

Half-sandwich Imido Complexes of Niobium and Tantalum†

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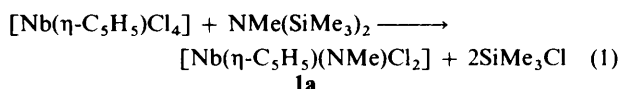
The half-sandwich methylimido complexes $[\text{Nb}(\eta\text{-C}_5\text{R}_5)(\text{NMe})\text{Cl}_2]$ ($\text{R} = \text{H}$ **1a**, or Me **1b**) have been prepared by treatment of $[\text{Nb}(\eta\text{-C}_5\text{R}_5)\text{Cl}_4]$ with $\text{NMe}(\text{SiMe}_3)_2$ in acetonitrile. The sterically hindered alkyl- and aryl-imido analogues $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{Cl}_2]$ ($\text{R} = \text{Bu}^t$ **1c**, or $\text{C}_6\text{H}_3\text{Pr}'_2\text{-2,6}$ **1d**), $[\text{Nb}(\eta\text{-C}_5\text{Me}_5)(\text{N-C}_6\text{H}_3\text{Pr}'_2\text{-2,6})\text{Cl}_2]$ **1e** and the tantalum compound $[\text{Ta}(\eta\text{-C}_5\text{Me}_5)(\text{N-C}_6\text{H}_3\text{Pr}'_2\text{-2,6})\text{Cl}_2]$ **1f** are obtained by treatment of $[\text{M}(\eta\text{-C}_5\text{R}_5)\text{Cl}_4]$ with two equivalents of $\text{NHR}(\text{SiMe}_3)$ in chloroform solvent. Crystal structures of **1a**, **1c**, **1d** and **1f** show that these complexes are mononuclear with quasi-linear imido ligands. The metal–nitrogen bond distances range from 1.744(3) to 1.780(5) Å consistent with pseudo triple bonds. Compounds **1a–1e** react with tertiary phosphines to give eighteen-electron adducts of the type $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{Cl}_2(\text{PR}'_3)]$ **2a–2e**. The crystal structure of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2(\text{PMe}_3)]$ shows a distorted four-legged piano-stool geometry in which the phosphine binds *cis* to the methylimido and *cis* to one of the chloride ligands. Alkoxide and aryloxo derivatives of the type $[\text{Nb}(\eta\text{-C}_5\text{R}_5)(\text{NR}')(\text{OR}'')_2]$ may be prepared *via* reactions of the dichlorides **1** with 2 equivalents of LiOR'' in Et_2O . Fenske–Hall quantum-chemical calculations indicate that there exists a close relationship between the $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})$ fragment and the bent metallocene moiety $\text{M}(\eta\text{-C}_5\text{H}_5)_2$ for the Group 4 elements.

Oxo and imido ligands are particularly suited to the stabilization of high-oxidation-state transition-metal complexes due to their ability to participate in extensive ligand-to-metal π donation.¹ An important additional facet of the imido ligand is the presence of an organo substituent through which the steric and electronic properties of the complex may be influenced. For example, large substituents may be exploited to reduce the tendency for imido-bridge formation, often leading to oligomeric or cluster species for analogous oxo systems of the early transition metals.² They may also be used to stabilize low-coordinate and in some cases highly reactive metal environments.³ Such compounds are also of interest due to their relevance to important transition-metal-catalysed industrial processes which utilize oxygen and nitrogen feedstocks.¹

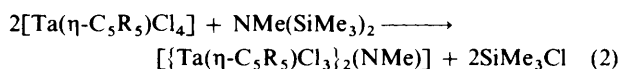
Part of our studies has focused on monocyclopentadienyl derivatives of the early transition metals containing ancillary oxo and imido ligands.^{2,4} To date, derivatives of this general type have not proved readily available for the heavier Group 5 metals. We describe herein a convenient and quite general synthetic strategy for the preparation of a variety of half-sandwich imido compounds of niobium and tantalum that contain either the C_5H_5 or the C_5Me_5 moiety and bear imido groups of differing steric and electronic requirements. Additionally, aspects of their derivative chemistry and an analysis of the bonding in these compounds are presented.

Results and Discussion

Synthesis of $[\text{M}(\eta\text{-C}_5\text{R}_5)(\text{NR}')\text{Cl}_2]$ Complexes.—We have recently reported the synthesis of the mononuclear methylimido complex $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2]$ **1a** *via* treatment of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_4]$ with $\text{NMe}(\text{SiMe}_3)_2$ [equation (1)].⁴ This approach turned out to be quite specific to the niobium compound **1a** and

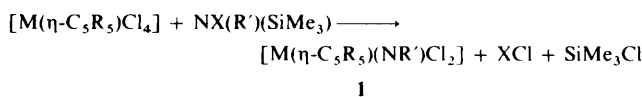


its pentamethylcyclopentadienyl analogue **1b**. Related reactions of $[\text{Ta}(\eta\text{-C}_5\text{R}_5)\text{Cl}_4]$ ($\text{R} = \text{H}$ or Me) with this reagent afforded binuclear tantalum species of the type shown in equation (2).



Here it is presumed that the $[\text{Ta}(\eta\text{-C}_5\text{R}_5)\text{Cl}_3\{\text{NMe}(\text{SiMe}_3)\}]$ intermediate reacts rapidly with the tetrachloride starting material to give the binuclear product.

Nevertheless, both niobium and tantalum analogues of **1a** and **1b** containing sterically demanding alkyl- and aryl-imido groups may be prepared by a slight modification of this synthetic strategy exploiting monosilylated amine reagents (Scheme 1). Compounds **1a–1f** are obtained in good to excel-



	R	M	X ^a	R'	Yield (%)
1a	H	Nb	SiMe ₃	Me	87
1b	Me	Nb	SiMe ₃	Me	60 ^b
1c	H	Nb	H	Bu ^t	78
1d	H	Nb	H	C ₆ H ₃ Pr' ₂ -2,6	81
1e	Me	Nb	H	C ₆ H ₃ Pr' ₂ -2,6	77
1f	Me	Ta	H	C ₆ H ₃ Pr' ₂ -2,6	72

Scheme 1 ^a In the case of X = H a second equivalent of amine is necessary for neutralizing the HCl which is formed during the reaction. ^b Not optimized.

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

lent yields as crystalline solids which are only slightly air sensitive. They are all highly soluble in polar solvents such as chloroform and dichloromethane, and the niobium complexes

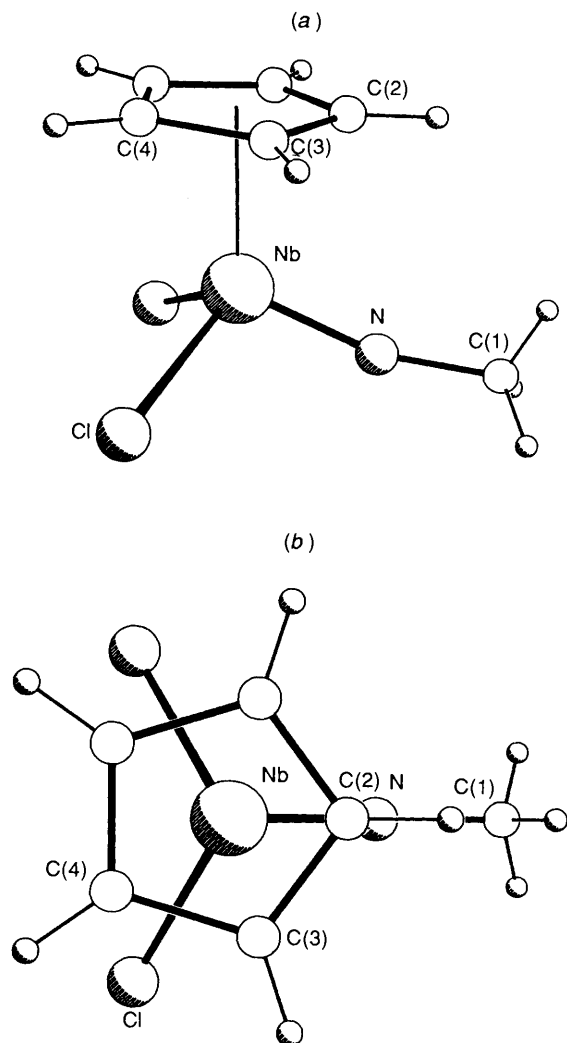
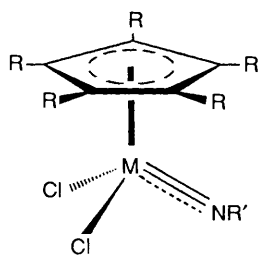


Fig. 1 The molecular structure of compound **1a** showing (a) the atom labelling, (b) view along the ring centroid–niobium vector



are also quite soluble in low-polarity hydrocarbon solvents such as toluene and pentane. Generally, more severe reaction conditions are required for the synthesis of the C_5Me_5 species than for their C_5H_5 counterparts; for example, **1d** is formed smoothly by stirring the reactants for 12 h at room temperature in dichloromethane, whereas **1e** is obtained in a comparable yield only after heating the reaction mixture for 2 d at 80 °C (dichloroethane solvent). Complex **1a** is known to be monomeric in the solid state⁴ adopting a three-legged piano-stool structure. The spectral data for **1b–1f** indicate that these species are isostructural with **1a**; a view of the basic structure type is shown above (the reader is referred to Scheme 1 for M, R and R'). In particular, their IR spectra give bands between 1200 and 1350 cm^{-1} characteristic of the terminal imido ligand. These findings are further corroborated by single-crystal X-ray studies on **1c**, **1d** and **1f**.

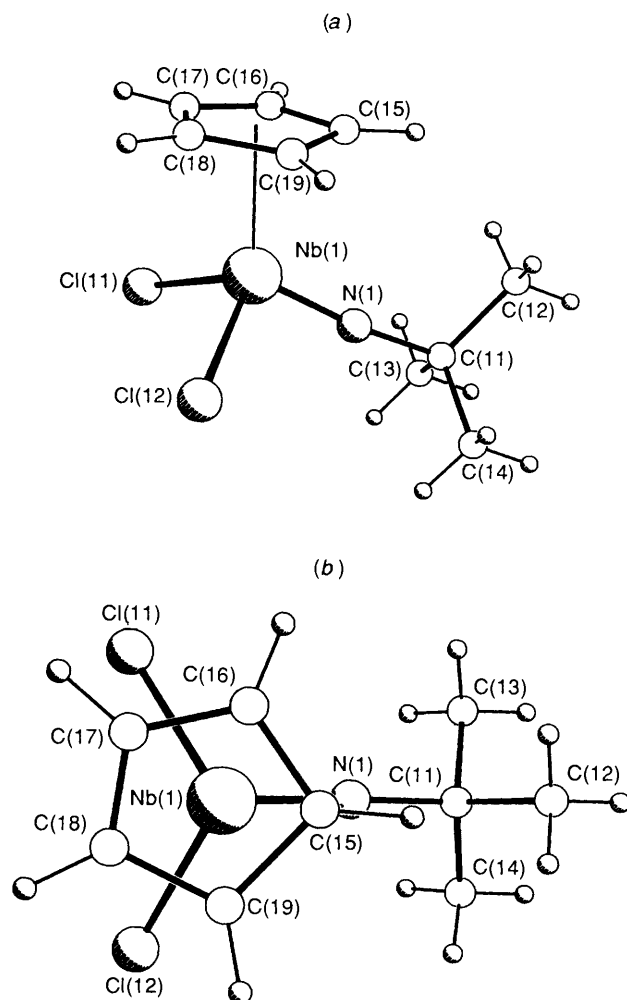


Fig. 2 The molecular structure of one of the independent molecules of compound **1c** showing (a) the atom labelling, (b) view along the ring centroid–niobium vector

Molecular Structures of $[M(\eta-C_5R_5)(NR')Cl_2]$ Derivatives.—The molecular structures of compounds **1a**, **1c**, **1d** and **1f**, are shown in Figs. 1–4 and the crystal data are given in Table 1. Atomic parameters and bond lengths and angles for all four species are collected in Tables 2–6. In each case, the metal–nitrogen distance lies within the range expected for a triple bond^{5–7} [1.752(2) for **1a**, 1.744(3) and 1.752(3) for the two independent molecules of **1c**, 1.761(6) for **1d**, and 1.780(5) Å for **1f**]. The imido unit is quasi-linear, the M–N–C angle being 163.4(3) for **1a**, 172.5(3) and 170.0(3) for **1c**, 165.6(5) for **1d** and 171.4(5)° for **1f**. The slight deviations from linearity are due to a bending of the organo substituent on the imido nitrogen toward the C_5 ring; these deviations range from 7.5 to 16.6°. This suggests that the primary interaction of the nitrogen lone pair-containing p orbital is with a lobe of a vacant metal orbital projecting *trans* to the cyclopentadienyl ring. The steric congestion around the metal centre (caused *e.g.* by the Bu' group in **1c** and by the C_5Me_5 ligand in **1f**) appears to favour a more linear M–N–C arrangement. From the structural and spectroscopic data, it is quite clear that **1a**, **1c**, **1d** and **1f** can be rationalized as formally sixteen-electron complexes containing a 'linear' terminal imido ligand which may be regarded as a four-electron (neutral) or six-electron (dianionic) donor ligand.

