)	0.2090(−)
Cyclopentadienyl b			
C(1)	0.9372(3)	0.1293(3)	−0.0046(3)
C(2)	1.0194(3)	0.1268(3)	0.0996(3)
C(3)	1.0703(3)	0.2216(3)	0.1170(3)
C(4)	1.0206(3)	0.2850(3)	0.0212(4)
C(5)	0.9386(3)	0.2266(3)	−0.0530(3)
C(0)	0.9972(−)	0.1978(−)	0.0360(−)
Ligand section a			
C(1)	0.7417(3)	0.2639(2)	−0.0261(3)
C(2)	0.6654(2)	0.2535(2)	0.0331(3)
C(3)	0.5966(3)	0.3365(3)	0.0320(3)
C(4)	0.5271(3)	0.3291(4)	0.0894(4)
C(5)	0.5235(3)	0.2425(4)	0.1493(4)
C(6)	0.5861(3)	0.1597(3)	0.1485(3)
C(7)	0.6576(2)	0.1632(3)	0.0905(3)
Ligand section b			
C(1)	0.8835(3)	0.1340(3)	0.2345(3)
C(2)	0.8229(3)	0.0520(3)	0.1560(3)
C(3)	0.8701(3)	−0.0437(3)	0.1497(3)
C(4)	0.8163(3)	−0.1192(3)	0.0771(4)
C(5)	0.7139(3)	−0.1043(3)	0.0076(4)
C(6)	0.6644(3)	−0.0120(3)	0.0138(3)
C(7)	0.7174(3)	0.0675(2)	0.0869(3)
Anion			
B	0.2647(5)	0.4458(5)	0.1654(6)
F(1)	0.3496(2)	0.4987(3)	0.1720(3)
F(2)	0.1725(3)	0.4888(3)	0.1129(3)
F(3)	0.2653(3)	0.3879(4)	0.2481(4)
F(4)	0.2592(5)	0.3722(5)	0.0774(7)

Preparation of [Ta{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$][BF_4] (**4b**).—The procedure was as described for the Nb analogue. (**3b**) (0.94 g, 1.9 mmol) and $AgBF_4$ (0.38 g, 1.9 mmol) afforded the *product* (**4b**), as red prisms 0.86 g (78%). M.p. 270 °C (decomp.) (Found: C, 49.8; H, 4.2. Calc. for $C_{24}H_{22}BF_4Ta$: C, 49.8; H, 3.85%). ^{1}H N.m.r. (60 MHz, CD_3NO_2), δ 2.81 (AB, J_{AB} 14.0 Hz, 4 H), 6.22 (s, 10 H), 7.11, 7.52 (m, 8 H); ^{13}C n.m.r. (^{1}H decoupled, CD_3NO_2), δ 65.0 (CH_2) 113.1 (C_5H_5), 126.6, 130.5, 131.8, 142.8, 145.9 (C_6H_4).

Preparation of [Na(18-crown-6)(thf)$_2$][Nb{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$] (**5**).—To a solution of (**3a**) (0.67 g, 1.7 mmol) in thf (30 cm^3) at −78 °C was added slowly a thf solution containing Na[$C_{10}H_8$] (16 cm^3, 0.11 mol dm^{-3}, 1.7 mmol) and 18-crown-6 (0.44 g, 1.7 mmol). After warming to room temperature the solution was stirred for 3 h. Solvent was then removed *in vacuo* and the residue washed with pentane (2 × 20 cm^3) and extracted with thf (30 cm^3). The brown solution was filtered and on concentration to *ca.* 15 cm^3 and addition of pentane (10 cm^3) red-brown acicular crystals of the *product*, (**5**), deposited (0.72 g, 52%); m.p. 258—260 °C (decomp.).

Preparation of [Nb{2-$CH_2(C_6H_4)_2$Me-2′}(CO)(η-$C_5H_5)_2$] (**6**).—*Method* 1. Sodium amalgam (0.044 g Na, 1.9 mmol, 4.4 g Hg) was added to a solution of (**3a**) (0.77 g, 1.9 mmol) in thf (200

Table 7. Non-hydrogen atom co-ordinates for (**5**)

