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Half-sandwich imido complexes of niobium bearing alkyne, benzyne and benzylidene ligands: relatives of the zirconocene family

Michael C. W. Chan,[a] Jacqueline M. Cole,[b] Vernon C. Gibson,*,[a] Judith A. K. Howard,[b] Christian Lehmann,[b] Andrew D. Poole[a] and Ulrich Siemeling[a]

[a] *Department of Chemistry, Imperial College, Exhibition Road, London, UK SW7 2AY*
[b] *Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE*

Reactions of $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ **1a** and $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ **1b** with 1 and 2 equivalents of benzylpotassium respectively gave the niobium benzyl derivatives $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl(CH_2Ph)]$ **2** and $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(CH_2Ph)_2]$ **3**. Treatment of **3** with trimethylphosphine afforded the benzylidene complex $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)({=}CHPh)]$ **4**. Complex **1a** reacted with phenylmagnesium chloride in the presence of PMe_3 to give $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Ph_2(PMe_3)]$ **5** which upon heating at 70 °C in heptane, converts to the η^2-benzyne complex $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}C_6H_4)(PMe_3)]$ **6**. The niobium(III) complexes $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PMe_3)_2]$ **8a** and $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_2]$ **8b** were obtained upon magnesium reduction of **1a** and **1b** respectively in the presence of an excess of PMe_3. They were converted into $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(\eta^2\text{-}R^1C{\equiv}CR^2)(PMe_3)$ ($R^1 = R^2 = Ph$ **9a**; $R^1 = Ph$, $R^2 = H$ **9b**) and $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)]$ **9c** upon treatment with the appropriate alkyne. The molecular structures of the 2-*tert*-butylimido complexes $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)Cl_2]$ **7** and **9a** have been determined.

Zirconocene complexes find widespread application as reagents in organic synthesis,[1] ranging from hydrozirconation[2] and carbomagnesiation,[3] through to C–C coupling reactions involving alkenes,[3a,4] alkynes,[4a,b,5] benzynes[1b,d,6] and imines,[7] and as catalysts for the polymerisation of, for example, alkenes,[8] α,ω-dienes[9] and silanes.[10]

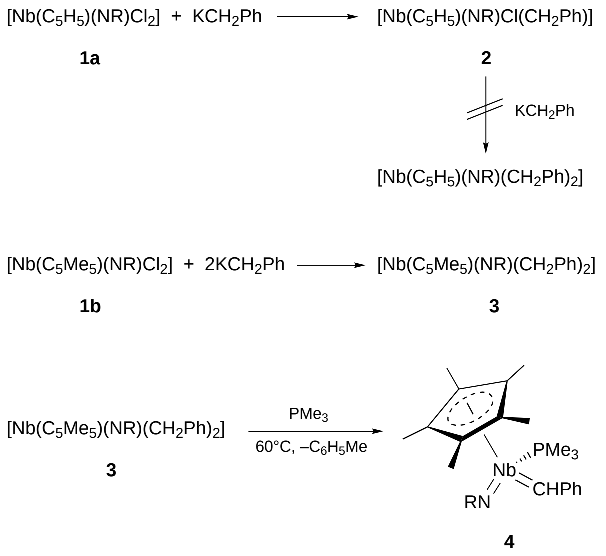
Half-sandwich imido compounds of the Group 5 metals offer an opportunity to extend the horizon of metallocene-like reactivity through the 'isolobal' relationship that exists between $[M(C_5H_5)(NR)]$ (M = Group 5 metal) and $[M(C_5H_5)_2]$ (M = Group 4 metal) fragments. Our earlier studies have been concerned with establishing the closeness of the analogy, through quantum-chemical calculations[11] and through a study of the extent to which $M(C_5H_5)(NR)L(L')$ complexes resemble $M(C_5H_5)_2L(L')$ structurally and in their reactivity. The structural relationship can be usefully probed through derivatives containing 'single-faced' π ligands since in a bent metallocene environment these groups adopt a strict orientational preference due to the competition between the ligands for metal π orbitals.[12]

Herein we describe half-sandwich niobium imido complexes containing alkyne, benzyne and benzylidene ligands, complexes that find direct analogues in zirconocene chemistry. These studies provide useful insight into the viability and extent of the 'isolobal' analogy and have helped to delineate some of the more subtle steric and electronic factors contributing to the stability of these metallocene-like molecules. We chose to start our investigations on derivatives containing either C_5H_5 or C_5Me_5 ligands in combination with arylimido ligands, combinations that we envisaged would allow sufficient flexibility for groups of differing steric requirements to be accommodated at the half-sandwich metal imido centres. Aspects of this work have been communicated.[13]

Results

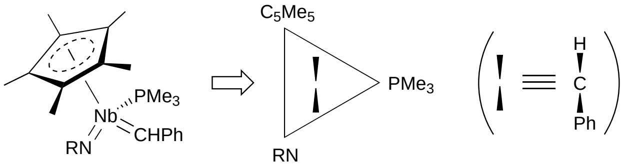
Benzyl and benzylidene derivatives

The starting points for these studies are the dichlorides **1a** and **1b**, whose syntheses have been described previously.[11] The monobenzyl complex **2** is obtained as a yellow crystalline solid upon treatment of **1a** with 1 equivalent of benzylpotassium (Scheme 1). Difficulties were encountered in extending this synthesis to the dibenzyl derivative *via* treatment of **2** with a further equivalent of KCH_2Ph; instead a complex mixture of products was obtained that could not be purified. A dibenzyl complex proved readily accessible, however, for the C_5Me_5 niobium system, and is stable indefinitely in hydrocarbon solutions to 100 °C. However, upon warming a solution of **3** at 65 °C in the presence of trimethylphosphine, a clean transformation occurs over several days to afford the benzylidene complex **4** with elimination of toluene.



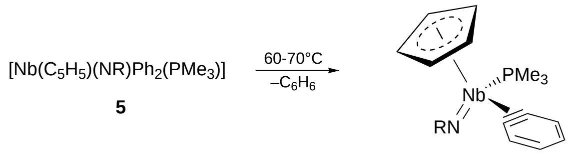
Scheme 1 $R = 2,6\text{-}Pr^i_2C_6H_3$

The ^1H NMR data (Table 1) for complex **4** reveal a high-frequency shift for the α-benzylidene hydrogen with a ^3J coupling constant of 5.4 Hz to the adjacent PMe_3 phosphorus nucleus. The corresponding α-carbon resonance occurs as a quadrupolar-broadened signal at δ 268.6, a shift comparable with other d^0 alkylidene complexes of niobium and tantalum.[15] Difference nuclear Overhauser effect (NOE) experiments indicated that the α-hydrogen is oriented towards the C_5Me_5 ring.



Scheme 2 Representation of complex **4** showing the orientation of the benzylidene ligand. R = 2,6-$Pr^i_2C_6H_4$

$$\underset{\mathbf{1a}}{[Nb(C_5H_5)(NR)Cl_2]} + 2MgPhCl \xrightarrow{PMe_3} \underset{\mathbf{5}}{[Nb(C_5H_5)(NR)Ph_2(PMe_3)]}$$



5 **6**

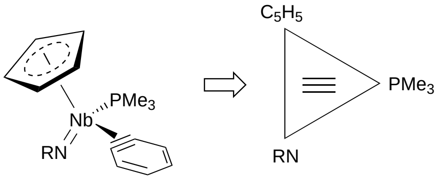
Scheme 3 R = 2,6-$Pr^i_2C_6H_3$

The molecular structure of complex **4** has been described previously[13a] and confirms that the benzylidene hydrogen projects towards the C_5Me_5 ring, with the phenyl substituent then pointing towards the imido ligand. This orientation allows the p orbital of the alkylidene to align with the metallocene-like π-symmetry frontier orbitals of the $Nb(C_5H_5)(NR)$ fragment. Thus, **4** is a direct analogue of $[Zr(C_5H_5)_2(CHCH_2CMe_3)(PPh_3)]$ described by Schwartz and co-workers.[16] There is no evidence from solution NMR data for the existence of the rotamer in which the positions of the phenyl and hydrogen substituents are interchanged. The orientation of the benzylidene ligand with respect to the other ligands around the metal is usefully illustrated using the representation[12] shown in Scheme 2 in which the molecule is viewed down the benzylidene carbon–metal bond.