In all four of the crystallographically characterized complexes the cyclopentadienyl moiety is not co-ordinated in an ideal η^5 fashion; instead, a trend towards η^3 co-ordination is observed leading invariably to three short and two long metal-to- C_5R_5 ring carbon distances and to a more or less pronounced

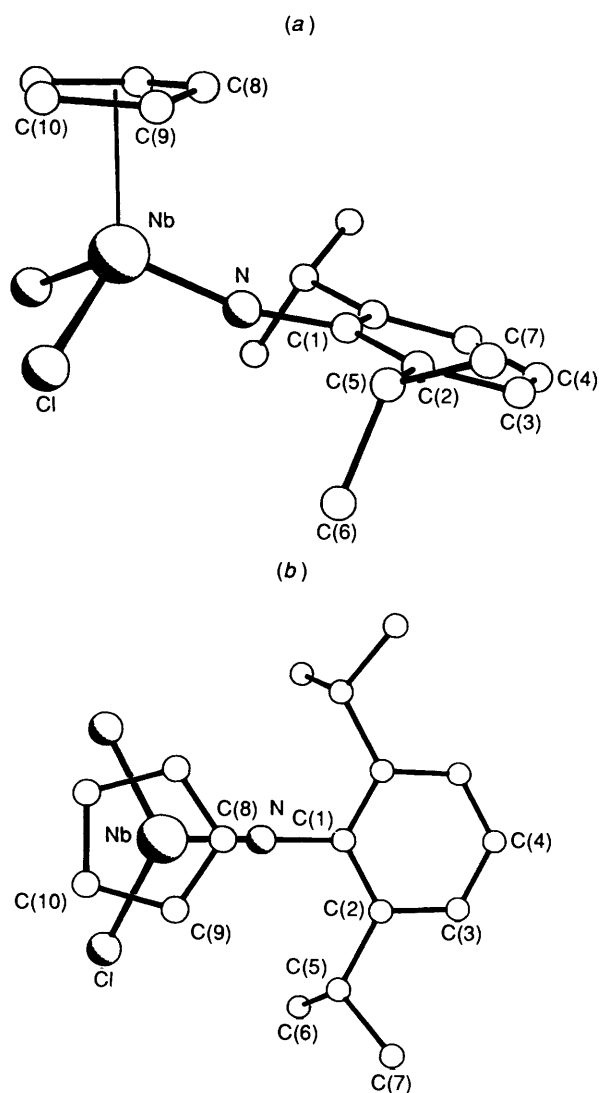


Fig. 3 The molecular structure of compound **1d** showing (a) the atom labelling (H atoms omitted for clarity), (b) view along the ring centroid-niobium vector

distortion of the cyclopentadienyl ring. Maximum deviations of metal-to- C_5R_5 ring carbon (ΔM) and inter-ring carbon distances (ΔR) are listed in Table 7 together with the distance ΔX between the C_5R_5 ring centroid and the point where the metal- C_5R_5 ring normal meets the 'best plane' for the C_5R_5 ring (hence, ΔX gives some indication of ring slippage); bend angles for the imido groups are also included in the Table for reference purposes. Interestingly, the two independent molecules of **1c** show markedly different ΔR (0.053 vs 0.173 Å) and ΔX (0.083 vs. 0.143 Å) values indicating that crystal-packing forces may also have a significant effect on the distortions.

Unlike the other structurally characterized derivatives, the two **1c** molecules lack a crystallographic mirror plane bisecting the cyclopentadienyl ring and the M-N-C unit. However, in all cases, the cyclopentadienyl rings are arranged in an eclipsed fashion with respect to the imido ligand; this leads to a bending of the eclipsed ring substituent away from the imido group. For example, in the tantalum complex **1f** the ring methyl subtends an angle of 5.2° to the C_5Me_5 ring plane (for comparison, the corresponding angles of the other ring methyl substituents are 2.3 and 2.8° respectively). Of the three symmetrical species, **1a** and **1f** adopt an allyl-ene structure similar to the rhenium imido complex $[Re(\eta-C_5Me_5)(NBu^t)Cl_2]$ recently described by Herrmann and co-workers.⁸ Two essential features of this structure type are that (i) the ring C-C bond *trans* to the imido

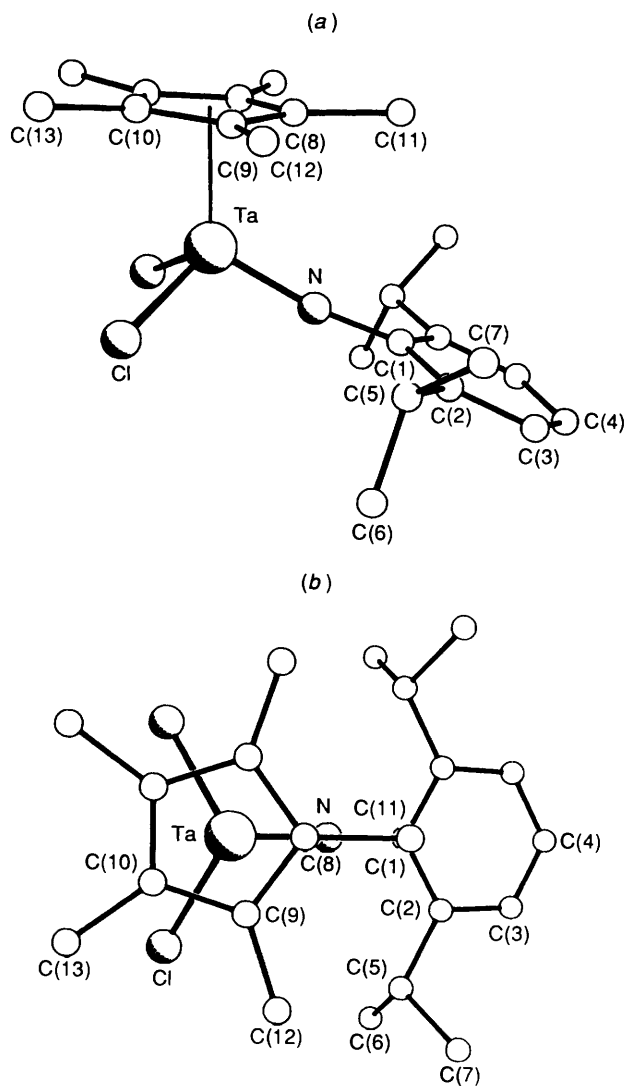
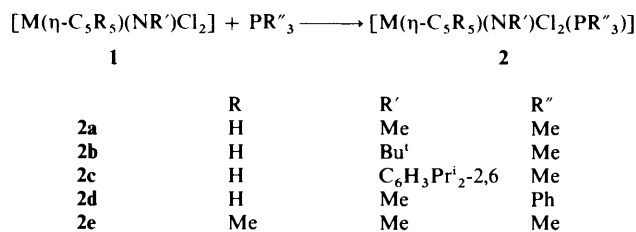


Fig. 4 The molecular structure of compound **1f** showing (a) the atom labelling (H atoms omitted for clarity), (b) view along the ring centroid-tantalum vector

ligand is the shortest bond within the cyclopentadienyl unit and (ii) the bonds between the metal and these two *trans* carbon atoms are considerably longer than the other three metal-to-ring carbon bonds. By contrast, the corresponding C-C bond in **1d** is not the shortest, but the *longest* in the C_5H_5 ring. Nevertheless, the distance between the metal centre and the two 'trans' carbon atoms is still considerably longer than the other three metal-to- C_5H_5 ring carbon distances (2×2.44 vs. 2×2.36 and 2.40 Å). Incidentally, C_5H_5 ring puckering, as measured by the root-mean-square deviation of the ring carbon atoms from their 'best plane', is more pronounced in this compound than in any of the other three species that were structurally investigated. The reason for this behaviour is not clear but again crystal-packing effects cannot be ruled out.

Tertiary Phosphine Adducts.—Compounds of type **1** are formally sixteen-electron species and therefore should coordinate good two-electron donors to afford eighteen-electron adducts. This is indeed found to be the case as shown for the tertiary phosphine donors in Scheme 2. The adducts **2a–2e** can be isolated in high yields as white to yellow air-sensitive solids which are not very soluble in low-polarity hydrocarbon solvents. Co-ordination of the phosphine is relatively weak for sterically congested species such as **2b** and **2c**. A qualitative assessment of co-ordination strength for the PMe_3 adducts is

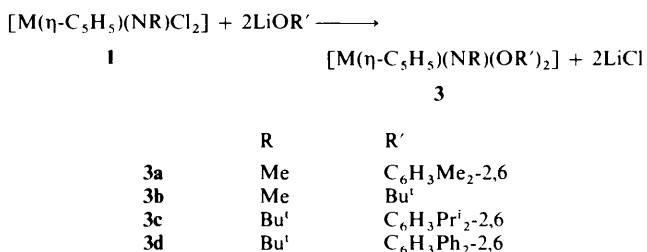


Scheme 2 M = Nb

possible by NMR spectroscopy, the chemical shift of the PMe₃ methyl protons being close to non-co-ordinated (δ 0.79 in [²H₆]benzene) for 'weak' adducts like **2b** and **2c** (δ 1.26 and 1.13 respectively), but shifted considerably downfield for 'strong' adducts like **2a** (δ 1.58).

Compounds **2b–2e** are presumed to adopt geometries similar to that established for **2a** by a single-crystal X-ray diffraction study. The molecular structure of **2a** is shown in Fig. 5 and the crystal data are given in Table 1; positional parameters and bond lengths and angles are collected in Tables 8 and 9. Overall, the molecular geometry may be described as a four-legged piano stool with the PMe₃ ligand binding *cis* to the methylimido group and therefore also *cis* to one of the chloride ligands. This would appear to be a sterically less-favourable position for the phosphine compared with the site bisecting the two chlorides; it is also found to lie not far out of the NbCl₂ plane (18°); for comparison, the PMe₃ ligand in the related half-sandwich tantalum complex [Ta(η -C₅Me₅)Cl₃(PMe₃)]⁹ lies about 40° (average) out of the analogous TaCl₂ planes. The origin of this effect is believed to result from the directional properties of the lowest unoccupied molecular orbital (LUMO) in [Nb(η -C₅H₅)(NMe)₂Cl₂]. Calculations indicate that this orbital lies essentially in the NbCl₂ plane (see later) and may be compared with the LUMO for the bent metallocene moiety.¹⁰ The co-ordination of PMe₃ to **1a** also appears to have a more pronounced effect on the Nb–Cl bonding than on the Nb–imido interaction. For example, while there is only a small increase in the Nb–N bond length and the Nb–N–C bond angle, the Nb–Cl bonds lengthen by nearly 0.15 Å. The Nb–C₅H₅ bonding remains essentially unaffected.

Alkoxide and Aryloxy Derivatives.—Further derivatization of compounds **1** may be achieved by exchange of the halide ligands through reaction with 2 equivalents of various lithium alkoxides to give alkoxo species of type **3** (Scheme 3). These compounds are isolated as white to yellow solids in generally good yields. It is assumed that they are isostructural with their chloride precursors of type **1**.



Scheme 3 M = Nb

¹³C NMR Spectroscopy.—The difference in ¹³C NMR chemical shift ($\Delta\delta$) between the quaternary carbon and the methyls of the *tert*-butylimido group [$\delta(\text{CMe}_3) - \delta(\text{CMe}_3)$] has been proposed to afford a qualitative indication of the degree of electron donation from the imido group to the metal centre.¹⁻¹¹ Although the main influence on $\Delta\delta$ values seems to

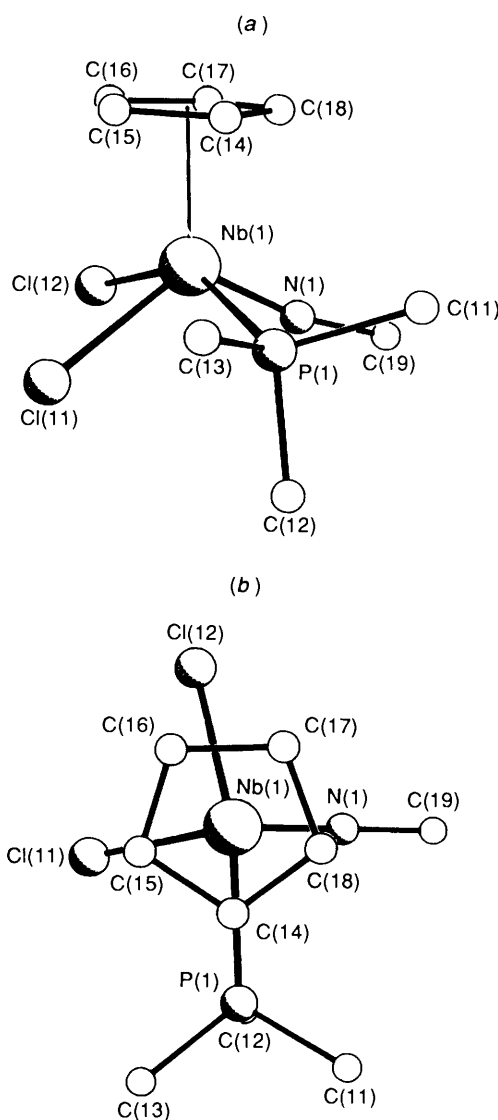


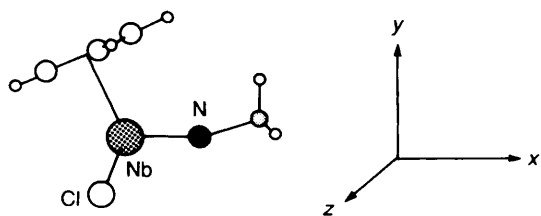
Fig. 5 The molecular structure of compound **2a** showing (a) the atom labelling (H atoms omitted for clarity). (b) view along the ring centroid niobium vector

stem from the nature of the metal centre attached to the imido nitrogen atom, the effect of ancillary ligands has also been studied for a constant metal imido system.¹² Large $\Delta\delta$ values are indicative of a relatively low electron density on the imido nitrogen due to a high degree of N→M donation. For our fairly limited series of four *tert*-butylimido niobium species the $\Delta\delta$ values lie between 28.8 and 40.6 ppm, which is within the range previously recorded for *tert*-butylimido species, 25 ppm for [$\{\text{Hf}(\mu\text{-NBu}^t)\}_2(\text{NMe}_2)$]¹³ to 55 ppm for [CrO(NBu^t)(OSiMe₃)₂]¹¹ with the dichloro derivatives lying at the high end of this range (39.6 for **1c**, 40.6 ppm for **2b**) and the phenoxide derivatives lying at the low end (28.8 for **3c**, 36.6 ppm for **3d**). This presumably reflects the higher electronegativity of the chloro *versus* phenoxide ligands. Interestingly, the $\Delta\delta$ value of the PMe₃ adduct **2b** is very similar to the PMe₃-free species. This is consistent with the findings of the X-ray structure determination which show that phosphine co-ordination has only a minimal effect on the niobium–imido bonding.