Atom	*x*	*y*	*z*
Anion			
Nb	0.4671(2)	0.1588(2)	0.1278(2)
Cyclopentadienyl a			
C(1)	0.597(2)	0.145(2)	0.043(5)
C(2)	0.582(3)	0.220(4)	0.100(2)
C(3)	0.513(3)	0.309(3)	0.044(4)
C(4)	0.480(4)	0.315(5)	−0.044(5)
C(5)	0.532(4)	0.203(6)	−0.055(3)
C(0)	0.541(−)	0.238(−)	0.018(−)
Cyclopentadienyl b			
C(1)	0.536(7)	0.016(6)	0.309(6)
C(2)	0.555(6)	−0.024(4)	0.233(8)
C(3)	0.500(7)	−0.025(5)	0.179(5)
C(4)	0.423(4)	0.016(6)	0.227(7)
C(5)	0.450(8)	0.039(3)	0.314(5)
C(0)	0.493(−)	0.005(−)	0.252(−)
Ligand section a			
C(1)	0.360(2)	0.287(2)	0.180(2)
C(2)	0.303(2)	0.398(2)	0.093(2)
C(3)	0.320(2)	0.487(2)	0.070(3)
C(4)	0.269(2)	0.585(3)	−0.010(3)
C(5)	0.198(2)	0.595(2)	−0.069(3)
C(6)	0.171(2)	0.504(2)	−0.049(2)
C(7)	0.227(2)	0.401(2)	0.036(2)
Ligand section b			
C(1)	0.347(2)	0.203(2)	0.005(2)
C(2)	0.260(2)	0.210(2)	0.047(2)
C(3)	0.229(2)	0.131(2)	0.077(2)
C(4)	0.151(2)	0.143(2)	0.116(2)
C(5)	0.096(2)	0.229(3)	0.129(3)
C(6)	0.120(2)	0.312(3)	0.103(2)
C(7)	0.202(2)	0.307(3)	0.067(2)
Cation a			
Na	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Crown ether ligand			
C(1)	0.603(2)	0.678(2)	0.369(2)
O(2)	0.427(1)	0.355(2)	0.522(2)
C(3)	0.480(3)	0.270(3)	0.490(3)
C(4)	0.520(2)	0.314(3)	0.376(3)
O(5)	0.570(1)	0.360(2)	0.386(2)
C(6)	0.601(2)	0.412(3)	0.271(3)
C(7)	0.661(2)	0.448(2)	0.300(2)
O(8)	0.611(1)	0.532(1)	0.338(1)
C(9)	0.662(2)	0.588(2)	0.344(3)
Tetrahydrofuran			
O(1)	0.382(2)	0.620(2)	0.365(2)
C(2)	0.345(3)	0.714(4)	0.342(3)
C(3)	0.276(2)	0.756(5)	0.223(4)
C(4)	0.326(9)	0.637(9)	0.193(12)
C(5)	0.362(3)	0.607(4)	0.280(4)
Cation b			
Na	0	$\frac{1}{2}$	$\frac{1}{2}$
Crown ether ligand			
C(1)	−0.204(3)	0.573(5)	0.642(6)
O(2)	−0.107(2)	0.516(2)	0.679(2)
C(3)	−0.090(3)	0.429(4)	0.786(4)
C(4)	0.004(3)	0.382(3)	0.818(3)
O(5)	0.053(1)	0.348(2)	0.725(2)
C(6)	0.138(4)	0.305(5)	0.745(6)
C(7)	0.183(3)	0.259(4)	0.667(7)
O(8)	0.173(1)	0.352(2)	0.557(2)
C(9)	0.210(3)	0.329(4)	0.449(6)
Tetrahydrofuran			
O(1)	−0.040(2)	0.379(2)	0.466(3)
C(2)	−0.085(9)	0.423(9)	0.327(9)
C(3)	−0.056(3)	0.313(5)	0.374(3)
C(4)	−0.072(3)	0.244(4)	0.493(5)
C(5)	−0.078(3)	0.331(4)	0.551(5)

cm^3). After stirring for 2 h the red-brown solution was filtered and CF_3CH_2OH (or CF_3CH_2OD) (0.14 cm^3, 1.4 mmol) in thf (30 cm^3) was added over 8 h under CO (1 atm) whereupon the solvent was removed *in vacuo* and the product extracted with pentane (70 cm^3). On filtration and concentration the green solution yielded a turquoise solid (0.63 g, 76%); m.p. 105 °C (Found: C, 68.6; H, 5.55. Calc. for $C_{25}H_{23}NbO$: C, 69.5; H, 5.55%). I.r. (KBr disc), 1 888 cm^{-1} (Nb–CO); ^{1}H n.m.r. (60 MHz, C_6D_6), δ 1.74 (AB, J_{AB} 9.5 Hz, 2 H), 2.28 (s, 3 H) 4.31, 4.33 (s, 2 × 5 H), 7.14 (m, 8 H); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ 5.7, (CH_2), 20.28 (CH_3), 92.5, 92.9 (C_5H_5), 120.7, 125.7, 126.8, 128.0, 129.2, 130.2, 131.4, 137.1 [$(C_6H_4)_2$], 157.5 (CO).