Phenyl and benzyne derivatives

Treatment of complex **1a** with 2 equivalents of MgPhCl in the presence of PMe_3 affords the diphenyl complex **5** in which trimethylphosphine is also bound to the niobium centre (Scheme 3). Large orange cubic crystals may be obtained from diethyl ether upon cooling a solution at −30 °C for several hours. It did not prove possible to obtain the base-free diphenyl complex by conducting the reaction in the absence of PMe_3. Upon warming a heptane solution of **5** at 70 °C the solution darkens first to red and then gradually to a brown colouration. After removal of the solvent, extraction of the residue with diethyl ether and prolonged cooling at −40 °C, green cubes of the η^2-benzyne complex, $[Nb(C_5H_5)(NR)(\eta^2\text{-}C_6H_4)(PMe_3)]$ **6** can be obtained.

The molecular structure of complex **6** has been described previously.[13a] We noted the close similarity between the bond lengths in the benzyne ring of **6** with those found for $[Zr(C_5H_5)_2(\eta^2\text{-}C_6H_4)(PMe_3)]$.[4a] For comparative purposes, key bond lengths and angles for these molecules are collected in Table 2. The Nb–P and Nb–C bond lengths are evidently shorter than the corresponding Zr–P and Zr–C distances. While the differences between the metal–carbon distances may be largely attributed to the difference in ionic radii of Zr *vs.* Nb (*ca.* 0.1 Å for the metals in their highest formal oxidation states), the difference in metal–phosphorus distances (0.16 Å) lies outside this limit and therefore there may be a significant lengthening of the Zr–P bond due to crowding within the co-ordination sphere of the $M(C_5H_5)_2$ fragment. A similar explanation has been forwarded for the observed differences in bond lengths between zirconocene and bis(imido)molybdenum derivatives.[14] This is likely to be a general consequence of the greater space available within the immediate co-ordination sphere of imidometal species compared with cyclopentadienylmetal fragments, since only one atom is directly involved in the metal–ligand bonding for imidometal species compared to five for the cyclopentadienyl–metal interaction, resulting in a higher effective co-ordination number for the latter. In addition, the quasi-linear arrangement of the imido group results in the substituent being directed away from the metal centre. A representation[12] illustrating the orientation of the benzyne ligand is shown in Scheme 4.



Scheme 4 Representation of complex **6** showing the orientation of the benzyne ligand. R = 2,6-$Pr^i_2C_6H_4$

$$[Nb(C_5R'_5)(NR)Cl_2] \xrightarrow[2PMe_3]{Mg} [Nb(C_5R'_5)(NR)(PMe_3)_2]$$

1b R′ = Me, R = 2,6-$Pr^i_2C_6H_3$ **8a,8b**
7 R′ = H, R = 2,6-$Bu^tC_6H_4$

$$[Nb(C_5R'_5)(NR)(PMe_3)_2] \xrightarrow[-PMe_3]{R^1C\equiv CR^2} [Nb(C_5R'_5)(NR)(R^1C\equiv CR^2)(PMe_3)]$$

8a,8b

9a R′ = H, R = 2,6-$Bu^tC_6H_4$,
$R^1 = R^2$ = Ph
9b R′ = H, R = 2,6-$Bu^tC_6H_4$,
$R^1 = R^2$ = H
9c R′ = Me, R = 2,6-$Pr^i_2C_6H_3$,
$R^1 = R^2$ = Ph

Scheme 5

Alkyne derivatives

Alkyne derivatives of niobium have been synthesized from the niobium(III) bis(trimethylphosphine) precursors **8a** and **8b** according to Scheme 5. We have found previously that the $C_5H_5/NC_6H_3Pr^i_2$-2,6 ligand combination affords a bis(phosphine) complex that is exceedingly sensitive, whereas the C_5H_5-$NC_6H_4Bu^t$-2 derivatives are quite robust. The $NC_6H_4Bu^t$-2 system was, therefore, preferred for these studies, and in order to gain further insight into the factors influencing the stability of these closely related arylimido derivatives the structure of the dichloride precursor **7** was investigated.

A view of the molecule is shown in Fig. 1 and bond lengths and angles are collected in Table 3. The key difference between **7** and **1a**, **1b**[11] lies in the orientation of the aryl ring which aligns in the plane that bisects the Cl–Nb–Cl angle, thus allowing the *tert*-butyl group to be directed away from the C_5H_5 ring. By contrast, the 2,6-disubstituted aryl rings of **1a**–**1c** are oriented perpendicular to this alignment, in order to avoid unfavourable steric interactions between the cyclopentadienyl ring and one of the *ortho* substituents.

The alkyne complexes **9a**–**9c** are obtained in good yield upon treatment of **8a** or **8b** with 1 equivalent of the alkyne. The phenylacetylene derivative **9b** forms at room temperature whereas the diphenylacetylene complexes **9a** and **9c** require prolonged warming at elevated temperature for appreciable conversion.

The molecular structure of complex **9a** is shown in Fig. 2. Bond lengths and angles are collected in Table 4. The angle at the imido nitrogen [166.3(2)°] is approximately the same as that found in **7** [165.1(3)°], the bending being imposed by the bulky *tert*-butyl substituent. The Nb–N bond distance in **9a** is substantially longer than for **7** [1.813(3) *cf.* 1.782(3) Å] reflecting the lower formal oxidation state of the metal in the alkyne