Calculations.—*Metal–imido bonding.* In order to gain further insight into the metal–imido ligand bonding and the nature of the frontier orbitals of the co-ordinatively unsaturated

Table 1 Crystallographic data

Complex	1a	1c	1d	1f	2a
Formula	C ₆ H ₈ Cl ₂ NNb	C ₉ H ₁₄ Cl ₂ NNb	C ₁₇ H ₂₂ Cl ₂ NNb	C ₂₂ H ₃₂ Cl ₂ NTa	C ₉ H ₁₇ Cl ₂ NNbP
<i>M</i>	258.0	300.0	404.2	562.4	334.0
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Cmc</i> 2 ₁	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.1778(6)	12.977(1)	16.641(3)	6.975(1)	12.952(5)
<i>b</i> /Å	9.8969(11)	16.530(2)	8.6011(3)	17.433(3)	14.453(7)
<i>c</i> /Å	7.1994(6)	12.726(1)	12.8733(9)	9.842(2)	15.349(6)
β/°	118.037(6)	111.815(6)		99.18(2)	107.65(4)
<i>U</i> /Å ³	451.4	2534.3	1842.5	1181.4	2738.2
<i>Z</i>	2	8	4	2	8
<i>D_c</i> /g cm ⁻³	1.897	1.572	1.457	1.581	1.620
μ/mm ⁻¹	1.81	1.30	8.13	4.83	1.32
<i>F</i> (000)	252	1200	824	556	1344
Crystal size/mm	0.24 × 0.30 × 0.32	0.10 × 0.20 × 0.70	0.13 × 0.38 × 0.73	0.20 × 0.38 × 0.56	0.18 × 0.20 × 0.52
2θ _{max} /°	50	50	130	50	50
Maximum indices <i>h</i> , <i>k</i> , <i>l</i>	8, 11, 8	15, 19, 15	19, 10, 14	8, 20, 11	15, 17, 18
Transmission factors	0.652–0.778	0.549–0.623	0.014–0.058	0.093–0.177	0.623–0.678
Reflections measured	2807	5485	3667	3894	9296
Unique reflections	848	4451	1592	2168	4801
Observed reflections	827	3506	1562	2004	3540
<i>R</i> _{int}	0.014	0.030	0.023	0.014	0.024
Weighting parameters <i>A_n</i>	1.6, -1.5, 1.1, -3.2, 1.8, 0.9	7, 9, 63, -15, 11, -38	-18, 17, 207, 46, -29, 2	9, -20, 86, -19, 9, 13	8, -14, 17, -19, 12, 8
Extinction parameter <i>x</i>	7.8(7) × 10 ⁻⁶	3.8(6) × 10 ⁻⁷	1.8(6) × 10 ⁻⁶	9(3) × 10 ⁻⁷	0
No. of parameters	53	236	109	134	278
<i>R</i>	0.0160	0.0325	0.0500	0.0322	0.0339
<i>R</i> '	0.0160	0.0340	0.0580	0.0399	0.0300
Goodness of fit	1.02	1.12	1.05	1.07	1.08
Mean, maximum shift/e.s.d.	<0.0005, 0.001	0.005, 0.020	0.002, 0.180	0.001, 0.011	0.005, 0.017
Maximum, minimum electron density/e Å ⁻³	0.36, -0.22	0.43, -0.35	1.72, -1.98	1.69, -1.01	0.62, -0.41

**Fig. 6** Axial framework for FHMO calculation on [Nb(η-C₅H₅)₂(NMe)Cl₂]

dihalides, Fenske–Hall quantum-mechanical calculations¹⁴ were carried out on the structurally characterized complex [Nb(η-C₅H₅)(NMe)Cl₂] **1a** and also its 18-electron PMe₃ adduct [Nb(η-C₅H₅)(NMe)Cl₂(PMe₃)] **2a**. For **1a** the interaction of the Nb(η-C₅H₅)Cl₂²⁺ fragment with a NMe²⁻ fragment along the *x*-axis (Fig. 6) was considered using the crystallographically determined co-ordinates for **1a**.

The compositions of the fragment frontier orbitals are collected in Tables 10 and 11; the resulting molecular orbital correlation diagram is shown in Fig. 7, and the most important interactions (in terms of % of the total net Mulliken overlap population) are given in Table 12.

The bonding picture for the imido ligand in compound **1a** involves (i) a σ-symmetry interaction found in complex MO 15 and (ii) two π-symmetry interactions found in complex MO 27 and 28, the latter being responsible for the complex highest occupied molecular orbital (HOMO). The σ interaction arises from overlap of the NMe²⁻ fragment orbital MO 5 with the σ-symmetry components of the Nb(η-C₅H₅)Cl₂²⁺ fragment MO 22 and 25 (16.4 and 29.4%, respectively, of the total net Mulliken overlap population). The π-bonding components arise from overlap of NMe²⁻ fragment orbitals 6 and 7 with the Nb(η-C₅H₅)Cl₂²⁺ fragment MO 22 and 23 respectively, a combined total of 54.2%, of the net Mulliken overlap population. The

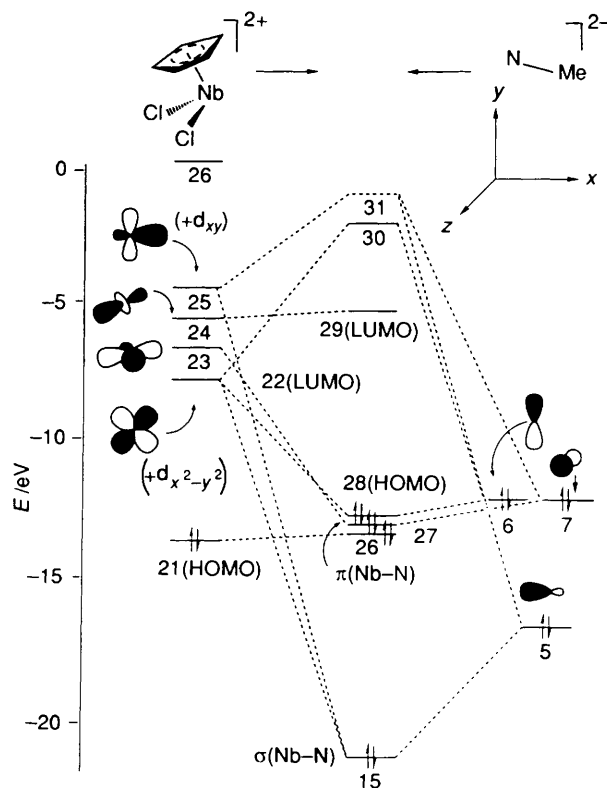
**Fig. 7** Molecular orbital correlation diagram, showing interaction of the fragments Nb(η-C₅H₅)Cl₂²⁺ and NMe²⁻. Representations of the fragment molecular orbitals show the most important orbital contributions only

Table 2 Atomic coordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
(a) For compound 1a				(c) For compound 1d			
Nb	1 287.7(4)	2 500	1 625.6(4)	Nb	0	296.2(5)	5 000
Cl	1 634.0(10)	616.4(6)	3 764.0(9)	Cl	1 136.2(13)	617.5(30)	6 045.9(18)
N	-1 403(4)	2 500	-199(4)	N	0	2 014(6)	4 256(5)
C(1)	-3 360(5)	2 500	-2 110(5)	C(1)	0	3 123(7)	3 451(6)
C(2)	1 983(5)	2 500	-1 297(4)	C(2)	738(3)	3 686(6)	3 088(4)
C(3)	2 984(4)	1 359(3)	-121(4)	C(3)	721(5)	4 890(11)	2 343(9)
C(4)	4 705(3)	1 798(3)	1 783(3)	C(4)	0	5 470(10)	1 989(10)
(b) For compound 1c				(d) For compound 1f			
Nb(1)	4 078.4(3)	2 055.4(2)	1 267.6(3)	Ta	6 548.1(3)	2 500	5 531.4(2)
Cl(11)	5 687.3(11)	1 834.8(8)	2 887.7(10)	Cl	4 970.7(20)	1 427.0(8)	6 273.9(14)
Cl(12)	2 566.8(13)	1 643.7(10)	1 743.5(13)	N	5 690(8)	2 500	3 728(5)
Nb(2)	8 791.7(3)	3 103.7(2)	2 653.1(3)	C(1)	5 317(10)	2 500	2 308(6)
Cl(21)	7 221.7(11)	3 351.7(8)	1 013.7(10)	C(2)	5 098(8)	1 799(3)	1 582(5)
Cl(22)	10 318.4(12)	3 531.2(8)	2 215.2(12)	C(3)	4 591(11)	1 823(4)	157(6)
N(1)	3 942(3)	3 106(2)	1 230(3)	C(4)	4 318(17)	2 500	-541(8)
C(11)	3 790(4)	3 966(2)	1 042(4)	C(5)	5 336(11)	1 038(3)	2 335(6)
C(12)	3 772(7)	4 170(4)	-120(6)	C(6)	3 356(18)	656(5)	2 302(14)
C(13)	4 769(8)	4 384(4)	1 926(6)	C(7)	6 736(15)	507(5)	1 757(10)
C(14)	2 735(8)	4 199(6)	1 169(11)	C(8)	9 806(10)	2 500	5 135(9)
C(15)	3 992(14)	2 008(5)	-605(6)	C(9)	9 590(8)	1 834(3)	5 934(7)
C(16)	4 978(10)	1 689(6)	20(9)	C(10)	9 380(8)	2 098(4)	7 272(6)
C(17)	4 840(7)	999(5)	383(5)	C(11)	10 288(13)	2 500	3 673(11)
C(18)	3 824(8)	818(4)	82(6)	C(12)	9 762(9)	1 024(4)	5 493(9)
C(19)	3 203(6)	1 420(8)	-538(6)	C(13)	9 261(13)	1 583(6)	8 485(8)
N(2)	8 952(3)	2 051(2)	2 648(2)				
C(21)	9 160(3)	1 195(2)	2 858(3)				
C(22)	9 178(5)	980(3)	4 023(4)				
C(23)	8 234(5)	738(3)	1 945(4)				
C(24)	10 270(5)	1 015(4)	2 760(6)				
C(25)	8 453(6)	3 063(3)	4 365(4)				
C(26)	7 753(5)	3 632(4)	3 752(5)				
C(27)	8 371(8)	4 291(3)	3 661(5)				
C(28)	9 483(7)	4 088(5)	4 222(6)				
C(29)	9 504(6)	3 318(5)	4 639(4)				

Table 3 Bond lengths (Å) and angles ($^\circ$) for compound 1a

Nb-Cl	2.355(1)	Nb-N	1.752(2)
Nb-C(2)	2.380(4)	Nb-C(3)	2.404(3)
Nb-C(4)	2.500(3)	N-C(1)	1.432(3)
C(2)-C(3)	1.392(3)	C(3)-C(4)	1.415(3)
C(4)-C(4')	1.390(6)		
Cl-Nb-N	103.3(1)	Cl-Nb-C(2)	125.2(1)
N-Nb-C(2)	87.3(1)	Cl-Nb-C(3)	92.6(1)
N-Nb-C(3)	105.0(1)	C(2)-Nb-C(3)	33.8(1)
Cl-Nb-C(4)	87.2(1)	N-Nb-C(4)	138.2(1)
C(2)-Nb-C(4)	55.3(1)	C(3)-Nb-C(4)	33.5(1)
Cl-Nb-Cl'	104.7(1)	C(3)-Nb-Cl'	142.2(1)
C(4)-Nb-Cl'	113.0(1)	C(3)-Nb-C(3')	56.1(1)
C(4)-Nb-C(3')	55.0(1)	C(4)-Nb-C(4')	32.3(1)
Nb-N-C(1)	163.4(3)	Nb-C(2)-C(3)	74.0(2)
C(3)-C(2)-C(3')	108.5(2)	Nb-C(3)-C(2)	72.2(2)
Nb-C(3)-C(4)	77.0(2)	C(2)-C(3)-C(4)	107.8(2)
Nb-C(4)-C(3)	69.5(2)	Nb-C(4)-C(4')	73.9(1)
C(3)-C(4)-C(4')	107.9(2)		

Symmetry operation for primed atoms: $x, \frac{1}{2} - y, z$.

complex LUMO (MO 29) arises from the empty metal fragment MO 24, which is mainly d_{z^2} in character and thus projects along the z axis. The final Mulliken population indicates that approximately 1.6 electrons are transferred from the NMe_2^- ligand to the metal fragment.