Method 2. A solution of (**7**) (0.5 g, 1.14 mmol) in thf (50 cm^3) and Na amalgam (0.05 g Na, 2.2 mmol, 5 g Hg) was stirred under an atmosphere of CO for 1 d. The procedure was then as for method 1. Yield 0.25 g, (51%).

Preparation of (**4a**) *from* (**5**).—*Method* 1. To a thf solution of (**5**), prepared from (**3a**) (0.5 g, 1.3 mmol) according to the above procedure but without 18-crown-6, was added $HBF_4{\cdot}OMe_2$ (0.54 cm^3, 2.6 mmol). After 1 h at room temperature the mixture was filtered and the solid subject to extraction with nitromethane. Procedure thereafter was as for the above synthesis of (**4a**). Yield 0.25 g (40%).

Method 2. $[CPh_3][BF_4]$ (0.43 g, 1.3 mmol) was added to a thf solution of (**5**) prepared from (**3a**) (0.26 g, 0.65 mmol). The procedure after 1 h of stirring at room temperature was as described in method 1.

Reduction of (**4a**) *to* (**3a**).—*Method* 1. To a suspension of (**4a**) (0.23 g, 0.47 mmol) in thf (30 cm^3) was added $NaBH_4$ (0.1 g, 2.82 mmol). After 3 h the solvent was removed *in vacuo* and the residue subjected to the same procedure as for the synthesis of (**3a**). Yield 0.11 g (58%).

Method 2. To a suspension of (**4a**) (0.15 g, 0.3 mmol) in thf (50 cm^3) was added $K[BHBu^s_3]$ (0.30 cm^3, 1 mol dm^{-3}, 0.3 mmol). The procedure was then as for method 1. Yield 0.06 g (49%).

Electrochemistry.—The electrochemical experiments were carried out using a P.A.R. 173 Potentiostat, P.A.R. 175 Programmer, and Bryans 26000 X-Y Chart Recorder. The cell, which was constructed at the School of Chemistry, University of Western Australia, consists essentially of a glass tube carrying gas lines and access ports with ground glass joints. One gas line was connected to the base of the cell *via* a glass frit. The electrode assembly comprised a platinum-ball working electrode of approximate area 0.24 cm^2 set in soda glass; surrounding this, a platinum-coil counter electrode set in soda glass; and a glass luggin capillary probe fitted with an Ag/Ag^+ reference electrode[41] separated from the working solution by a P.A.R. Vycor frit. These electrodes were mounted through a

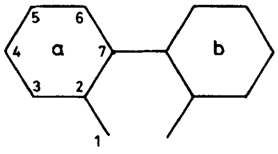
Teflon bung which was fitted into a ground glass joint at the top of the cell.

Prior to an experiment the thf was freshly distilled from $LiAlH_4$ and freeze-degassed under vacuum. The platinum working electrode was cleaned electrochemically by cycling its potential between the onset of H_2 and O_2 evolution in 1 mol dm^{-3} H_2SO_4 until a satisfactory cyclic voltammogram was obtained.[42] The electrode was then washed with deionised water, and subsequently with dried thf. The cell, containing weighed solid samples of the materials for study and of tetrabutylammonium tetrafluoroborate supporting electrolyte was repeatedly evacuated and flushed with high purity argon, as was the electrode assembly in a separate vessel. All subsequent manipulations were carried out in an air- and moisture-free environment using Schlenk techniques and a positive pressure of argon. The silver wire of the reference electrode was immersed in a fresh solution of $AgBF_4$ (0.10 mol dm^{-3}) and $[NBu_4][BF_4]$ (0.10 mol dm^{-3}) in dried thf. An aliquot of dried thf was introduced into the cell containing the solid samples which were dissolved by bubbling argon through the bottom glass frit. The electrodes were then transferred, under argon, to the cell. The above procedure was varied slightly with the more sensitive compounds studied which were added directly from a sealed glass ampoule to the prepared electrolyte solution in the cell through an access port, the instant before beginning the electrochemical studies. All solutions for electrochemical study were prepared to be 0.20 mol dm^{-3} in $[NBu_4][BF_4]$ and 1.0×10^{-3} mol dm^{-3} in the active species.