Table 1 The NMR data

Compound	Assignment	δ, multiplicity, J/Hz ^{1}H[a]	^{13}C[b]	^{31}P[c]
2	$\mathrm{CH}Me_2$	1.28 (d, $^3J_{\mathrm{HH}}$ 7.0)	24.14 (q, $^1J_{\mathrm{CH}}$ 131)	
		1.30 (d, $^3J_{\mathrm{HH}}$ 7.0)	24.66 (q, $^1J_{\mathrm{CH}}$ 131)	
	$CH_2\mathrm{Ph}$	2.85 (d, $^2J_{\mathrm{HH}}$ 7.5)	50.90 (d, $^1J_{\mathrm{CH}}$ 134)	
		3.29 (d, $^2J_{\mathrm{HH}}$ 7.5)		
	$CH\mathrm{Me}_2$	4.01 (spt, $^3J_{\mathrm{HH}}$ 7.0)	27.83 (d, $^1J_{\mathrm{CH}}$ 129)	
	$\mathrm{C_5H_5}$	5.64 (s)	108.21 (d, $^1J_{\mathrm{CH}}$ 176)	
	o-$\mathrm{C_6H_5}$	6.72 (d, $^3J_{\mathrm{HH}}$ 7.4)	132.68 (d, $^1J_{\mathrm{CH}}$ 159)	
	m-$\mathrm{C_6H_5}$	6.98 (t, $^3J_{\mathrm{HH}}$ 7.4)	131.00 (d, $^1J_{\mathrm{CH}}$ 160)	
	p-$\mathrm{C_6H_5}$	7.37 (t, $^3J_{\mathrm{HH}}$ 7.4)	131.38 (d, $^1J_{\mathrm{CH}}$ 161)	
	ipso-$\mathrm{C_6H_5}$		124.52 (s)	
	o-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		144.69 (s)	
	m-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	7.05 (d, $^3J_{\mathrm{HH}}$ 7.5)	122.82 (d, $^1J_{\mathrm{CH}}$ 156)	
	p-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	6.95 (t, $^3J_{\mathrm{HH}}$ 7.5)	125.19 (d, $^1J_{\mathrm{CH}}$ 160)	
	ipso-$C_6\mathrm{H_3Pr}^{\mathrm{i}}_2$-2,6		152.79 (s)	
3[d,e]	$\mathrm{CH}Me_2$	1.29 (d, $^3J_{\mathrm{HH}}$ (6.8)	24.76 (q, $^1J_{\mathrm{CH}}$ 131)	
	$\mathrm{C_5}Me_5$	1.61 (s)	10.96 (s)	
	$C_5\mathrm{Me_5}$		115.48 (s)	
	$CH_2\mathrm{Ph}$	2.18 (d, $^2J_{\mathrm{HH}}$ 10.8)	57.68 (s, br)	
		2.45 (d, $^2J_{\mathrm{HH}}$ 10.8)		
	$CH\mathrm{Me}_2$	3.89 (spt, $^3J_{\mathrm{HH}}$ 6.8)	27.48 (s)	
	o-$\mathrm{C_6H_5}$		145.54 (s)	
	m-$\mathrm{C_6H_5}$		128.51 (s)	
	p-$\mathrm{C_6H_5}$		130.73 (s)	
	ipso-$\mathrm{C_6H_5}$	6.84–7.11	124.53 (s)	
	o-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		143.15 (s)	
	m-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		122.92 (s)	
	p-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		124.09 (s)	
	ipso-$C_6\mathrm{H_3Pr}^{\mathrm{i}}_2$-2,6		150.55 (s)	
4	$\mathrm{PMe_3}$	0.85 (d, $^2J_{\mathrm{PH}}$ 7.6)	16.75 (dq, $^1J_{\mathrm{CH}}$ 129, $^1J_{\mathrm{CP}}$ 24)	−1.56 (s)
	$\mathrm{C_5}Me_5$	1.96 (s)	11.52 (q, $^1J_{\mathrm{CH}}$ 126)	
	$C_5\mathrm{Me_5}$		112.38 (s)	
	$\mathrm{CH}Me_2$	1.21 (d, $^3J_{\mathrm{HH}}$ 6.7)	24.76 (q, $^1J_{\mathrm{CH}}$ 128)	
		1.32 (d, $^3J_{\mathrm{HH}}$ 6.7)		
	$CH\mathrm{Me}_2$	4.21 (spt, $^3J_{\mathrm{HH}}$ 6.7)	26.93 (d, $^1J_{\mathrm{CH}}$ 127)	
	o-$\mathrm{C_6H_5}$	7.75 (t, $^3J_{\mathrm{HH}}$ 8.3)		
	m-$\mathrm{C_6H_5}$		122.69, 127.54, 127.80 (s)	
	p-$\mathrm{C_6H_5}$	6.95–7.18 (m)		
	m-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		121.58 (q, $^1J_{\mathrm{CH}}$ 159)	
	ipso-$\mathrm{C_6H_5}$		148.20 (s)	
	o-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		143.20 (s)	
	p-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	6.91 (t, $^3J_{\mathrm{HH}}$ 7.2)	124.24 (d, $^1J_{\mathrm{CH}}$ 158)	
	ipso-$C_6\mathrm{H_3Pr}^{\mathrm{i}}_2$-2,6		150.50 (s)	
	$CH\mathrm{Ph}$	11.23 (d, $^3J_{\mathrm{PH}}$ 5.4)	268.60 (s, br)	
5	$\mathrm{PMe_3}$	0.60 (d, $^2J_{\mathrm{PH}}$ 5.9)	14.78 (dq, $^1J_{\mathrm{CH}}$ 129, $^1J_{\mathrm{CP}}$ 17)	−18.30 (br, $\nu_{\frac{1}{2}}$ *ca.* 500 Hz)
	$\mathrm{CH}Me_2$	1.32 (d, $^3J_{\mathrm{HH}}$ 6.8)	25.07 (q, $^1J_{\mathrm{CH}}$ 125)	
	$CH\mathrm{Me}_2$	4.19 (spt, $^3J_{\mathrm{HH}}$ 6.8)	27.15 (d, $^1J_{\mathrm{CH}}$ 129)	
	$\mathrm{C_5H_5}$	5.72 (s)	108.90 (d, $^1J_{\mathrm{CH}}$ 175)	
	o-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		142.44 (br, $\nu_{\frac{1}{2}} = 30$ Hz)	
	m-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	7.09 (d, $^3J_{\mathrm{HH}}$ 7.2)	123.52 (d, $^1J_{\mathrm{CH}}$ 156)	
	p-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	6.97 (t, $^3J_{\mathrm{HH}}$ 8.0)	124.01 (d, $^1J_{\mathrm{CH}}$ 160)	
	ipso-$C_6\mathrm{H_3Pr}^{\mathrm{i}}_2$-2,6		154.17 (br, $\nu_{\frac{1}{2}} = 50$ Hz)	
	o-$\mathrm{C_6H_5}$	7.56 (br, $\nu_{\frac{1}{2}} = 16$ Hz)	137.86 (d, $^1J_{\mathrm{CH}}$ 154)	
	m-$\mathrm{C_6H_5}$	7.21 (t, $^3J_{\mathrm{HH}}$ 7.2)	126.95 (d, $^1J_{\mathrm{CH}}$ 157)	
	p-$\mathrm{C_6H_5}$	7.08 (t, $^3J_{\mathrm{HH}}$ 6.0)	124.46 (d, $^1J_{\mathrm{CH}}$ 159)	
	ipso-$\mathrm{C_6H_5}$		177.62 (br, $\nu_{\frac{1}{2}} = 80$ Hz)	
6	$\mathrm{CH}Me_2$	0.97 (d, $^3J_{\mathrm{HH}}$ 6.8)	24.00 (q, $^1J_{\mathrm{CH}}$ 125)	
		1.16 (d, $^3J_{\mathrm{HH}}$ 6.8)	23.52 (q, $^1J_{\mathrm{CH}}$ 125)	
	$\mathrm{PMe_3}$	1.13 (d, $^2J_{\mathrm{PH}}$ 8.0)	17.93 (qd, $^1J_{\mathrm{CH}}$ 130, $^1J_{\mathrm{CP}}$ 25)	7.5 (s, br, $\nu_{\frac{1}{2}} = 600$ Hz)
	$CH\mathrm{Me}_2$	3.56 (spt, $^3J_{\mathrm{HH}}$ 6.8)	27.35 (d, $^1J_{\mathrm{CH}}$ 130)	
	$\mathrm{C_5H_5}$	5.67 (s)	103.37 (d, $^1J_{\mathrm{CH}}$ 173)	
	α,α′-$\mathrm{C_6H_4}$		153.7, 162.7 (br)	
	β-$\mathrm{C_6H_4}$	7.71 (d, $^3J_{\mathrm{HH}}$ 6.0)	130.8	
	γ-$\mathrm{C_6H_4}$	7.53 (m)	130.2	
	β′-$\mathrm{C_6H_4}$	8.30 (dd, $^3J_{\mathrm{HH}}$ 6.0, $^4J_{\mathrm{PH}}$ 0.9)	132.1	
	γ′-$\mathrm{C_6H_4}$	7.60 (m)	130.6	
	o-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6		143.74 (s)	
	m-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	6.99 (d, $^3J_{\mathrm{HH}}$ 7.2)	122.21 (d, $^1J_{\mathrm{CH}}$ 154)	
	p-$C_6H_3\mathrm{Pr}^{\mathrm{i}}_2$-2,6	6.89 (t, $^3J_{\mathrm{HH}}$ 7.2)	122.87 (d, $^1J_{\mathrm{CH}}$ 159)	
	ipso-$C_6\mathrm{H_3Pr}^{\mathrm{i}}_2$-2,6		152.05 (s, br, $\nu_{\frac{1}{2}} = 33$ Hz)	

Table 1 (*Contd.*)