The interaction diagram for the PMe_3 adduct **2a**, generated by interacting the neutral fragments $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2$ and PMe_3 , is shown in Fig. 8. There is only one major interaction

evident, that of the PMe_3 lone pair (MO 13) interacting strongly with the LUMO (MO 29) of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2]$. The final Mulliken population shows that 0.55 of an electron is transferred from the neutral phosphine to the metal fragment.

Relationship between $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{X}_2]$ ($\text{M} = \text{Nb}$ or Ta) and $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ ($\text{M} = \text{Zr}$ or Hf). The close similarities between the symmetry properties of the frontier orbitals of the imido fragment NR^{2-} and those of the cyclopentadienyl anion $\eta^5\text{-C}_5\text{H}_5^-$ raises the possibility that there could exist a close relationship between $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{Cl}_2]$ and the Group 4 metallocene species $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$. Both NR and $\eta\text{-C}_5\text{H}_5$ ligands contain an orbital of a_1 symmetry and a set of degenerate e_1 orbitals. In bonding to a transition metal the C_5H_5 group in $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ engages in strong π -type interactions between metal d_{xz} and d_{yz} (e) and C_5H_5 e_1 orbitals, and a σ -type bonding interaction between metal s and p_z orbitals and the C_5H_5 a_1 orbital. The remaining three d orbitals of the metal remain essentially non-bonding.* These similarities imply that sixteen-electron d^0 species of the type $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})\text{Cl}_2]$ and therefore even non-cyclopentadienyl species such as the Group 6 series $[\text{M}(\text{NR})_2\text{Cl}_2]$ ($\text{M} = \text{Cr}, \text{Mo},$ or W) (see below) may have closely related electronic and chemical properties.

In order further to evaluate this relationship, calculations were carried out on the $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})^{2+}$ fragment in a bent metallocene orientation so as to allow a direct comparison with

* It might have been expected that the d_{z^2} would also interact with the C_5H_5 a_1 orbital, but the π -orbital lobes probe the region of the d_{z^2} nodal surface, see ref. 10.

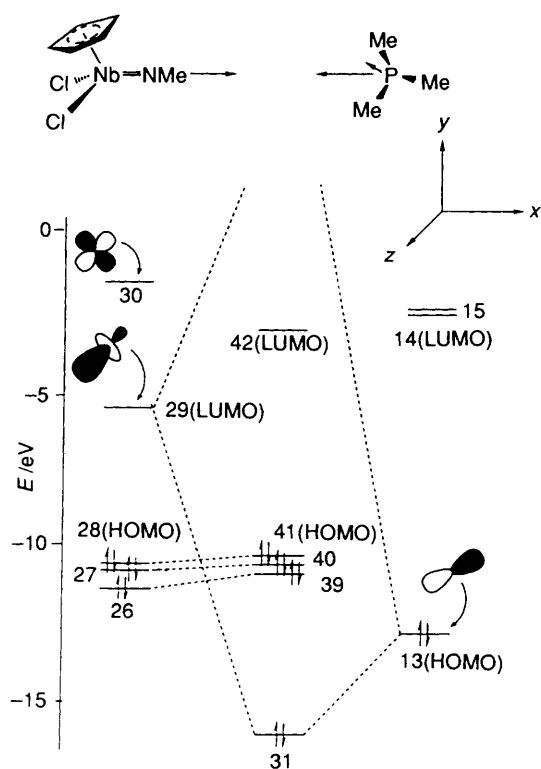


Fig. 8 Molecular orbital correlation diagram, showing interaction of the fragments $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2$ and PMe_3 . Representations of the fragment molecular orbitals show the most important orbital contributions only

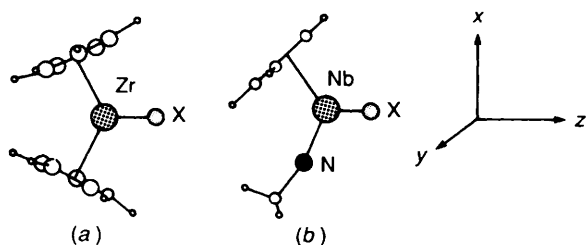
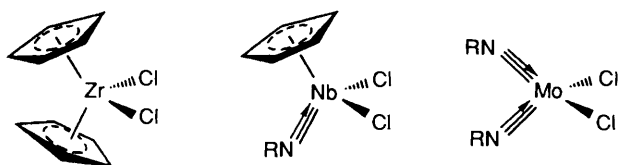


Fig. 9 Axial framework for FHMO calculations on (a) $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ and (b) $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{X}_2]$



$\text{Zr}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ {the geometry here was taken from the crystal structure of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]^{15}$ }. It should be noted that the metallocene system has been investigated thoroughly by Lauher and Hoffmann¹⁰ using extended-Hückel molecular orbital (EHMO) calculations, and also by Zhu and Kostic¹⁶ using the Fenske-Hall method. The orbital compositions for $\text{Zr}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ using the Fenske-Hall method are recorded here for direct comparative purposes; the co-ordinate axes chosen for these calculations are the same as those adopted by Lauher and Hoffmann in their study of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ [see Fig. 9(a)].

The compositions of the unoccupied frontier orbitals of the $\text{M}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ fragment generated by the two methods are compared in Table 13. The $1a_1$, b_2 and $2a_1$ orbitals (MO 27–29) are the energetically accessible frontier orbitals responsible for ligand binding in the bent metallocene fragment. The higher-

energy orbitals of b_1 and a_2 symmetry (fragment MO 30 and 31) are generally found to be too high in energy to participate to any significant extent in metallocene-to-ligand bonding¹⁰ and therefore are not central to this discussion. Although on initial inspection there appear to be some differences in the compositions of complex MO 27 and 29 with those generated by the EHMO calculations, closer inspection reveals that the orbital contributions described by Lauher and Hoffmann lead to complex MOs with shapes and directions similar to 27 and 29 (the reader is referred to the earlier work¹⁰ for the shapes of these orbitals). For example, these authors note that the $1a_1$ orbital comprising 51% $d_{x^2-y^2}$ and 30% d_{z^2} has a significant component in the y direction and may be described as being similar to a d_{yz} orbital (cf. MO 27 which contains 84% d_{yz} character). Similarly, MO 29 which is hybridized along the z axis away from the C_5H_5 ligands is closely related to the $2a_1$ orbital found in Hoffmann's calculations. Therefore, the Fenske-Hall molecular orbital (FHMO) calculations are in good general agreement with Lauher and Hoffmann's EHMO calculations.

Now turning to the $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})^{2+}$ fragment, the compositions of the frontier molecular orbitals generated by FHMO calculations [using the axial framework shown in Fig. 9(b)] are collected in Table 14. Striking similarities are immediately evident with the frontier orbitals (MO 27–29) of $\text{Zr}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ (cf. left-hand side of Table 13). The only significant difference appears to be in the composition of fragment orbital 23 ($2a_1$) which for $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})^{2+}$ contains a significant contribution (19%) from the niobium d_{xz} orbital. This lies out of the normal 'equatorial' ligand binding plane of a $\text{M}(\eta\text{-C}_5\text{H}_5)_2$ fragment, and therefore may be where differences in the chemistries of $[\text{M}(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Ti}, \text{Zr}$ or Hf) and $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{NR})]$ ($\text{M} = \text{Nb}$ or Ta) could occur. Thus, the imido ligand, by comparison with a cyclopentadienyl group, may allow greater flexibility for bonding interactions above and below the 'normal' equatorial binding plane of a bent metallocene fragment. This may be viewed as a consequence of only a single atom interacting with the metal centre in the imido case whereas the additional metal-carbon interactions present in an $\eta^5\text{-C}_5\text{H}_5$ ligand will tend to 'tie-up' more of the energetically accessible metal orbitals. Still, it is clear from these calculations that a close relationship *does exist* between the fragments $\text{Zr}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ and $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})^{2+}$ and one which is likely to lead to some general similarities in their coordination chemistries. In future studies we shall endeavour to probe further the similarities and differences between the chemistries of these systems.

Experimental

All manipulations were carried out under an atmosphere of inert gas (argon or dinitrogen) using standard Schlenk and cannula techniques or a conventional glove-box. Solvents were distilled from an appropriate drying agent and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry, Durham University. The following instruments were used: NMR spectra, Varian VXR 400 S (399.952, ^1H ; 100.577 MHz, ^{13}C), Bruker AC 250 (250.13, ^1H ; 62.90 MHz, ^{13}C); chemical shifts are referenced to the residual protio impurities of the deuterated solvent, and, where necessary, assignments of ^{13}C resonances were made using proton-coupled or distortionless enhancement by polarization transfer (DEPT) spectra; IR spectra (Nujol mulls, KBr or CsI windows), Perkin-Elmer 577 and 457 grating spectrophotometers; mass spectra, VG 7070E [70 eV (*ca.* 1.12×10^{-17} J), 100 μA emission; for chemical ionization (CI) spectra, NH_3 was used as carrier gas], only characteristic fragments are listed. The following chemicals were prepared by previously published procedures: $[\text{Nb}(\text{C}_5\text{H}_5)\text{Cl}_4]$,¹⁷ $[\text{Nb}(\text{C}_5\text{Me}_5)\text{Cl}_4]$,¹⁸ $[\text{Ta}(\text{C}_5\text{Me}_5)\text{Cl}_4]$,¹⁹ PMe_3 ,²⁰ and LiOR .²¹ Reagents $\text{NHR}(\text{SiMe}_3)$ ($\text{R} = \text{Bu}^t$ or $\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$) were prepared by treatment of NH_2R with LiBu^t followed by SiMe_3Cl . All other