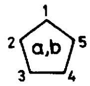
All potentials were internally referenced by adding ferrocene or bis(biphenyl)chromium(I) tetraphenylborate through an access port, and are reported against the $[Fe(\eta\text{-}C_5H_5)_2]^{+/0}$ reference redox system (in thf), as recommended by Gritzner and Kuta.[43] Potentials could usually be determined to ± 0.002 V. Half-lives of unstable species were determined from the cyclic voltammetry using the method of Nicholson and Shain.[44,45] The uncertainty in these values, due to difficulty in obtaining reproducible measurements, gives error limits such that the true value can be considered to lie between half the value quoted and twice the value quoted.

Crystallography.—Unique data sets were measured at 295 K on crystals mounted in capillaries to a $2\theta_{max.}$ limit determined by the scope of the data using a Syntex $P2_1$ four-circle diffractometer, fitted with a monochromatic Mo-K_α radiation source ($\lambda = 0.710\,69$ Å), in conventional $2\theta/\theta$ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the (basically) 9×9 block-diagonal least-squares refinement in each case after absorption correction and solution of the structures by the heavy-atom method. [In the case of (**3a**) very little coarsely crystalline material was available; an oversize crystal was employed, and the precision of the determination reflects this.] At convergence, reflection weights were $[\sigma^2(F_o) + 0.0003(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[46] Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were constrained in the refinement with idealized (x,y,z,U). Computation used the *X*-RAY 76 program system[47] implemented on a Perkin-Elmer 3240 computer by Dr. S. R. Hall.

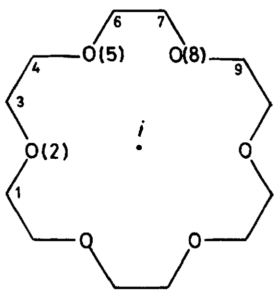
Selected bond lengths and angles are in Table 3, independent cation geometries of (**5**) in Table 4, and atomic co-ordinates are in Tables 5—7. The cation of (**4a**) is shown in Figure 3 and that of (**5**) in Figure 4. Non-hydrogen atom labelling in the various species is given below; hydrogen atom labelling follows that of the parent atom, suffixed A, B, C *etc.* if required.



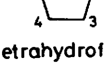
biphenyl derivatives



cyclopentadienyl



18-crown-6



tetrahydrofuran

Crystal data for (**3a**). $C_{24}H_{22}Nb$, $M = 403.3$, orthorhombic, space group *Pnn*2 (no. 34, C_{2v}^{10}), $a = 31.985(9)$, $b = 10.875(3)$, $c = 10.527(3)$ Å, $U = 3\,662(1)$ Å^3, $D_c = 1.46$ g cm^{-3} ($Z = 8$), $F(000) = 1\,656$, $\mu_{Mo} = 6.4$ cm^{-1}, $2\theta_{max.} = 50°$; $N = 3\,427$, $N_o = 2\,326$, $R = 0.045$, $R' = 0.046$.

Crystal data for (**4a**). $(C_{24}H_{22}Nb)(BF_4)$, $M = 490.1$, monoclinic, space group $P2_1/n$ [no. 14, C_{2h}^5 (variant)], $a = 13.602(6)$, $b = 12.934(5)$, $c = 12.623(5)$ Å, $\beta = 110.26(3)°$, $U = 2\,083(1)$ Å^3, $D_c = 1.46$ g cm^{-3} ($Z = 4$), $F(000) = 944$, $\mu_{Mo} = 6.4$ cm^{-3}, $2\theta_{max.} = 60°$, $N = 6\,124$, $N_o = 4\,163$, $R = 0.040$, $R' = 0.053$.

Crystal data for (**5**). $(C_{24}H_{22}Nb)\,Na(C_{12}H_{24}O_6)\cdot 2(C_4H_8O)$, $C_{44}H_{54}NaNbO_8$, $M = 834.8$, triclinic, space group $P\bar{1}$ (no. 2, C_i^1), $a = 16.77(8)$, $b = 14.68(3)$, $c = 12.53(2)$ Å, $\alpha = 66.2(2)$, $\beta = 85.4(3)$, $\gamma = 66.2(3)°$, $U = 2\,569(13)$ Å^3, $D_c = 1.08$ g cm^{-3} ($Z = 2$), $F(000) = 884$, $\mu_{Mo} = 2.8$ cm^{-1}, $2\theta_{max.} = 45°$; $N = 4\,665$, $N_o = 3\,430$, $R = 0.13$, $R' = 0.18$.