		δ, multiplicity, J/Hz		
Compound	Assignment	^{1}H^a	^{13}C^b	^{31}P^c
7	$\mathrm{C}\mathit{Me}_3$	1.55 (s)	30.44 (q, $^1J_{\mathrm{CH}}$ 126)	
	$\mathit{C}\mathrm{Me}_3$		35.62 (s)	
	$\mathrm{C_5H_5}$	5.80 (s)	113.20 (dpnt, $^1J_{\mathrm{CH}}$ 178, $^2J_{\mathrm{CH}} = {}^3J_{\mathrm{CH}} = 6.7$)	
	o-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.95 (d, $^3J_{\mathrm{HH}}$ 8.0)	131.10 (d, $^1J_{\mathrm{CH}}$ 160) 143.17 (s)	
	m-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.99 (t, $^3J_{\mathrm{HH}}$ 7.3) 7.19 (d, $^3J_{\mathrm{HH}}$ 7.8)	125.98 (d, $^1J_{\mathrm{CH}}$ 156) 126.55 (d, $^1J_{\mathrm{CH}}$ 156)	
	p-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.86 (t, $^3J_{\mathrm{HH}}$ 7.4)	126.50 (d, $^1J_{\mathrm{CH}}$ 160)	
	ipso-$\mathit{C}_6\mathrm{H_4Bu^t}$-2		155.46 (s)	
8a	$\mathrm{PMe_3}$	0.91 (s, br, $\nu_{\frac{1}{2}} = 45$ Hz)	17.22 (br, $\nu_{\frac{1}{2}} = 180$ Hz)	25 (vbr, $\nu_{\frac{1}{2}} = 4500$ Hz)
	$\mathrm{C}\mathit{Me}_3$	1.48 (s)	29.29 (q, $^1J_{\mathrm{CH}}$ 125)	
	$\mathit{C}\mathrm{Me}_3$		35.97 (s)	
	$\mathrm{C_5H_5}$	5.06 (s)	93.85 (dpnt, $^1J_{\mathrm{CH}}$ 171, $^2J_{\mathrm{CH}} = {}^3J_{\mathrm{CH}} = 7.0$)	
	o-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	7.39 (d, $^3J_{\mathrm{HH}}$ 7.6)	131.28 (d, $^1J_{\mathrm{CH}}$ 152) 140.27 (s)	
	m-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	7.18 (t, $^3J_{\mathrm{HH}}$ 7.6) 7.33 (d, $^3J_{\mathrm{HH}}$ 8.0)	126.30 (d, $^1J_{\mathrm{CH}}$ 152) 119.05 (d, $^1J_{\mathrm{CH}}$ 157)	
	p-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.91 (t, $^3J_{\mathrm{HH}}$ 7.4)	125.91 (d, $^1J_{\mathrm{CH}}$ 151)	
	ipso-$\mathit{C}_6\mathrm{H_4Bu^t}$-2		Not observed	
8b	PMe_3	1.20 (d, $^2J_{\mathrm{PH}}$ 5.2)	23.60 (m)	
	$\mathrm{CH}\mathit{Me}_2$	1.33 (d, $^3J_{\mathrm{HH}}$ 7.2)	24.74	
	$\mathit{CH}\mathrm{Me}_2$	4.75 (spt, $^3J_{\mathrm{HH}}$ 7.2)	26.46	
	$\mathrm{C_5}\mathit{Me}_5$	1.90 (s)	12.64	
	$\mathit{C}_5\mathrm{Me}_5$		105.09	
	o-$\mathit{C}_6\mathit{H}_3\mathrm{Pr^i}_2$-2,6		141.32	
	m-$\mathit{C}_6\mathit{H}_3\mathrm{Pr^i}_2$-2,6	7.14 (d, $^3J_{\mathrm{HH}}$ 7.6)	120.48	
	p-$\mathit{C}_6\mathit{H}_3\mathrm{Pr^i}_2$-2,6	7.01 (t, $^3J_{\mathrm{HH}}$ 7.6)	122.71	
	ipso-$\mathit{C}_6\mathrm{H_3Pr^i}_2$-2,6		150.47	
9a	$\mathrm{PMe_3}$	0.89 (d, $^2J_{\mathrm{PH}}$ 8.4)	16.92 (qd, $^1J_{\mathrm{CH}}$ 129, $^1J_{\mathrm{CP}}$ 24)	9.8 (br, $\nu_{\frac{1}{2}} = 405$ Hz)
	$\mathrm{C}\mathit{Me}_3$	1.45 (s)	30.06 (q, $^1J_{\mathrm{CH}}$ 125)	
	$\mathit{C}\mathrm{Me}_3$		35.65 (s)	
	$\mathrm{C_5H_5}$	5.72 (d, $^3J_{\mathrm{PH}}$ 1.6)	102.5 (dpnt, $^1J_{\mathrm{CH}}$ 173, $^2J_{\mathrm{CH}} = {}^3J_{\mathrm{CH}} = 7.0$)	
	o-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	7.39 (d, $^3J_{\mathrm{HH}}$ 7.6)	130.71 (d, $^1J_{\mathrm{CH}}$ 157) 142.33 (s)	
	m-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2		122.58 (d, $^1J_{\mathrm{CH}}$ 158) 126.04 (d, $^1J_{\mathrm{CH}}$ 155)	
	p-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2		125.95 (d, $^1J_{\mathrm{CH}}$ 157)	
	ipso-$\mathit{C}_6\mathrm{H_4Bu^t}$-2		156.88 (s)	
	o-$\mathrm{C_6H_5}$ (*endo*)		125.00 (d, $^1J_{\mathrm{CH}}$ 160)	
	m-$\mathrm{C_6H_5}$ (*endo*)		128.43 (d, $^1J_{\mathrm{CH}}$ 157)	
	p-$\mathrm{C_6H_5}$ (*endo*)		123.65 (d, $^1J_{\mathrm{CH}}$ 158)	
	ipso-$\mathrm{C_6H_5}$ (*endo*)	6.8–7.3 (m)	138.64 (s)^f	
	o-$\mathrm{C_6H_5}$ (*exo*)		131.16 (d, $^1J_{\mathrm{CH}}$ 158)	
	m-$\mathrm{C_6H_5}$ (*exo*)		128.48 (d, $^1J_{\mathrm{CH}}$ 157)	
	p-$\mathrm{C_6H_5}$ (*exo*)		126.98 (d, $^1J_{\mathrm{CH}}$ 159)	
	ipso-$\mathrm{C_6H_5}$ (*exo*)		151.82 (s)^f	
	$\mathrm{PhC{\equiv}}\mathit{C}\mathrm{Ph}$		157.44 (d, $^2J_{\mathrm{CP}}$ 22.1) *endo* 162.01 (s) *exo*	
9b	$\mathrm{PMe_3}$	1.02 (d, $^2J_{\mathrm{PH}}$ 8.0)	16.88 (qd, $^1J_{\mathrm{CH}}$ 129, $^1J_{\mathrm{CP}}$ 25)	14.2 (br, $\nu_{\frac{1}{2}} = 530$ Hz)
	$\mathrm{C}\mathit{Me}_3$	1.39 (s)	29.98 (q, $^1J_{\mathrm{CH}}$ 126)	
	$\mathit{C}\mathrm{Me}_3$		35.67 (s)	
	$\mathrm{C_5H_5}$	5.67 (d, $^3J_{\mathrm{PH}}$ 1.6)	102.19 (dpnt, $^1J_{\mathrm{CH}}$ 172, $^2J_{\mathrm{CH}} = {}^3J_{\mathrm{CH}} = 6.8$)	
	o-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.92 (d, $^3J_{\mathrm{HH}}$ 7.6)	130.26 (d, $^1J_{\mathrm{CH}}$ 157) 141.67 (s)	
	m-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	7.22 (d, $^3J_{\mathrm{HH}}$ 8.0) 7.07 (t, $^3J_{\mathrm{HH}}$ 7.2)	125.87 (d, $^1J_{\mathrm{CH}}$ 156) 125.94 (d, $^1J_{\mathrm{CH}}$ 156)	
	p-$\mathit{C}_6\mathit{H}_4\mathrm{Bu^t}$-2	6.84 (t, $^3J_{\mathrm{HH}}$ 7.6)	121.88 (d, $^1J_{\mathrm{CH}}$ 158)	
	ipso-$\mathit{C}_6\mathrm{H_4Bu^t}$-2		157.23 (s)	
	o-$\mathrm{C_6H_5}$	8.03 (d, $^3J_{\mathrm{HH}}$ 8.0)	131.49 (d, $^1J_{\mathrm{CH}}$ 158)	
	m-$\mathrm{C_6H_5}$	7.43 (t, $^3J_{\mathrm{HH}}$ 7.8)	128.53 (d, $^1J_{\mathrm{CH}}$ 158)	
	p-$\mathrm{C_6H_5}$	7.21 (t, $^3J_{\mathrm{HH}}$ 7.4)	127.24 (d, $^1J_{\mathrm{CH}}$ 156)	
	ipso-$\mathrm{C_6H_5}$		139.05 (s)	
	$\mathrm{Ph}\mathit{C}{\equiv}\mathrm{CH}$		157.44 (d, $^2J_{\mathrm{CP}}$ 22.1)	
	$\mathrm{PhC{\equiv}}\mathit{CH}$	8.47 (d, $^3J_{\mathrm{PH}}$ 12.4)	143.53 (dd, $^1J_{\mathrm{CH}}$ 179, $^2J_{\mathrm{CP}}$ 29.4)	