Table 4 Bond lengths (Å) and angles (°) for compound **1c**

Nb(1)–Cl(11)	2.354(1)	Nb(2)–Cl(21)	2.348(1)	C(11)–C(12)	1.508(10)	C(21)–C(22)	1.517(7)
Nb(1)–Cl(12)	2.358(2)	Nb(2)–Cl(22)	2.357(2)	C(11)–C(13)	1.515(8)	C(21)–C(23)	1.525(6)
Nb(1)–N(1)	1.744(3)	Nb(2)–N(2)	1.752(3)	C(11)–C(14)	1.488(13)	C(21)–C(24)	1.520(9)
Nb(1)–C(15)	2.345(10)	Nb(2)–C(25)	2.379(7)	C(15)–C(16)	1.339(17)	C(25)–C(26)	1.339(8)
Nb(1)–C(16)	2.372(14)	Nb(2)–C(26)	2.437(8)	C(15)–C(19)	1.437(18)	C(25)–C(29)	1.344(10)
Nb(1)–C(17)	2.474(9)	Nb(2)–C(27)	2.513(7)	C(16)–C(17)	1.269(14)	C(26)–C(27)	1.382(11)
Nb(1)–C(18)	2.489(7)	Nb(2)–C(28)	2.471(7)	C(17)–C(18)	1.264(13)	C(27)–C(28)	1.392(12)
Nb(1)–C(19)	2.395(8)	Nb(2)–C(29)	2.373(5)	C(18)–C(19)	1.338(13)	C(28)–C(29)	1.375(11)
N(1)–C(11)	1.444(5)	N(2)–C(21)	1.447(5)				
Cl(11)–Nb(1)–Cl(12)	106.4(1)	Cl(21)–Nb(2)–Cl(22)	105.4(1)	C(16)–Nb(1)–C(19)	54.7(3)	C(26)–Nb(2)–C(29)	54.2(2)
Cl(11)–Nb(1)–N(1)	103.1(1)	Cl(21)–Nb(2)–N(2)	103.6(1)	C(17)–Nb(1)–C(19)	51.8(3)	C(27)–Nb(2)–C(29)	54.0(2)
Cl(12)–Nb(1)–N(1)	102.1(1)	Cl(22)–Nb(2)–N(2)	100.7(1)	C(18)–Nb(1)–C(19)	31.7(3)	C(28)–Nb(2)–C(29)	32.9(3)
Cl(11)–Nb(1)–C(15)	125.2(4)	Cl(21)–Nb(2)–C(25)	115.1(2)	Nb(1)–N(1)–C(11)	172.5(3)	Nb(2)–N(2)–C(21)	170.0(3)
Cl(12)–Nb(1)–C(15)	121.4(4)	Cl(22)–Nb(2)–C(25)	133.1(2)	N(1)–C(11)–C(12)	109.5(4)	N(2)–C(21)–C(22)	110.1(4)
N(1)–Nb(1)–C(15)	92.2(2)	N(2)–Nb(2)–C(25)	92.2(2)	N(1)–C(11)–C(13)	107.5(4)	N(2)–C(21)–C(23)	107.7(3)
Cl(11)–Nb(1)–C(16)	92.8(2)	Cl(21)–Nb(2)–C(26)	88.0(1)	C(12)–C(11)–C(13)	109.3(6)	C(22)–C(21)–C(23)	110.5(4)
Cl(12)–Nb(1)–C(16)	139.6(3)	Cl(22)–Nb(2)–C(26)	136.1(2)	N(1)–C(11)–C(14)	108.2(5)	N(2)–C(21)–C(24)	107.1(4)
N(1)–Nb(1)–C(16)	107.8(3)	N(2)–Nb(2)–C(26)	145.7(2)	C(12)–C(11)–C(14)	111.7(6)	C(22)–C(21)–C(24)	111.3(4)
C(15)–Nb(1)–C(16)	33.0(5)	C(25)–Nb(2)–C(26)	32.2(2)	C(13)–C(11)–C(14)	110.6(6)	C(23)–C(21)–C(24)	110.1(4)
Cl(11)–Nb(1)–C(17)	85.1(1)	Cl(21)–Nb(2)–C(27)	92.0(2)	Nb(1)–C(15)–C(16)	74.6(7)	Nb(2)–C(25)–C(26)	76.2(4)
Cl(12)–Nb(1)–C(17)	115.1(2)	Cl(22)–Nb(2)–C(27)	104.3(2)	Nb(1)–C(15)–C(19)	74.3(6)	Nb(2)–C(25)–C(29)	73.3(4)
N(1)–Nb(1)–C(17)	138.1(2)	N(2)–Nb(2)–C(27)	145.7(2)	C(16)–C(15)–C(19)	104.1(8)	C(26)–C(25)–C(29)	109.5(6)
C(15)–Nb(1)–C(17)	52.4(3)	C(25)–Nb(2)–C(27)	53.5(2)	Nb(1)–C(16)–C(15)	72.4(8)	Nb(2)–C(26)–C(25)	71.5(4)
C(16)–Nb(1)–C(17)	30.3(3)	C(26)–Nb(2)–C(27)	32.4(3)	Nb(1)–C(16)–C(17)	79.3(8)	Nb(2)–C(26)–C(27)	76.8(5)
Cl(11)–Nb(1)–C(18)	106.2(2)	Cl(21)–Nb(2)–C(28)	122.5(2)	C(15)–C(16)–C(17)	109.7(11)	C(25)–C(26)–C(27)	108.3(6)
Cl(12)–Nb(1)–C(18)	89.0(3)	Cl(22)–Nb(2)–C(28)	84.8(2)	Nb(1)–C(17)–C(16)	70.4(7)	Nb(2)–C(27)–C(26)	70.8(4)
N(1)–Nb(1)–C(18)	144.3(2)	N(2)–Nb(2)–C(28)	130.4(2)	Nb(1)–C(17)–C(18)	75.9(6)	Nb(2)–C(27)–C(28)	72.1(5)
C(15)–Nb(1)–C(18)	53.9(3)	C(25)–Nb(2)–C(28)	54.1(3)	C(16)–C(17)–C(18)	112.0(8)	C(26)–C(27)–C(28)	106.8(6)
C(16)–Nb(1)–C(18)	51.1(4)	C(26)–Nb(2)–C(28)	54.0(3)	Nb(1)–C(18)–C(17)	74.6(5)	Nb(2)–C(28)–C(27)	75.4(4)
C(17)–Nb(1)–C(18)	29.5(3)	C(27)–Nb(2)–C(28)	32.4(3)	Nb(1)–C(18)–C(19)	70.2(5)	Nb(2)–C(28)–C(29)	69.6(4)
Cl(11)–Nb(1)–C(19)	136.3(2)	Cl(21)–Nb(2)–C(29)	141.8(2)	C(17)–C(18)–C(19)	109.6(8)	C(27)–C(28)–C(29)	106.9(7)
Cl(12)–Nb(1)–C(19)	88.7(2)	Cl(22)–Nb(2)–C(29)	100.3(2)	Nb(1)–C(19)–C(15)	70.5(5)	Nb(2)–C(29)–C(25)	73.8(3)
N(1)–Nb(1)–C(19)	113.8(3)	N(2)–Nb(2)–C(29)	98.8(2)	Nb(1)–C(19)–C(18)	78.1(4)	Nb(2)–C(29)–C(28)	77.5(4)
C(15)–Nb(1)–C(19)	35.3(4)	C(25)–Nb(2)–C(29)	32.9(2)	C(15)–C(19)–C(18)	104.6(8)	C(25)–C(29)–C(28)	108.5(6)

Table 5 Bond lengths (Å) and angles (°) for compound **1d**

Nb–Cl	2.338(2)	Nb–N	1.761(6)
Nb–C(8)	2.396(11)	Nb–C(9)	2.362(14)
Nb–C(10)	2.442(10)	N–C(1)	1.408(9)
C(1)–C(2)	1.401(6)	C(2)–C(3)	1.411(12)
C(2)–C(5)	1.524(8)	C(3)–C(4)	1.378(10)
C(5)–C(6)	1.507(10)	C(5)–C(7)	1.487(10)
C(8)–C(9)	1.285(13)	C(9)–C(10)	1.360(21)
C(10)–C(10')	1.404(27)		
Cl–Nb–N	102.4(1)	Cl–Nb–C(8)	123.0(1)
N–Nb–C(8)	90.7(3)	Cl–Nb–C(9)	141.2(3)
N–Nb–C(9)	105.1(4)	C(8)–Nb–C(9)	31.3(3)
Cl–Nb–C(10)	114.0(3)	N–Nb–C(10)	137.8(4)
C(8)–Nb–C(10)	52.0(4)	C(9)–Nb–C(10)	32.8(5)
Cl–Nb–Cl'	108.0(1)	C(9)–Nb–Cl'	92.4(3)
C(10)–Nb–Cl'	86.6(3)	C(9)–Nb–C(9')	54.2(5)
C(10)–Nb–C(9')	54.7(4)	C(10)–Nb–C(10')	33.4(6)
Nb–N–C(1)	165.6(5)	N–C(1)–C(2)	118.7(3)
C(2)–C(1)–C(2')	122.6(7)	C(1)–C(2)–C(3)	117.6(5)
C(1)–C(2)–C(5)	122.1(5)	C(3)–C(2)–C(5)	120.4(5)
C(2)–C(3)–C(4)	120.5(8)	C(3)–C(4)–C(3')	121.2(11)
C(2)–C(5)–C(6)	109.5(5)	C(2)–C(5)–C(7)	113.5(5)
C(6)–C(5)–C(7)	112.8(6)	Nb–C(8)–C(9)	72.9(8)
C(9)–C(8)–C(9')	113.8(15)	Nb–C(9)–C(8)	75.8(7)
Nb–C(9)–C(10)	76.8(8)	C(8)–C(9)–C(10)	106.7(10)
Nb–C(10)–C(9)	70.3(7)	Nb–C(10)–C(10')	73.3(3)
C(9)–C(10)–C(10')	106.0(7)		

Symmetry operation for primed atoms: $-x, y, z$.

chemicals were obtained commercially and used as received unless stated otherwise.

Computational Methods. The Fenske–Hall calculations¹⁴ employed single ζ Slater functions for the 1s, 2s and 3s functions of N, O, C, S, P and Cl. The exponents were obtained by curve

Table 6 Bond lengths (Å) and angles (°) for compound **1f**

Ta–Cl	2.345(2)	Ta–N	1.780(5)
Ta–C(8)	2.366(8)	Ta–C(9)	2.396(5)
Ta–C(10)	2.500(6)	N–C(1)	1.380(8)
C(1)–C(2)	1.412(6)	C(2)–C(3)	1.392(8)
C(2)–C(5)	1.516(8)	C(3)–C(4)	1.363(8)
C(5)–C(6)	1.529(14)	C(5)–C(7)	1.520(13)
C(8)–C(9)	1.424(8)	C(8)–C(11)	1.529(14)
C(9)–C(10)	1.425(9)	C(9)–C(12)	1.488(9)
C(10)–C(13)	1.506(11)	C(10)–C(10')	1.402(14)
Cl–Ta–N	102.2(1)	Cl–Ta–C(8)	124.2(1)
N–Ta–C(8)	90.8(3)	Cl–Ta–C(9)	90.5(1)
N–Ta–C(9)	108.2(2)	C(8)–Ta–C(9)	34.8(2)
Cl–Ta–C(10)	85.5(2)	N–Ta–C(10)	141.9(2)
C(8)–Ta–C(10)	55.8(2)	C(9)–Ta–C(10)	33.8(2)
Cl–Ta–Cl'	105.8(1)	C(9)–Ta–Cl'	141.5(1)
C(10)–Ta–Cl'	111.6(2)	C(9)–Ta–C(9')	58.0(3)
C(10)–Ta–C(9')	56.0(2)	C(10)–Ta–C(10')	32.6(3)
Ta–N–C(1)	171.4(5)	N–C(1)–C(2)	120.0(3)
C(2)–C(1)–C(2')	120.0(6)	C(1)–C(2)–C(3)	118.2(5)
C(1)–C(2)–C(5)	121.1(5)	C(3)–C(2)–C(5)	120.7(5)
C(2)–C(3)–C(4)	121.8(6)	C(3)–C(4)–C(3')	119.9(8)
C(2)–C(5)–C(6)	110.0(6)	C(2)–C(5)–C(7)	112.1(6)
C(6)–C(5)–C(7)	111.1(7)	Ta–C(8)–C(9)	73.8(4)
Ta–C(8)–C(11)	121.1(5)	C(9)–C(8)–C(11)	125.3(4)
C(9)–C(8)–C(9')	109.3(8)	Ta–C(9)–C(8)	71.5(4)
Ta–C(9)–C(10)	77.1(3)	C(8)–C(9)–C(10)	106.4(5)
Ta–C(9)–C(12)	121.5(4)	C(8)–C(9)–C(12)	126.4(7)
C(10)–C(9)–C(12)	127.0(6)	Ta–C(10)–C(9)	69.1(3)
Ta–C(10)–C(13)	125.0(5)	C(9)–C(10)–C(13)	124.6(6)
Ta–C(10)–C(10')	73.7(2)	C(9)–C(10)–C(10')	108.8(4)
C(13)–C(10)–C(10')	126.6(4)		

Symmetry operation for primed atoms: $x, \frac{1}{2} - y, z$.

Table 7 Distortions in M-C₅R₅ bonding (see text for definition of Δ*M*, Δ*R* and Δ*X*)

Compound	Δ <i>M</i> /Å	Δ <i>R</i> /Å	Δ <i>X</i> /Å	Imido bend angle (°)
1a	0.120	0.025	0.115	16.6
1c*	0.144	0.173	0.143	7.5
	0.140	0.053	0.083	10.0
1d	0.080	0.119	0.048	14.4
1f	0.134	0.023	0.165	8.6

* Two independent molecules.