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References

1 L. M. Engelhardt, W.-P. Leung, C. L. Raston, P. Twiss, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 321.
2 L. M. Engelhardt, W.-P. Leung, C. L. Raston, P. Twiss, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 331.
3 L. M. Engelhardt, W.-P. Leung, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1983, 386.
4 W.-P. Leung and C. L. Raston, *J. Organomet. Chem.*, 1982, **240**, C1.
5 G. S. Bristow, M. F. Lappert, T. R. Martin, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1984, 399; M. F. Lappert, C. L. Raston, G. L. Rowbottom, B. W. Skelton, and A. H. White, *ibid.*, p. 883.
6 E. A. Mintz, K. G. Moloy, T. J. Marks, and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 4692.
7 P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.
8 N. G. Connelly, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 24.
9 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 893.
10 L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525.
11 T. M. V. der Huizen and J. H. Teuben, *J. Organomet. Chem.*, 1976, **105**, 321.

12 J. Sala-Pala, J. Amaudrut, J. E. Guerchais, R. Mercier, J. Douglade, and J. G. Theobald, *J. Organomet. Chem.*, 1981, **204**, 347.

13 O. A. Lemenovskii, T. V. Bavkova, G. Zyzik, V. A. Knizhnikov, V. P. Fedin, and E. G. Perevalova, *Koord. Khim.*, 1978, **4**, 1033; *Chem. Abstr.*, 1978, **89**, 109856.

14 J. Roncin and R. Debuyst, *J. Chem. Phys.*, 1969, **51**, 577.

15 D. F. Froust, M. D. Rausch, and E. Samuel, *J. Organomet. Chem.*, 1980, **193**, 209.

16 N. G. Connelly, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 23.

17 I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374.

18 R. S. Threlkel and J. E. Bercaw, *J. Am. Chem. Soc.*, 1981, **103**, 2650.

19 R. Broussier, H. Normant, and G. Gautheron, *J. Organomet. Chem.*, 1978, **155**, 337.

20 M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Chem. Commun.*, 1978, 925.

21 P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219; R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243.

22 R. J. Klingher, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 208.

23 R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.

24 R. R. Schrock and P. R. Sharp, *J. Am. Chem. Soc.*, 1978, **100**, 2389.

25 A. Antiñolo, M. Fajardo, A. Otero, and P. Royo, *J. Organomet. Chem.*, 1982, **234**, 309; S. Serrano and P. Royo, *ibid.*, 1983, **247**, 33; A. Fakhr, Y. Mugnier, R. Broussier, and B. Gautheron, *ibid.*, 1984, **269**, 53.

26 L. Acedo, A. Otero, and P. Royo, *J. Organomet. Chem.*, 1983, **258**, 181.

27 A. Fakhr, Y. Mugnier, R. Broussier, B. Gautheron, and E. Laviron, *J. Organomet. Chem.*, 1983, **255**, C8.

28 A. Antiñolo, M. Fajardo, A. Otero, and P. Royo, *J. Organomet. Chem.*, 1983, **246**, 269.

29 G. S. Bristow, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1981, 1145.

30 S. J. Fredericks and J. L. Thomas, *J. Am. Chem. Soc.*, 1978, **100**, 350.

31 F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.*, 1971, **93**, 3793.

32 J. A. Labinger and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 1596.

33 R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1967, 1155.

34 J. D. Holloway and W. E. Geiger, *J. Am. Chem. Soc.*, 1979, **101**, 2038.

35 S. I. Bailey, W.-P. Leung, C. L. Raston, and I. M. Ritchie, unpublished work.

36 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

37 M. F. Lappert, T. R. Martin, C. R. C. Milne, J. L. Attwood, W. E. Hunter, and R. E. Pentilla, *J. Organomet. Chem.*, 1980, **192**, C35.

38 L. M. Engelhardt, W.-P. Leung, C. L. Raston, and A. H. White, *Aust. J. Chem.*, in the press.

39 W. S. Sheldrick, J. Kroner, F. Zwaschka, and A. Schmidpeter, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 934.

40 A. van Baalen, C. J. Groenenboom, and H. J. De Liefde Meijer, *J. Organomet. Chem.*, 1974, **74**, 245.

41 H. Lund and P. Iverson, in 'Organic Electrochemistry,' ed. M. Baizer, Marcel Dekker, New York, 1973.

42 E. Gileadi, E. Kirowa-Eisner, and J. Penciner, 'Interfacial Electrochemistry: An Experimental Approach,' Addison–Wesley, Reading, 1975.

43 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1982, **54**, 1527.

44 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.

45 A. J. Bard and L. R. Faulkner, 'Electrochemical Methods – Fundamentals and Applications,' Wiley, New York, 1980.

46 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

47 'The *X*-RAY System – Version of March, 1976,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Centre, University of Maryland, U.S.A.

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