Table 1 (*Contd.*)

		δ, multiplicity, *J*/Hz		
Compound	Assignment	$^{1}H^{a}$	$^{13}C^{b}$	$^{31}P^{c}$
9c	PMe_3	0.95 (d, $^{2}J_{PH}$ 8.0)	16.79 (d, $^{1}J_{CP}$ 10.9)	2.8 (br, $\nu_{\frac{1}{2}}$ = 350 Hz)
	$CH\mathit{Me}_2$	1.14 (d, $^{3}J_{HH}$ 6.8)	25.41	
		1.23 (d, $^{3}J_{HH}$ 6.8)	25.80	
	$\mathit{CH}Me_2$	4.09 (spt, $^{3}J_{HH}$ 6.8)	26.24	
	$C_5\mathit{Me}_5$	1.87 (s)	12.17	
	C_5Me_5		113.16	
	o-C_6H_5	7.76 (m)		
	Ph*C*≡*C*Ph		159.64 (d, $^{2}J_{CP}$ 23.6) *endo* 167.60 (s) *exo*	
	Aromatic H	6.9–7.3		
	Aromatic C		151.85, 151.61, 144.45, 137.00, 131.95, 128.53, 128.09, 126.62, 125.85, 123.83, 123.01, 122.53	

[a] In C_6D_6 at 400 MHz. [b] In C_6D_6 at 100.58 MHz. [c] In C_6D_6 at 161.9 MHz, referenced to aqueous H_3PO_4 (external). [d] ^{13}C NMR shifts and assignments from distortionless enhancements of polarisation transfer spectra. [e] Aromatic hydrogens and carbons included only where unambiguous assignments could be made. [f] Assignment made by comparison with [Mo(NBu^t)$_2$(PhC≡CPh)(PMe$_3$)] (ref. 14).

Table 2 Comparison of key structural parameters for 'isolobal' zirconocene and $Nb(C_5H_5)(NR)$ complexes

Parameter	[Nb(C$_5$H$_5$)(NC$_6$H$_3$Pr$^i_2$-2,6)-(PMe$_3$)(η^2-C$_6$H$_4$)] **6**[a]	[Zr(C$_5$H$_5$)$_2$(PMe$_3$)-(η^2-C$_6$H$_4$)][b]	[Nb(C$_5$H$_5$)(NC$_6$H$_4$Bu^t-2)-(Ph≡CPh)(PMe$_3$)] **9a**[c]	[Zr(C$_5$H$_5$)(PhC≡CPh)-(PMe$_3$)][d]
M–P/Å	2.528(3)	2.687(3)	2.546(1)	2.70(1)
M–C(*endo*)[e]/Å	2.190(8)	2.267(5)	2.200(3)	2.25(4)
M–C(*exo*)[f]/Å	2.138(7)	2.228(5)	2.144(3)	2.20(4)
C(*exo*)–C(*endo*)	1.342(11)	1.364(8)	1.309(5)	1.36(6)

[a] See ref. 13(*a*) and this work. [b] See ref. 4(*a*). [c] This work. [d] See ref. 17. [e] C(*endo*) refers to the metal-bound olefinic or acetylenic carbon closest to the PMe$_3$ ligand. [f] C(*exo*) refers to the metal-bound olefinic or acetylenic carbon furthest from the PMe$_3$ ligand.

Table 3 Bond lengths (Å) and angles (°) for complex **7**

Nb–N	1.782(3)	C(2)–C(3)	1.375(6)
Nb–Cl	2.3455(8)	C(3)–C(4)	1.374(7)
Nb–C(12)	2.379(3)	C(4)–C(5)	1.385(7)
Nb–C(11)	2.464(3)	C(5)–C(6)	1.397(6)
Nb–C(10)	2.523(4)	C(6)–C(7)	1.531(6)
Nb–Centroid	2.128(5)	C(7)–C(9)	1.540(4)
N(1)–C(1)	1.394(5)	C(7)–C(8)	1.541(6)
C(1)–C(2)	1.397(6)	C(10)–C(11)	1.404(4)
C(1)–C(6)	1.423(6)	C(11)–C(12)	1.409(5)
N–Nb–Cl	101.76(7)	C(1)–N–Nb	165.1(3)
Cl–Nb–Cl(a)	104.58(4)	N–C(1)–C(2)	117.3(4)
Centroid–Nb–N(1)	119.7(3)	N–C(1)–C(6)	122.9(4)
Centroid–Nb–Cl	113.6(8)	C(1)–C(6)–C(7)	122.6(4)

Symmetry transformations used to generate equivalent atoms: $x, -y + \frac{1}{2}, z$.

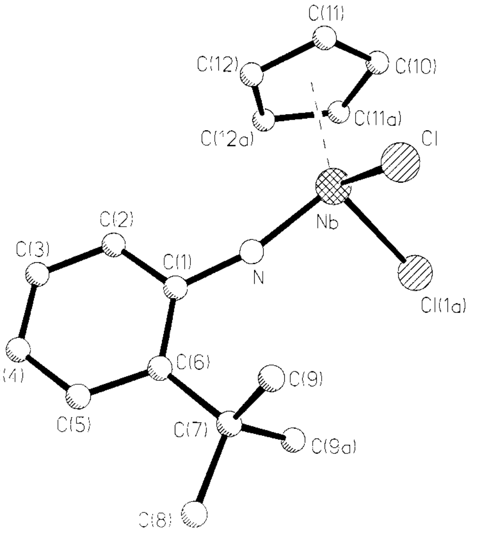


Fig. 1 Molecular structure of complex **7**, without H atoms and with key atoms labelled

complex. The phenyl ring of the imido substituent is twisted by 51(1)° relative to its position in **7** such that the *tert*-butyl substituent is accommodated in a pocket beneath the alkyne group. The phosphorus atom of the PMe$_3$ ligand lies close to the Nb–C(1)–C(2) plane (displacement 0.021 Å) consistent once again with the metallocene-like characteristics of the Nb(C$_5$H$_5$)(NR) fragment; a representation that illustrates the orientation of the alkyne ligand is shown in Scheme 6. The alkyne C–C bond length is identical within experimental error to the distance found in the 'isolobal' molybdenum complex, [Mo(NBu^t)$_2$(PhC≡CPh)(PMe$_3$)],[14] while the Nb–P and Nb–C distances lie intermediate between those determined for the zirconocene[17] and bis(imido)molybdenum[14] analogues of **9a**.