Table 8 Atomic coordinates (× 10⁴) for compound **2a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Nb(1)	7 667.5(3)	9 045.5(3)	7 182.4(3)
Cl(11)	8 357.8(11)	7 468.5(9)	6 989.1(9)
Cl(12)	8 501.9(10)	9 370.5(12)	5 948.1(9)
P(1)	7 745.1(10)	8 185.5(9)	8 691.3(8)
Nb(2)	6 910.5(3)	3 481.3(3)	6 693.0(3)
Cl(21)	6 500.3(11)	2 392.8(8)	7 799.9(9)
Cl(22)	5 295.9(12)	2 717.8(12)	5 646.3(10)
P(2)	7 923.3(9)	4 149.8(8)	8 297.9(8)
C(11)	7 341(5)	8 883(4)	9 516(4)
C(12)	9 118(4)	7 864(5)	9 308(4)
C(13)	6 990(5)	7 128(3)	8 638(4)
C(14)	5 815(3)	9 008(4)	7 262(3)
C(15)	5 738(3)	8 590(4)	6 420(3)
C(16)	6 002(4)	9 234(4)	5 880(4)
C(17)	6 242(4)	10 067(4)	6 369(4)
C(18)	6 109(4)	9 921(4)	7 218(4)
N(1)	8 532(3)	9 836(3)	7 947(3)
C(19)	9 014(5)	10 567(4)	8 532(4)
C(21)	6 925(4)	4 512(4)	8 842(3)
C(22)	8 703(4)	5 177(3)	8 280(4)
C(23)	8 871(4)	3 438(4)	9 138(3)
C(24)	8 841(4)	3 418(6)	6 808(4)
C(25)	8 471(7)	2 525(6)	6 523(6)
C(26)	7 710(7)	2 615(6)	5 674(6)
C(27)	7 621(5)	3 535(6)	5 435(4)
C(28)	8 330(5)	4 033(5)	6 129(4)
N(2)	6 276(3)	4 589(3)	6 537(2)
C(29)	5 894(5)	5 495(4)	6 322(4)

fitting the double- ζ function of Clementi²² while maintaining orthogonal functions; the double- ζ functions were used directly for the 2p and 3p orbitals. For phosphorus an expanded atomic orbital basis set used an exponent of 1.80 for the 3d functions. An exponent of 1.20 was used for hydrogen corresponding to the minimum-energy exponent for methane.²³ The niobium and zirconium functions, chosen for the +1 oxidation state, were based on the results of Richardson *et al.*,²⁴ and augmented by 5s and 5p functions with an exponent of 2.20. Two Slater-type orbitals (STOs) were used to represent the valence-shell 4d orbitals.²⁵

Preparations.—[Nb(η -C₅H₅)(NMe)Cl₂] **1a**. The compound [Nb(η -C₅H₅)Cl₄] (5.0 g, 16.7 mmol) and heptamethyldisilazane (2.93 g, 16.7 mmol) were stirred in acetonitrile (20 cm³) for 2 h. The red suspension was consumed to give a yellow-orange solution, which was stirred for 6 h. Removal of the volatile components, followed by washing with light petroleum (2 × 25 cm³, b.p. 40–60 °C) and drying *in vacuo*, gave a yellow powder which was recrystallized from toluene to afford orange crystals of compound **1a**. Yield 3.74 g (87%) (Found: C, 27.95; H, 3.30; Cl, 27.85; N, 5.15. C₆H₈Cl₂NNb requires C, 27.95; H, 3.15; Cl, 27.50; N, 5.45%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 5.72 (s, 5 H, C₅H₅) and 3.21 (s, 3 H, NMe); ¹³C-{¹H}, δ 54.3 (NMe) and 112.9 (C₅H₅). IR (Nujol, CsI): 3045w, 1446(sh), 1427m, 1250m, 1007s, 928w, 852s, 840m, 820vs, 720w, 593w, 428m, 381vs, 343m and 289w cm⁻¹. Mass spectrum: *m/z* 257, [M]⁺; 242, [M - Me]⁺; and 228, [M - NMe]⁺.

[Nb(η -C₅Me₅)(NMe)Cl₂] **1b**. The compound [Nb(η -C₅Me₅)Cl₄] (700 mg, 1.89 mmol) and heptamethyldisilazane (280 mg, 1.90 mmol) were stirred in acetonitrile (20 cm³) for 14 h. The volatile components were removed *in vacuo*, and the resultant dark orange solid was recrystallized from toluene-pentane to give light orange crystals of compound **1b**. Yield 372 mg (60%) (Found: C, 40.20; H, 5.60; N, 3.80. C₁₁H₁₈Cl₂NNb requires C, 40.25; H, 5.55; N, 4.25%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 1.77 (s, 15 H, C₅Me₅) and 3.25 (s, 3 H, NMe); ¹³C-{¹H}, δ 11.3 (C₅Me₅), 49.1 (NMe) and 122.2 (C₅Me₅). IR (Nujol, CsI): 1255s, 1025w, 810vw, 590m, 445m, 405s, 385s and 340 cm⁻¹. Mass spectrum: *m/z* 327, [M]⁺; and 298, [M - NMe]⁺.

[Nb(η -C₅H₅)(NBu^t)Cl₂] **1c**. A solution of NBu^t(SiMe₃) (9.69 g, 66.7 mmol) in dichloromethane (50 cm³) was added dropwise to a stirred suspension of [Nb(η -C₅H₅)Cl₄] (10.0 g, 33.4 mmol) in dichloromethane (150 cm³). The red suspension was consumed over 12 h to give an orange-red solution. Removal of the volatile components, followed by washing with cold light petroleum (15 cm³) and drying *in vacuo* gave a brown solid, which was extracted with diethyl ether (2 × 100 cm³). The combined extracts were concentrated and cooled to -78 °C to afford yellow crystals of compound **1c**. Yield 7.77 g (78%) (Found: C, 36.20; H, 4.90; N, 4.80. C₉H₁₄Cl₂NNb requires C, 36.05; H, 4.70; N, 4.65%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 1.02 (s 9 H, CMe₃) and 5.88 (s, 5 H, C₅H₅); ¹³C-{¹H}, δ 30.4 (CMe₃), 70.0 (CMe₃) and 112.4 (C₅H₅). IR (Nujol, CsI): 3040w, 1378m, 1242s, 1218s, 1150m, 1020m, 1010m, 844m, 812s, 805s, 720w, 576w, 550m, 535m, 395vs, 378s, 343s and 305m cm⁻¹. Mass spectrum: *m/z* 299, [M]⁺; 284, [M - Me]⁺; 269, [M - 2Me]⁺; and 228, [M - NBu^t]⁺.

[Nb(η -C₅H₅)(NC₆H₃Pr₂-2,6)Cl₂] **1d**. A solution of 2,6-diisopropylphenyl(trimethylsilyl)amine (3.33 g, 26.7 mmol) in dichloromethane (30 cm³) was added dropwise to a stirred suspension of [Nb(η -C₅H₅)Cl₄] (4.00 g, 13.3 mmol) in dichloromethane (40 cm³). The red suspension was consumed over 12 h to give a red solution. Removal of the volatile components under reduced pressure, followed by washing with cold light petroleum (15 cm³) and drying *in vacuo*, gave a red solid, which was extracted with pentane (2 × 50 cm³). Concentration and cooling of the combined extracts to -78 °C afforded red crystals of compound **1d**. Yield 4.26 g (79%). Alternatively, the reaction may be performed using 1 equivalent of 2,6-diisopropylphenyl(trimethylsilyl)amine and 1 equivalent of 2,6-dimethylpyridine; in this case, the reaction mixture was reduced to dryness and the resultant oily solid extracted with diethyl ether. This solution was filtered and the solvent removed under reduced pressure. The residue was then dried, washed with light petroleum and recrystallized from pentane (Found: C, 50.10; H, 5.30; Cl, 17.80; N, 3.15. C₁₇H₂₂Cl₂NNb requires C, 50.50; H, 5.50; Cl, 17.55; N, 3.45%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 1.24 [d, ³J = 6.9, 12 H, CHMe₂], 3.72 [spt, ³J = 6.9 Hz, 2 H, CHMe₂], 5.82 (s, 5 H, C₅H₅) and 6.88–6.98 (m, 3 H, aryl); ¹³C-{¹H}, δ 24.1 (CHMe₂), 28.5 (CHMe₂), 113.5 (C₅H₅), 122.8, 126.7, 145.5 and 152.0 (all aryl). IR (Nujol, CsI): 3052w, 3029w, 1622w, 1588w, 1425w, 1350w, 1310(sh)w, 1332m, 1285m, 1114w, 1024w, 986w, 934w, 856m, 843w, 831w, 819s, 798s, 758vs, 457w, 402m, 382m and 321w cm⁻¹. Mass spectrum: *m/z* 403, [M]⁺; 388 [M - Me]⁺; 368, [M - Cl]⁺; and 228, [M - NC₆H₃Pr₂-2,6]⁺.

[Nb(η -C₅Me₅)(NC₆H₃Pr₂-2,6)Cl₂] **1e**. The compound [Nb(η -C₅Me₅)Cl₄] (7.10 g, 19.2 mmol) and 2,6-diisopropylphenyl(trimethylsilyl)amine (9.57 g, 38.4 mmol) were stirred in 1,2-dichloroethane (150 cm³) at 80 °C for 2 d. After cooling to room temperature, the volatile components were removed under reduced pressure, the crude product was washed with pentane (30 cm³) and recrystallized from toluene to give dark red crystals of compound **1e**. Yield 7.36 g (81%) (Found: C, 56.10; H, 7.25; N, 2.55. C₂₂H₃₂Cl₂NNb requires C, 55.70; H, 6.80; N, 2.95%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 1.29 (d, ³J = 6.8, 12 H, CHMe₂), 1.78 (s, 15 H, C₅Me₅), 3.52 (spt, ³J =

Table 9 Bond lengths (Å) and angles (°) for compound **2a**

Nb(1)–Cl(11)	2.499(2)	Nb(2)–Cl(21)	2.488(2)	P(1)–C(11)	1.814(7)	P(2)–C(21)	1.816(6)
Nb(1)–Cl(12)	2.494(2)	Nb(2)–Cl(22)	2.477(2)	P(1)–C(12)	1.804(5)	P(2)–C(22)	1.800(5)
Nb(1)–P(1)	2.604(2)	Nb(2)–P(2)	2.601(1)	P(1)–C(13)	1.803(6)	P(2)–C(23)	1.808(5)
Nb(1)–C(14)	2.440(5)	Nb(2)–C(24)	2.454(6)	C(14)–C(15)	1.403(8)	C(24)–C(25)	1.399(12)
Nb(1)–C(15)	2.504(4)	Nb(2)–C(25)	2.526(9)	C(14)–C(18)	1.380(8)	C(24)–C(28)	1.378(9)
Nb(1)–C(16)	2.472(4)	Nb(2)–C(26)	2.462(10)	C(15)–C(16)	1.358(8)	C(25)–C(26)	1.381(11)
Nb(1)–C(17)	2.399(5)	Nb(2)–C(27)	2.379(7)	C(16)–C(17)	1.403(8)	C(26)–C(27)	1.375(12)
Nb(1)–C(18)	2.397(5)	Nb(2)–C(28)	2.395(7)	C(17)–C(18)	1.381(10)	C(27)–C(28)	1.379(9)
Nb(1)–N(1)	1.772(4)	Nb(2)–N(2)	1.782(4)	N(1)–C(19)	1.404(7)	N(2)–C(29)	1.404(7)
Cl(11)–Nb(1)–Cl(12)	80.1(1)	Cl(21)–Nb(2)–Cl(22)	81.3(1)	Cl(12)–Nb(1)–N(1)	92.8(2)	Cl(22)–Nb(2)–N(2)	92.8(1)
Cl(11)–Nb(1)–P(1)	75.6(1)	Cl(21)–Nb(2)–P(2)	74.9(1)	P(1)–Nb(1)–N(1)	82.7(1)	P(2)–Nb(2)–N(2)	82.7(1)
Cl(12)–Nb(1)–P(1)	149.0(1)	Cl(22)–Nb(2)–P(2)	149.8(1)	C(14)–Nb(1)–N(1)	114.5(2)	C(24)–Nb(2)–N(2)	117.5(2)
Cl(11)–Nb(1)–C(14)	112.2(1)	Cl(21)–Nb(2)–C(24)	110.5(2)	C(15)–Nb(1)–N(1)	145.0(2)	C(25)–Nb(2)–N(2)	145.9(3)
Cl(12)–Nb(1)–C(14)	134.6(1)	Cl(22)–Nb(2)–C(24)	132.2(2)	C(16)–Nb(1)–N(1)	133.3(2)	C(26)–Nb(2)–N(2)	129.5(2)
P(1)–Nb(1)–C(14)	73.6(1)	P(2)–Nb(2)–C(24)	74.7(2)	C(17)–Nb(1)–N(1)	100.4(2)	C(27)–Nb(2)–N(2)	97.9(2)
Cl(11)–Nb(1)–C(15)	92.7(1)	Cl(21)–Nb(2)–C(25)	93.9(2)	C(18)–Nb(1)–N(1)	90.7(2)	C(28)–Nb(2)–N(2)	91.5(2)
Cl(12)–Nb(1)–C(15)	107.2(1)	Cl(22)–Nb(2)–C(25)	103.5(2)	Nb(1)–P(1)–C(11)	114.4(2)	Nb(2)–P(2)–C(21)	108.5(1)
P(1)–Nb(1)–C(15)	93.1(1)	P(2)–Nb(2)–C(25)	96.4(2)	Nb(1)–P(1)–C(12)	110.8(2)	Nb(2)–P(2)–C(22)	114.6(2)
C(14)–Nb(1)–C(15)	32.9(2)	C(24)–Nb(2)–C(25)	32.6(3)	C(11)–P(1)–C(12)	103.0(3)	C(21)–P(2)–C(22)	104.5(3)
Cl(11)–Nb(1)–C(16)	105.1(2)	Cl(21)–Nb(2)–C(26)	109.3(2)	Nb(1)–P(1)–C(13)	119.3(2)	Nb(2)–P(2)–C(23)	120.2(2)
Cl(12)–Nb(1)–C(16)	80.6(1)	Cl(22)–Nb(2)–C(26)	78.3(2)	C(11)–P(1)–C(13)	103.6(3)	C(21)–P(2)–C(23)	105.1(2)
P(1)–Nb(1)–C(16)	124.1(1)	P(2)–Nb(2)–C(26)	127.0(2)	C(12)–P(1)–C(13)	103.9(3)	C(22)–P(2)–C(23)	102.6(2)
C(14)–Nb(1)–C(16)	54.0(2)	C(24)–Nb(2)–C(26)	53.9(2)	Nb(1)–C(14)–C(15)	76.1(3)	Nb(2)–C(24)–C(25)	76.6(5)
C(15)–Nb(1)–C(16)	31.7(2)	C(25)–Nb(2)–C(26)	32.1(3)	Nb(1)–C(14)–C(18)	71.7(3)	Nb(2)–C(24)–C(28)	71.1(4)
Cl(11)–Nb(1)–C(17)	138.3(1)	Cl(21)–Nb(2)–C(27)	142.2(2)	C(15)–C(14)–C(18)	108.0(5)	C(25)–C(24)–C(28)	108.6(6)
Cl(12)–Nb(1)–C(17)	86.0(2)	Cl(22)–Nb(2)–C(27)	86.9(2)	Nb(1)–C(15)–C(14)	71.0(2)	Nb(2)–C(25)–C(24)	70.9(4)
P(1)–Nb(1)–C(17)	125.0(2)	P(2)–Nb(2)–C(27)	123.3(2)	Nb(1)–C(15)–C(16)	72.9(3)	Nb(2)–C(25)–C(26)	71.4(5)
C(14)–Nb(1)–C(17)	55.0(2)	C(24)–Nb(2)–C(27)	54.8(2)	C(14)–C(15)–C(16)	107.9(5)	C(24)–C(25)–C(26)	106.6(7)
C(15)–Nb(1)–C(17)	54.3(2)	C(25)–Nb(2)–C(27)	54.2(3)	Nb(1)–C(16)–C(15)	75.5(3)	Nb(2)–C(26)–C(25)	76.5(6)
C(16)–Nb(1)–C(17)	33.4(2)	C(26)–Nb(2)–C(27)	32.9(3)	Nb(1)–C(16)–C(17)	70.4(3)	Nb(2)–C(26)–C(27)	70.2(5)
Cl(11)–Nb(1)–C(18)	144.9(1)	Cl(21)–Nb(2)–C(28)	143.5(1)	C(15)–C(16)–C(17)	108.5(5)	C(25)–C(26)–C(27)	108.7(7)
Cl(12)–Nb(1)–C(18)	118.7(2)	Cl(22)–Nb(2)–C(28)	120.2(1)	Nb(1)–C(17)–C(16)	76.2(3)	Nb(2)–C(27)–C(26)	76.9(5)
P(1)–Nb(1)–C(18)	92.2(2)	P(2)–Nb(2)–C(28)	89.8(1)	Nb(1)–C(17)–C(18)	73.2(3)	Nb(2)–C(27)–C(28)	73.8(4)
C(14)–Nb(1)–C(18)	33.1(2)	C(24)–Nb(2)–C(28)	33.0(2)	C(16)–C(17)–C(18)	107.6(5)	C(26)–C(27)–C(28)	108.4(6)
C(15)–Nb(1)–C(18)	54.6(2)	C(25)–Nb(2)–C(28)	54.4(3)	Nb(1)–C(18)–C(14)	75.1(3)	Nb(2)–C(28)–C(24)	75.9(4)
C(16)–Nb(1)–C(18)	54.9(2)	C(26)–Nb(2)–C(28)	54.7(3)	Nb(1)–C(18)–C(17)	73.3(3)	Nb(2)–C(28)–C(27)	72.6(4)
C(17)–Nb(1)–C(18)	33.5(2)	C(27)–Nb(2)–C(28)	33.6(2)	C(14)–C(18)–C(17)	108.0(5)	C(24)–C(28)–C(27)	107.6(7)
Cl(11)–Nb(1)–N(1)	119.3(1)	Cl(21)–Nb(2)–N(2)	118.3(1)	Nb(1)–N(1)–C(19)	167.9(4)	Nb(2)–N(2)–C(29)	170.1(4)