Discussion

The results described herein highlight a number of half-sandwich niobium imido derivatives which find direct analogues in zirconocene chemistry. The stabilities of these molecules are largely dependent upon the steric properties of the cyclopentadienyl and imido coligands, with certain combinations clearly being less suitable than others. For example, the dibenzyl complex containing the C$_5$H$_5$N/C$_6$H$_3$Pr$^i_2$-2,6 combination could not be isolated whereas the bulkier C$_5$Me$_5$ derivative with the same imido coligand (**3**) is readily synthesized and is thermally stable. We have noted previously a similar instability for the cyclopentadienylniobium dialkyl complex [Nb(C$_5$H$_5$)(NR)(CH$_2$CMe$_3$)$_2$][18] which, although isolable at room temperature, slowly decomposes at this temperature with loss of CMe$_4$ to give paramagnetic niobium products (Scheme 7). Neopentane is formed during decomposition indicating that a niobium alkylidene species may be generated, but attempts to trap this species either with added base or unsaturated hydrocarbons were unsuccessful. A good indication that a niobium alkylidene had formed was provided by the ability of these mixtures to promote the ring-opening metathesis polymerisation (ROMP) of norbornene (bicyclo[2.2.1]hept-2-ene), but no

Table 4 Selected bond lengths (Å) and angles (°) for complex **9a**

Nb–N	1.813(3)	N–C(31)	1.392(4)
Nb–C(2)	2.144(3)	C(1)–C(2)	1.309(5)
Nb–C(1)	2.200(3)	C(1)–C(11)	1.457(5)
Nb–P	2.5462(12)	C(2)–C(21)	1.469(5)
Nb–Centroid	2.154(6)		
N–Nb–C(2)	105.90(12)	Centroid–Nb–C(2)	111.8(2)
N–Nb–C(1)	109.52(12)	C(31)–N–Nb	166.3(2)
C(2)–Nb–C(1)	35.05(12)	C(2)–C(1)–C(11)	137.7(3)
N–Nb–P	88.46(10)	C(2)–C(1)–Nb	70.1(2)
C(2)–Nb–P	116.11(9)	C(11)–C(1)–Nb	152.2(2)
C(1)–Nb–P	81.18(9)	C(1)–C(2)–C(21)	136.0(3)
Centroid–Nb–P	111.5(1)	C(1)–C(2)–Nb	74.8(2)
Centroid–Nb–N	121.5(2)	C(21)–C(2)–Nb	149.0(2)
Centroid–Nb–C(1)	127.1(2)	C(31)–C(32)–C(320)	121.9(3)

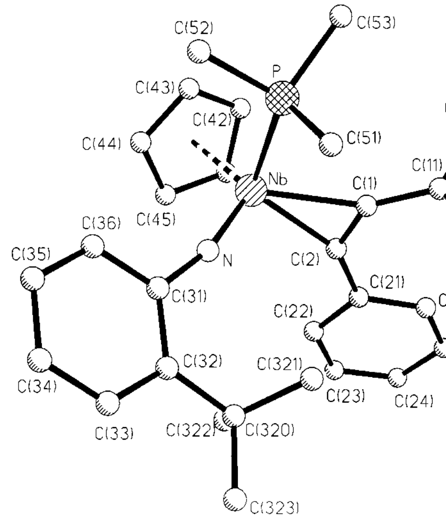
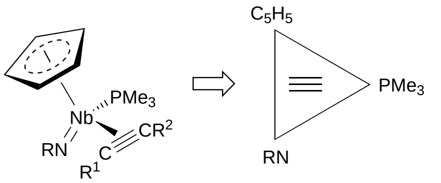


Fig. 2 Molecular structure of complex **9a**, without H atoms and with key atoms labelled

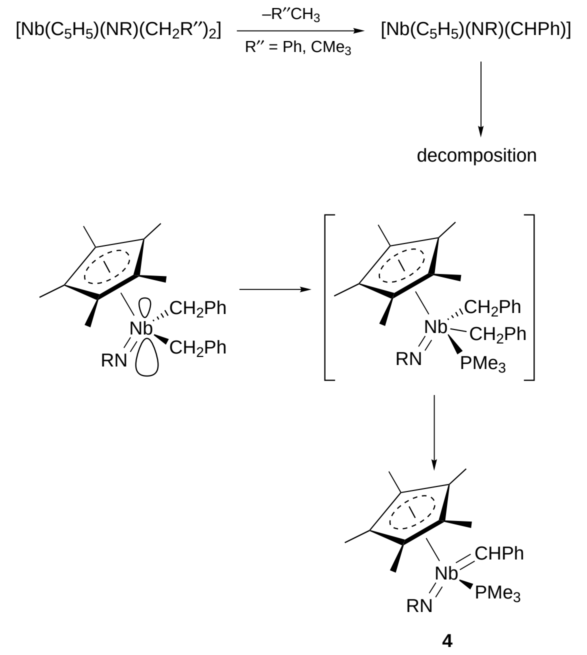


Scheme 6 Representation of complex **9a** showing the orientation of the alkyne ligand. R = 2-Bu^{t}C$_6$H$_4$, R^1 = R^2 = Ph

identifiable propagating niobium alkylidene species could be observed.

By contrast, the C$_5$Me$_5$ dibenzyl complex is stable to temperatures in excess of 100 °C and it proved possible to induce elimination of toluene only upon addition of PMe$_3$. Although there is no direct evidence for the formation of an intermediate PMe$_3$ adduct, it is believed that the added phosphine may force the two alkyl groups closer together by binding at the lowest unoccupied molecular orbital (LUMO),[11] which projects either side rather than between the two benzyl ligands. Owing to strong binding of the PMe$_3$ ligand in the resultant benzylidene complex **4**, it is not an efficient initiator for ring-opening metathesis polymerisation, requiring several days at 80 °C to polymerise 10 equivalents of norbornene to completion. A propagating alkylidene species is not observable. It may prove possible to increase the ROMP efficiency of molecules of this type by increasing the size and decreasing the basicity of the coordinated phosphine.

For phenyl derivatives, the C$_5$H$_5$ complex **5** is quite stable but only as a phosphine adduct. Its conversion into the benzyne complex is inhibited by added phosphine which probably reflects a requirement for sufficient space to be generated at the metal to facilitate β-H transfer. Unlike its zirconocene analogue, the niobium benzyne compound **6** is remarkably unreactive towards unsaturated reagents such as ethene, carbon monoxide and acetonitrile, being stable to >100 °C in the presence of ethene and decomposing to paramagnetic products only after prolonged heating at 80 °C in the presence of CO and MeCN. Again the stability of **6** is attributed to strong binding of the PMe$_3$ ligand.



Scheme 7 R = 2,6-Pr$^i_2$C$_6$H$_4$

In conclusion, the complexes described here lend strong support to the isolobal relationship between zirconocene and half-sandwich niobium imido complexes. Differences are seen in the stabilities of the half-sandwich imido derivatives containing differing cyclopentadienyl/NR combinations. The influence of the cyclopentadienyl and imido ligands on the reactivity of these complexes will form a focus of future work.

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^{1}H), 100.6 (^{13}C) and 161.9 MHz (^{31}P); chemical shifts are referenced to the residual protio impurity of the deuteriated solvent. Infrared spectra (Nujol mulls, CsI windows) were obtained on Perkin-Elmer 577 and 457 grating spectrophotometers, mass spectra on a VG 7070E instrument [70 eV (*ca.* 1.12 × 10^{-17} J), 100 μA emission. Trimethylphosphine was prepared by a previously published procedure.[19] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

[Nb(C$_5$H$_5$)(NC$_6$H$_3$Pr$^i_2$-2,6)Cl(CH$_2$Ph)] 2. Diethyl ether (50 cm^3) was condensed onto a mixture of [Nb(C$_5$H$_5$)(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2$] (1.20 g, 2.97 mmol) and KCH$_2$Ph (0.41 g, 3.12 mmol) in an ampoule at −196 °C. The mixture was allowed to warm over 2 h to room temperature (r.t.) and stirred for 6 h to afford a red-brown suspension. The supernatant solution was filtered from the KCl residue and the solvent removed under reduced pressure to give an oily red solid. The solid was extracted into *n*-pentane (15 cm^3) and prolonged cooling at *ca.* −30 °C afforded pale yellow crystals. Yield 0.3 g, 22%. (Found: C, 62.7; H, 6.4; N, 3.1. Calc. for $C_{24}H_{29}ClNNb$: C, 62.7; H, 6.5; N, 2.9%). *m*/*z* (^{35}Cl) 459 (M^+) and 421 ($[M - Cl]^+$). IR (Nujol, CsI, cm^{-1}): 3040w, 2910s, 2840s, 1590w, 1515w, 1455s, 1375s, 1365m, 1330m, 1280m, 1175w, 1095m (br), 1055m (br), 1015s, 810s, 800s, 755s, 750s, 685m, 450w and 370w (br).

$[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(CH_2Ph)_2]$ 3. Diethyl ether (30 cm^3) was condensed onto a mixture of $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ (1.75 g, 3.69 mmol) and KCH_2Ph (1.10 g, 8.39 mmol) at −196 °C. The mixture was allowed to warm to 0 °C and stirred for 2 h. The volatile components were then removed under reduced pressure and the residue extracted with *n*-pentane (50 cm^3). The resulting orange solution was filtered, concentrated to *ca.* 20 cm^3 and stored at −78 °C whereupon dark yellow crystals were obtained. Yield 0.90 g, 42% (Found: C, 73.6; H, 8.2; N, 2.2. Calc. for $C_{36}H_{46}NNb$: C, 73.8; H, 7.9; N, 2.4%). *m*/*z* 585 (M^+) and 494 ($[M - C_7H_8]^+$). IR (Nujol, CsI, cm^{-1}): 3030w, 1600m, 1490s, 1465s, 1430m, 1385s, 1335m, 1275m, 970w, 800w, 755s, 750m, 740s, 700m, 690s, 470m, 455m and 370m.

$[Nb(C_5Me_5)(NC_6H_3Pr^i\text{-}2,6)(PMe_3)(CHPh)]$ 4. Trimethylphosphine (0.08 g, 0.99 mmol) was condensed onto a frozen solution of $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(CH_2Ph)_2]$ (0.39 g, 0.66 mmol) in *n*-heptane (30 cm^3). On warming to 65 °C the solution adopted a yellow colouration, and after stirring for 14 d it was concentrated to 10 cm^3 to afford a red solution. Subsequent cooling to *ca.* −40 °C gave orange needles which were collected and dried *in vacuo*. Yield 0.10 g, 28% (Found: C, 68.1; H, 8.3; N, 2.2. Calc. for $C_{32}H_{47}NNbP$: C, 67.5; H, 8.3; N, 2.5%). *m*/*z* 569 (M^+) and 493 ($[M - PMe_3]^+$). IR (Nujol, CsI, cm^{-1}): 3040w, 2930s, 2840s, 1585w, 1515w, 1460s, 1425m, 1380m, 1335m, 1285m, 1215m (sh), 1120m, 1025w, 955w (br), 815m, 795m, 770w, 750s, 735w, 695m and 380m (br).

$[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Ph_2(PMe_3)]$ 5. Trimethylphosphine (0.23 g, 3.0 mmol) was condensed onto a frozen solution of $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ (0.60 g, 1.5 mmol) and MgPhCl (0.41 g, 3.0 mmol) in diethyl ether (30 cm^3) at −196 °C. Upon warming to r.t. an orange suspension was formed. After stirring for 4 h the supernatant solution was filtered from the $MgCl_2$ residue and concentrated. Recrystallisation from the diethyl ether solution (20 cm^3) at *ca.* −30 °C afforded cubic orange crystals. Yield 0.25 g, 30% (Found: C, 68.3; H, 7.7; N, 2.3. Calc. for $C_{32}H_{41}NNbP$: C, 68.3; H, 7.3; N, 2.5%). *m*/*z* 485 ($[M - C_6H_6]^+$) and 409 ($[M - C_6H_6 - PMe_3]^+$). IR (Nujol, CsI, cm^{-1}): 2940s (br), 2850s, 2720w (br), 1565w, 1465s, 1430m (sh), 1380s, 1370m (sh), 1330w, 1270m, 1155w (br), 1100w (br), 1010w, 805m, 760m, 755w (sh), 725s, 705m, 330w and 310w.

$[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)(\eta^2\text{-}C_6H_4)]$ 6. A *n*-heptane solution of $[Nb(C_5H_5)(NC_6H_3Pr^i_2\text{-}2,6)Ph_2(PMe_3)]$ (0.40 g, 0.71 mmol) in *n*-heptane (20 cm^3) was stirred at 60 °C for 3 d to afford a brown solution. The solution was then filtered and the volatile components were removed under reduced pressure to give a yellow-black powder. Extraction with diethyl ether (15 cm^3) and prolonged cooling at *ca.* −40 °C afforded green cubic crystals. Yield 0.27 g, 78% (Found: C, 64.0; H, 7.3; N, 2.7. Calc. for $C_{26}H_{35}NNbP$: C, 64.3; H, 7.3; N, 2.9%). *m*/*z* 485 (M^+) and 409 ($[M - C_6H_4]^+$). IR (Nujol, CsI, cm^{-1}): 3020m, 2920s, 2850s, 1565m, 1460s, 1450m (sh), 1425m, 1415m (sh), 1380m, 1360w, 1345m, 1335s, 1310w, 1285s, 1245w, 1150m, 1100w (br), 1015w (br), 980w, 970m, 955m, 940w (sh), 795s, 760s, 740s, 730w, 395w and 295w.

$[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)Cl_2]$ 7. To a stirred suspension of $[Nb(C_5H_5)Cl_4]$ (3.00 g, 10.0 mmol) in CH_2Cl_2 (70 cm^3) was added a solution of 2,6-dimethylpyridine (1.07 g, 10.0 mmol) in CH_2Cl_2 (20 cm^3). To this was added dropwise at 0 °C a solution of $Me_3SiNH(C_6H_4Bu^t\text{-}2)$ (2.22 g, 10.0 mmol) in CH_2Cl_2 (40 cm^3). The mixture was then stirred at r.t. for 8 h to afford a clear red solution. The solvent was removed under reduced pressure to give an orange-yellow solid. Extraction of the solid with hot (70 °C) heptane (3 × 100 cm^3) afforded an orange solution which was filtered, concentrated and cooled at *ca.* −20 °C to give orange needle crystals (yield 2.71 g, 72%) (Found: C, 47.9; H, 4.9; N, 3.6. Calc. for $C_{15}H_{18}Cl_2NNb$: C, 47.9; H, 4.8; N, 3.7%). *m*/*z* (^{35}Cl) 375 (M^+). IR (Nujol, CsI, cm^{-1}): 3090m, 3060w, 1480m, 1430s, 1365m, 1310w, 1290s, 1280m (sh), 1160w, 1090m, 1050w, 1020s, 980s, 930w, 840s (sh), 830w, 820vs, 815m, 750s, 740s, 600w, 390s, 350m and 340m.