Table 10 Compositions of Nb(η -C₅H₅)Cl₂²⁺ fragment frontier orbitals

Orbital	Composition (%)	
	Ligands (C ₅ H ₅ , Cl)	Metal
21 (HOMO)	95	3 d _{yz} , 2 p _z
22 (LUMO)	22	30 d _{xy} , 26 d _{x²-y²} , 15 d _{z²} , 7 s
23	25	65 d _{xy} , 10 p _z
24	23	48 d _{z²} , 11 p _y , 10 d _{xy} , 8 d _{x²-y²}
25	28	26 d _{xy} , 23 d _{x²-y²} , 12 s, 11 p _x
26	42	47 d _{yz} , 11 p _z

Table 11 Composition of NMe₂⁻ fragment frontier molecular orbitals

Orbital	Composition (% N)
5	59 p _x , 28 s
6	91 p _y
7	99 p _z

Table 12 Percentage total overlap populations for the principal interactions between the Nb(η -C₅H₅)Cl₂²⁺ and NMe₂⁻ fragments

Metal fragment MO	Ligand fragment MO	% Of total net Mulliken overlap population
22 (LUMO)	5	16.4
22 (LUMO)	6	20.6
23	7	33.6
25	5	29.4

6.8, 2 H, CHMe₂), 6.92 (t, ³J = 7.6, 1 H, aryl) and 7.03 (d, ³J = 7.6 Hz, 2 H, aryl); ¹³C-{¹H}, δ 11.6 (C₅Me₅), 24.3 (CHMe₂), 28.5 (CHMe₂), 122.7 (aryl), 123.3 (C₅Me₅), 125.8, 145.6 and 148.9 (all aryl). IR (Nujol, CsI): 1570w, 1330s, 1285s, 1110m, 1030m, 985m, 805s, 760vs, 460m, 445m, 390s, 375vs, 360s and 320m cm⁻¹. Mass spectrum: m/z 473, [M]⁺; and 298, [M - NC₆H₃Prⁱ₂-2,6]⁺.

[Ta(η -C₅Me₅)(NC₆H₃Prⁱ₂-2,6)Cl₂] **If**. The compound [Ta(η -C₅Me₅)Cl₄] (7.64 g, 16.7 mmol) and 2,6-diisopropylphenyl(trimethylsilyl)amine (8.32 g, 33.4 mmol) were stirred in 1,2-dichloroethane (250 cm³) at 70 °C for 10 d to give an orange solution. This was filtered and reduced to dryness to give an orange residue which was washed with cold pentane (2 × 20 cm³). Extraction of the residue with toluene (150 cm³) followed by concentration and cooling to ca. -50 °C afforded orange crystals of compound **If**. Yield 6.80 g (72.5%) (Found: C, 47.45; H, 5.75; N, 2.20. C₂₂H₃₂Cl₂NTa requires C, 47.00; H, 5.75; N, 2.50%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 1.33 (d, ³J = 6.8, 6 H, CHMe₂), 1.86 (s, 15 H, C₅Me₅), 3.53 (spt, ³J = 6.8, 2 H, CHMe₂), 6.87 (t, ³J = 7.6, 1 H, aryl) and 7.16 (d, ³J = 7.6 Hz, 2 H, aryl); ¹³C-{¹H}, δ 11.2 (C₅Me₅), 24.4 (CHMe₂), 28.1 (CHMe₂), 121.4 (C₅Me₅), 122.2, 124.9, 145.4 and 148.3 (all aryl). IR (Nujol, CsI): 1300m, 805s, 760vs, 375s and 360s cm⁻¹. Mass spectrum: m/z 561, [M]⁺; 546, [M - Me]⁺; and 386 [M - NC₆H₃Prⁱ₂-2,6]⁺.

[Nb(η -C₅H₅)(NMe)Cl₂(PMe₃)] **2a**. Trimethylphosphine (1.18 g, 15.5 mmol) was condensed onto a frozen solution of [Nb(η -C₅H₅)(NMe)Cl₂] (2.00 g, 7.75 mmol) in toluene (40 cm³). On warming the mixture to room temperature an immediate reaction ensued leading to the formation of a pale

Table 13 Comparison of the frontier orbital compositions for metallocene fragments

Fenske-Hall for $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2]^a$			Extended Hückel for $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2]^b$		
% Composition			% Composition		
Orbital	Ligands	Metal ^c	Orbital	Ligands	Metal ^c
27(1a ₁)	11	84 d _{y²} , 5 s	1a ₁	18	51 d _{x²-y²} , 30 d _{z²} , 1 s
28(b ₂)	27	66 d _{y²} , 7 p _y	b ₂	34	64 d _{y²} , 2 p _y
29(2a ₁)	14	36 d _{x²-x²} , 33 s, 17 p _z	2a ₁	21	33 d _{x²} , 27 d _{x²-y²} , 11 s, 8 p _z
30(b ₁)	33	60 d _{x²} , 7 p _y	b ₁	57	43 d _{x²}
31(a ₂)	40	60 d _{xy}	a ₂	69	31 d _{xy}

^a Using the crystallographically determined coordinates for $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ taken from ref. 15. ^b Taken from ref. 10. ^c Metal orbitals are defined with respect to the coordinate system in Fig. 9.

Table 14 Composition of the frontier orbitals of the $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})_2^+$ fragment

Composition (%)		
Orbital*	Ligands	Metal
21(1a ₁)[1a ₁]	12	79 d _{y²} , 9 s
22(a ⁺)[b ₂]	41	57 d _{y²} , 2 d _{xy}
23(2a ⁺)[2a ₁]	24	23 d _{x²-x²} , 19 d _{x²} , 18 s, 14 p _z , 2 p _x
24	21	35 d _{x²} , 17 s, 14 p _x , 7 d _{x²-x²} , 6 p _z
25	40	55 d _{xy} , 3 p _x , 2 d _{yz}

* C_{2v} symmetry labels of the $\text{Zr}(\eta\text{-C}_5\text{H}_5)_2^{2+}$ system (Table 13) are shown in square brackets to assist comparison.

precipitate and a yellow solution. After stirring for 12 h the off-white solid was collected by filtration, washed with light petroleum (2 × 10 cm³) and dried *in vacuo*. Recrystallization from hot toluene afforded pale yellow needles of compound **2a**. Yield 2.21 g (85%) (Found: C, 32.20; H, 5.20; Cl, 21.00; N, 4.00; Nb, 28.10. C₉H₁₇Cl₂NNbP requires C, 32.35; H, 5.15; Cl, 21.25; N, 4.20; Nb 27.80%). NMR (250 MHz, [²H]chloroform, 296 K): ¹H, δ 1.58 (d, ²J_{PH} = 9.2, 9 H, PMe₃), 3.85 (s, 3 H, NMe) and 6.16 (s, 5 H, C₅H₅); ¹³C-{¹H}, δ 14.7 (d, ¹J_{CP} = 26 Hz, PMe₃), 54.9 (NMe) and 109.9 (C₅H₅). IR (Nujol, CsI): 3040w, 1445(sh)w, 1419m, 1289w, 1278w, 1240s, 960s, 945m(sh), 814vs, 807vs, 741w, 734w, 577w, 394m and 282m cm⁻¹.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^t)\text{Cl}_2(\text{PMe}_3)]$ **2b**. By a procedure analogous to that described for compound **2a**, trimethylphosphine (250 mg, 3.33 mmol) was treated with $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^t)\text{Cl}_2]$ (500 mg, 1.67 mmol) in toluene (30 cm³) to give **2b** in the form of orange crystals. Yield 0.56 g (89%) (Found: C, 38.00; H, 6.10; Cl, 18.85; N, 4.00; Nb, 24.45. C₁₂H₂₃Cl₂NNbP requires C, 38.30; H, 6.10; Cl, 18.85; N, 3.70; Nb, 24.70%). NMR (250 MHz, [²H]chloroform, 296 K): ¹H, δ 1.26 (s, 9 H, CMe₃), 1.63 (d, ²J_{PH} = 9.1, 9 H, PMe₃) and 6.20 (s, 5 H, C₅H₅). ¹³C-{¹H}, δ 16.2 (d, ¹J_{CP} = 26 Hz, PMe₃), 30.8 (CMe₃), 71.4 (CMe₃) and 109.7 (C₅H₅). IR (Nujol, CsI): 3043w, 1430m, 1380m, 1295m, 1289m, 1238s, 1219m, 1125w, 1029m, 1015w, 965s, 950m(sh), 928w, 843s, 836s, 805vs, 742m, 630w, 580w, 549w, 532w, 332w, 232w and 289m cm⁻¹.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NC}_6\text{H}_3\text{Pr}^i\text{-2,6})\text{Cl}_2(\text{PMe}_3)]$ **2c**. Trimethylphosphine (0.26 g, 3.38 mmol) was condensed onto a frozen solution of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NC}_6\text{H}_3\text{Pr}^i\text{-2,6})\text{Cl}_2]$ **1d** (1.00 g, 2.47 mmol) in toluene (50 cm³). The mixture was warmed to room temperature and stirred for 30 min to give a yellow suspension. The solid was isolated by filtration, and dried *in vacuo* to give compound **2c** as a yellow microcrystalline solid. Yield 0.91 g (77%) (Found: C, 53.2; H, 6.8; N, 2.6. C₂₀H₃₁Cl₂NNbP requires C, 50.0; H, 6.3; N, 2.9%). NMR (250 MHz, [²H₈]toluene, 296 K): ¹H, δ 1.13 [s(br), 9 H, PMe₃], 1.23 (d, ³J = 6.9, 12 H, CHMe₂), 3.87 (spt, ³J = 6.9 Hz, 2 H, CHMe₂), 6.03 (s, 5 H, C₅H₅) and 6.87-6.99 (m, 3 H, aryl); ¹³C-{¹H}, δ 14.9 [s(br), PMe₃], 24.4 (CHMe₂), 27.88 (CHMe₂), 114.0 (C₅H₅), 123.1,