$[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PMe_3)_2]$ 8a. Trimethylphosphine (0.67 g, 8.76 mmol) was condensed at −196 °C onto a frozen tetrahydrofuran (thf) (100 cm^3) solution of $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)Cl_2]$ (0.82 g, 2.19 mmol) over activated magnesium turnings (0.06 g, 2.47 mmol). Upon warming to r.t. a yellow suspension characteristic of the PMe_3 adduct $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)Cl_2(PMe_3)]$, was formed. After stirring for 20 h a dark green solution was observed. Removal of the volatile components under reduced pressure gave a dark green solid, which was extracted with pentane, concentrated and cooled to −30 °C to afford extremely air-sensitive dark green crystals. Yield 0.74 g, 74%. Satisfactory elemental analysis could not be obtained for this compound due to its extreme air and moisture sensitivity. *m*/*z* 457 (M^+). IR (Nujol, CsI, cm^{-1}): 3070w, 3030w, 1885w, 1580s, 1550w, 1460vs, 1350w, 1310vs, 1280s (sh), 1240w, 1200w, 1160w, 1120m, 1100m (sh), 1050s, 1020s, 995s (sharp), 950vs (sh), 850m, 820m, 800s (sh), 760vs, 740s, 710s, 660vs, 590w, 520m, 450m (sh), 380m, 365m and 340m.

$[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_2]$ 8b. In an analogous procedure to that for complex **8a**, $[Nb(C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ (0.496 g, 1.046 mmol) was treated with PMe_3 (0.44 g, 5.80 mmol) in the presence of activated magnesium (0.032 g, 1.37 mmol) in thf (15 cm^3). The mixture was stirred for 4 d at room temperature during which time it changed from deep orange to dark brown. After removal of the volatile components under reduced pressure, the solid residue was extracted with pentane (120 cm^3) to give a brown solution which was filtered and pumped to dryness to give dark brown crystals. Yield 0.33 g, 57% (Found: C, 61.1; H, 9.4; N, 2.5. Calc. for $C_{28}H_{50}NNbP$: C, 60.5; H, 9.1; N, 2.5%). IR (Nujol, CsI, cm^{-1}): 1585w, 1460s, 1425m, 1380s, 1335s, 1280s, 950s, 935s, 840w, 795w, 750s, 720m, 710m, 650s, 400w and 360m.

$[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PhC{\equiv}CPh)(PMe_3)]$ 9a. Pentane (30 cm^3) was added to $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PMe_3)_2]$ (0.167 g, 0.37 mmol) and diphenylacetylene (0.065 g, 0.37 mmol) at r.t. and the mixture was stirred at 40 °C for 4 weeks. The brown solution was filtered, concentrated and cooled to 0 °C to yield yellow-brown crystals. Yield 0.14 g, 68% (Found: C, 68.3; H, 6.7; N, 2.3. Calc. for $C_{32}H_{37}NNbP$: C, 68.7; H, 6.7; N, 2.5%). *m*/*z* 560 (M^+). IR (Nujol, CsI, cm^{-1}): 3070w, 3040w, 1695s (sh), 1595m (sh), 1440m, 1360m, 1310s, 1290s, 1265s (sh), 1120w, 1090w, 1070w, 1050m, 1010m (sh), 955s (sh), 890w, 840w, 790vs, 780m, 760m, 750s, 740m, 730m, 700s (sharp), 695s (sharp), 580m, 455m and 400w.

$[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PhC{\equiv}CH)(PMe_3)]$ 9b. Pentane (50 cm^3) was added to $[Nb(C_5H_5)(NC_6H_4Bu^t\text{-}2)(PMe_3)_2]$ (0.210 g, 0.46 mmol) and phenylacetylene (0.056 g, 0.55 mmol) at r.t. and the mixture was stirred for 2 d. The red-brown solution was filtered, concentrated and cooled to −40 °C to give a yellow-brown crystalline solid. Yield 0.13 g, 59% (Found: C, 64.5; H, 7.3; N, 2.9. Calc. for $C_{26}H_{33}NNbP$: C, 64.6; H, 6.9; N, 2.9%). *m*/*z* 483 (M^+). IR (Nujol, CsI, cm^{-1}): 3090w, 3040w, 1640m,

Table 5 Crystallographic data for compounds **7** and **9a**[a]

	7	**9a**
Formula	$C_{15}H_{18}Cl_2NNb$	$C_{32}H_{37}NNbP$
M	376.11	559.51
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/n$
a/Å	11.897(2)	11.731(6)
b/Å	9.400(2)	12.624(3)
c/Å	14.081(3)	19.282(4)
β/°		95.24(3)
U/Å^3	1574.7(5)	2844(2)
D_c/g cm^{-3}	1.586	1.307
F(000)	760	1168
Colour	Red	Yellow-brown
Size/mm	0.75 × 0.55 × 0.40	0.3 × 0.25 × 0.25
Scan type	ω	ω–2θ
θ Range/°	2.61–25.0	3.08–27.02
hkl Ranges	$-14 \leqslant h \leqslant 1$, $-11 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 16$	$0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 16$, $-24 \leqslant l \leqslant 24$
Data measured	1975	6058
Data unique	1471	5705
Data observed	1471	5505
R_{merg}	0.0166	0.0673
Parameters	133	389
μ/mm^{-1}	1.090	1.307
$t_{\min}$, $t_{\max}$	0.850, 1.000	0.96, 1.00
R [$I > 2\sigma(I)$]	0.0223	0.0357
wR' [$I > 2\sigma(I)$]	0.0615	0.0800
Goodness of fit	1.299	1.028
$\rho_{\max}$, $\rho_{\min}$/e Å^{-3}	0.307, −0.341	0.451, −0.597
$(\Delta/\sigma)_{\max}$	0.000	−2.983[b]

[a] Details in common: $Z = 4$; block morphology; empirical ψ-scan absorption correction. [b] This value is large because the methyl hydrogen atoms, H32A-X and H51A-X, are badly resolved and are consequently fixed at idealised positions in the model.

1590m, 1480m, 1360w, 1310vs, 1285s (sharp), 1270m (sh), 1205w, 1165w, 1150w, 1125m, 1090m, 1065m, 1050m, 1010m, 1005m, 965s, 960s, 950s, 940m, 840w, 810m, 790vs, 760s, 740vs, 720m, 690s, 665w, 625w, 580w, 520m (sh), 470m (sh) and 380w.

[Nb(C_5Me_5)($NC_6H_3Pr^i_2$-2,6)(PhC≡CPh)(PMe_3)] 9c. Benzene (30 cm^3) was added to [Nb(C_5Me_5)($NC_6H_3Pr^i_2$-2,6)(PMe_3)$_2$] (0.111 g, 0.20 mmol) and diphenylacetylene (0.036 g, 0.20 mmol) at r.t. and the mixture was stirred at 60 °C for 2 weeks. The volatile components were removed under reduced pressure and the residue was extracted with pentane (30 cm^3). The solution was then filtered, concentrated and cooled to 0 °C to yield yellow-brown crystals. Yield: 0.14 g, 68% (Found: C, 70.7; H, 7.5; N, 1.9. Calc. for $C_{39}H_{51}NNbP$: C, 71.2; H, 7.8; N, 2.1%). m/z 560 (M^+). IR (Nujol, CsI, cm^{-1}): 1695m, 1670m, 1590m, 1320s, 1270s, 1170w, 1155w, 1105w, 1065w, 1025w, 950s (sh), 930s, 770s, 755s, 730m, 720m, 695s, 585w, 575w, 450m and 340m.

X-Ray crystallography

Crystal data for complexes **7** and **9a** are given in Table 5. The air-sensitive samples were mounted on glass fibres using a perfluoropolyether oil.[20] Crystal data were collected at 150 K, using a four-circle Rigaku AFC6S diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Three standard reflections measured every 147 during the data collection showed no variation in intensity. Cell parameters were determined from 20 reflections located using a systematic zig-zag search through reciprocal space and data were reduced using TEXSAN.[21]

The structures were solved by Patterson methods using the SHELXS 86 program[22] and refined by full-matrix least-squares methods on F^2 using SHELXL 93.[23] The weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (2F_c^2 + F_o^2)/3$ and a and b are refinable parameters in the least-squares program. Atomic scattering factors were taken from ref. 24.

Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model (including free rotation about C–C bonds for methyl groups). Isotropic atomic displacement parameters were constrained to be 1.2 (1.5 for methyl groups) times the equivalent isotropic atomic displacement parameter for the adjacent heavy atom.

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