126.4 and 145.0 (all aryl). IR (Nujol, CsI): 3120w, 3090w, 3050w, 2850s, 1460s, 1420m, 1380m, 1330m, 1290m, 1280m, 1020m, 960s, 820s, 760s, 370w, 330w and 300m cm⁻¹. Mass spectrum: *m/z* 404, [*M* - PMe₃]⁺.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2(\text{PPh}_3)]$ **2d**. To a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2]$ (0.9 g, 3.45 mmol) and triphenylphosphine (0.92 g, 3.45 mmol) was added toluene (30 cm³) chilled to -78 °C. The mixture was allowed to warm to room temperature and stirred for 24 h to give an orange solution. The solution was filtered, concentrated under reduced pressure and cooled to ca. -50 °C to give white crystals of compound **2d**. Yield 1.38 g (76%) (Found: C, 55.4; H, 4.4; N, 2.7. C₂₄H₂₃Cl₂NNbP requires C, 55.0; H, 4.4; N, 2.6%). NMR (250 MHz, [²H₆]benzene, 296 K): ¹H, δ 3.17 (s, 3 H, Me), 5.70 (s, 5 H, C₅H₅), 7.02-7.04 and 7.35-7.42 (m, 15 H, Ph); ¹³C-{¹H}, δ 53.4 (Me), 112.4 (C₅H₅), 128.7, 128.8, 134.1 and 137.9 (Ph). IR (Nujol, CsI): 3080w, 3050w, 2900s, 2840s, 1440s, 1380s, 1240m, 1095m, 1025w, 1010w, 845w, 830s, 755m, 745m, 710m, 695m, 595w, 530m, 510m, 500w, 405m and 385m cm⁻¹. Mass spectrum: *m/z* 258, [*M* - PPh₃]⁺.

$[\text{Nb}(\eta\text{-C}_5\text{Me}_5)(\text{NMe})\text{Cl}_2(\text{PMe}_3)]$ **2e**. Trimethylphosphine (0.05 g, 6.10 mmol) was condensed onto a frozen solution of $[\text{Nb}(\eta\text{-C}_5\text{Me}_5)(\text{NMe})\text{Cl}_2]$ (0.1 g, 3.05 mmol) in pentane (30 cm³). The mixture was allowed to warm to room temperature and stirred for 30 min to give a pale yellow suspension. The solvent was then removed under reduced pressure, while maintaining the surroundings at 0 °C, to give a yellow powder. Yield 0.090 g (70%) (Found: C, 42.0; H, 6.6; N, 3.5. C₁₄H₂₇Cl₂NNbP requires C, 41.6; H, 6.7; N, 3.5%). NMR (250 MHz, [²H₈]toluene, 296 K): ¹H, δ 0.75 [s(br), 9 H, PMe₃], 1.82 (s, 15 H, C₅Me₅) and 3.35 (s, 3 H, Me); ¹³C-{¹H}, δ 11.5 (C₅Me₅), 12.4 (d, ¹J_{CP} = 36 Hz, PMe₃), 49.3 (Me) and 121.2 (C₅Me₅). IR (Nujol, CsI): 2920s, 2820s, 2480w, 1580m, 1540w, 1460s, 1440m, 1380s, 1295w, 1060w, 1020w, 1000m, 960m, 845m, 785s, 720m, 670s, 650s, 605m, 590s, 365m and 310m cm⁻¹. Mass spectrum: *m/z* 328, [*M* - PMe₃]⁺.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2]$ **3a**. Chilled toluene (40 cm³) was added to a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2]$ (0.5 g, 1.94 mmol) and LiOC₆H₃Me₂-2,6 (0.5 g, 3.88 mmol). The mixture was allowed to warm to room temperature and stirred for 12 h, during which time a pale yellow solution and a pale gelatinous precipitate were formed. Filtration of the supernatant solution from the solid, followed by concentration to half volume and cooling to -50 °C, afforded pale yellow crystals of compound **3a**, which were collected, washed with cold light petroleum (2 × 5 cm³) and dried *in vacuo*. Yield 0.62 g (74%) (Found: C, 61.20; H, 6.20; N, 3.00; Nb, 21.30. C₂₂H₂₆NNbO₂ requires C, 61.55; H, 6.10; N, 3.25; Nb, 21.65%). NMR (250 MHz, [²H]chloroform, 296 K): ¹H, δ 2.50 (s, 12 H, C₆H₃Me₂), 3.30 (s, 3 H, NMe), 6.16 (s, 5 H, C₅H₅) and 7.02-7.23 (m, 6 H, aryl); ¹³C-{¹H}, δ 17.4 (C₆H₃Me₂), 111.4 (C₅H₅), 120.0, 126.0, 128.3 and 162.7 (all aryl). IR (Nujol, CsI): 3024w(sh), 1589m, 1276vs, 1225vs(sh), 1215vs, 1088s, 1062w, 1020m, 1010m, 890s, 866s, 819s, 811s, 798vs, 761vs, 752vs, 738s, 730s,

599w, 572m, 561m, 400m, 380s and 266w cm^{-1} . Mass spectrum: m/z 429 $[M]^+$; and 308, $[M - \text{OC}_5\text{H}_5\text{Me}_2-2,6]^+$.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})(\text{OBU}^i)_2]$ **3b**. Chilled diethyl ether (40 cm^3) was added to a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NMe})\text{Cl}_2]$ (0.5 g, 1.94 mmol) and LiOBU^i (0.31 g, 3.88 mmol). The mixture was allowed to warm to room temperature and stirred for 12 h, during which time a pale yellow solution and a pale gelatinous precipitate were formed. The suspension was filtered, the solvent removed under reduced pressure, and the residue dried *in vacuo*. The resultant brown oily solid was washed with cold pentane (10 cm^3) to give 0.6 g (95%) of crude product. Sublimation at 50 °C (5×10^{-4} Torr, ca. 0.067 Pa) afforded compound **3b** as a white crystalline solid (Found: C, 50.10; H, 7.30; N, 4.00. $\text{C}_{14}\text{H}_{26}\text{NNbO}_2$ requires C, 50.10; H, 7.85; N, 4.20%). NMR (250 MHz, $[\text{C}_6\text{H}_6]$ benzene, 296 K): ^1H , δ 1.31 (s, 18 H, CMe_3), 3.43 (s, 3 H, Me), and 6.08 (s, 5 H, C_5H_5), ^{13}C - $\{^1\text{H}\}$, δ 32.2 (CMe_3), 50.8 (NMe), 77.3 (CMe_3) and 109.4 (C_5H_5). IR (Nujol, CsI): 3042w, 2960vs, 2920vs(sh), 2765w, 1458m, 1420m(sh), 1385m, 1361vs, 1272vs, 1232s, 1186vs, 1010s(sh), 975vs, 800s, 780vs, 595m, 552s, 480m, 391m, 377m and 360m cm^{-1} .

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^i)(\text{OC}_6\text{H}_3\text{Pr}^i-2,6)_2]$ **3c**. Chilled diethyl ether (40 cm^3) was added to a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^i)\text{Cl}_2]$ (0.5 g, 1.67 mmol) and $\text{LiOC}_6\text{H}_3\text{Pr}^i-2,6$ (0.61 g, 3.33 mmol). The solution was allowed to warm to room temperature and stirred for 12 h, during which time a pale yellow solution and a pale gelatinous precipitate were formed. The mixture was filtered and the solvent removed from the filtrate under reduced pressure. The resultant oily solid was washed with cold light petroleum ($2 \times 5 \text{ cm}^3$) and dried *in vacuo* to afford compound **3c** as an off-white crystalline solid. Yield 0.74 g (76%) (Found: C, 67.80; H, 8.55; N, 2.15; Nb, 15.95. $\text{C}_{33}\text{H}_{48}\text{NNbO}_2$ requires C, 67.90; H, 8.30; N, 2.40; Nb, 15.90%). NMR (250 MHz, $[\text{C}_6\text{H}_6]$ -benzene, 296 K): ^1H , δ 0.87 (s, 9, CMe_3), 1.28 (d, $^3J = 6.8$, 24 H, CHMe_2), 3.60 (spt, 4 H, $^3J = 6.8$ Hz, CHMe_2), 6.28 (s, 5 H, C_5H_5) and 6.99–7.13 (m, 6 H, aryl); ^{13}C - $\{^1\text{H}\}$ ($[\text{C}_6\text{H}_6]$ chloroform), δ 23.6 (CHMe_2), 26.0 (CHMe_2), 31.2 (CMe_3), 60.0 (CMe_3), 110.3 (C_5H_5), 120.4, 122.8, 136.2 and 161.3 (all aryl). IR (Nujol, CsI): 3039w(sh), 3028w, 1590m, 1435vs, 1362s, 1332vs, 1326vs, 1265vs, 1250vs, 1239vs, 1206vs, 1190vs, 1162w, 1137w, 1110m, 1096m, 1042m, 1012m, 937w, 892s, 871s, 855s, 815s, 798vs, 756vs, 700s, 593m, 524w, 420w, 392m, 380m and 338w cm^{-1} . Mass spectrum: m/z 583, $[M]^+$; and 568, $[M - \text{Me}]^+$.

$[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^i)(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)_2]$ **3d**. Chilled diethyl ether (40 cm^3) was added to a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^i)\text{Cl}_2]$ (0.3 g, 1.00 mmol) and $\text{LiOC}_6\text{H}_3\text{Ph}_2-2,6$ (0.5 g, 2.00 mmol). The solution was allowed to warm to room temperature and stirred for 12 h, during which time a pale yellow solution and a pale gelatinous precipitate were formed. The suspension was filtered and the filtrate cooled to -78 °C to afford pale yellow crystals of compound **3d**, which were collected, washed with cold light petroleum ($2 \times 5 \text{ cm}^3$) and dried *in vacuo*. Yield 0.72 g (87%) (Found: C, 75.20; H, 5.55; N, 1.85; Nb, 12.50. $\text{C}_{45}\text{H}_{40}\text{NNbO}_2$ requires C, 75.00; H, 5.60; N, 1.95; Nb, 12.90%). NMR (250 MHz, $[\text{C}_6\text{H}_6]$ benzene, 296 K): ^1H , δ 0.64 (s, 9 H, CMe_3), 5.13 (s, 5 H, C_5H_5), 6.88 (m, 2 H, aryl), 7.10 (m, 4 H, aryl), 7.25 (m, 4 H, aryl), 7.27 (m, 8 H, aryl) and 7.54 (m, 8 H, aryl); ^{13}C - $\{^1\text{H}\}$, δ 31.3 (CMe_3), 67.9 (CMe_3), 110.2 (C_5H_5), 121.0, 126.8, 128.5, 130.6, 130.7, 132.4, 140.7 and 162.7 (all aryl). IR (Nujol, CsI): 3030w(sh), 1602w, 1583w, 1495w, 1412vs, 1358w(sh), 1311w, 1230s, 1085w, 1071w, 1029w, 877w, 859m, 811w, 800m, 762s, 758s, 708s, 702vs, 632w, 612w, 599w, 585w and 391w cm^{-1} . Mass spectrum: m/z 264, $[M - 2\text{C}_6\text{H}_3\text{Ph}_2-2,6]^+$.

X-Ray Crystallography.—Crystal data for complexes **1a**, **1c**, **1d**, **1f** and **2a** are given in Table 1. Crystals were examined at room temperature on a Stoe-Siemens four-circle diffractometer with graphite-monochromated radiation (Cu-K α for **1d**, with $\lambda = 1.54184$ Å; Mo-K α otherwise with $\lambda = 0.71073$ Å). Cell parameters were refined from 20 values of 32 reflections

measured at $\pm\omega$ in each case. Intensity data were collected by an on-line profile-fitting procedure,²⁶ and corrected semi-empirically for absorption; no significant variation was seen in periodically monitored standard reflections. Each data set consisted of a unique set of reflections, together with at least one partial set of equivalent reflections.

The structures were determined from Patterson and difference syntheses,²⁷ and refined²⁸ by blocked-cascade least-squares methods to minimize $\sum w\Delta^2$, with $\Delta = |F_o| - |F_c|$; data with $F > 4\sigma_c(F)$ were employed (σ_c from counting statistics only). The weighting scheme²⁹ was $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$, with $G = F_o/F_{\text{max}}$, $H = \sin\theta/\sin\theta_{\text{max}}$, and the coefficients A derived from an analysis of the data. Atomic scattering factors were taken from ref. 30.

Non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were constrained to normal geometries (C–H 0.96 Å, H–C–H 109.5°, aromatic H on ring-angle external bisectors) with $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Refinement included an isotropic extinction parameter x , whereby $F'_c = F_c/(1 + xF_c^2/\sin^2\theta)^{1/2}$. In the case of compound **1d** the absolute structure was confirmed by refinement of $\eta = 0.84(7)$.³¹ The parameters R and R' , given in Table 1, are defined as $\Sigma|\Delta|/\Sigma|F_o|$ and $(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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