Mono(cyclopentadienyl) and *ansa*-bis(cyclopentadienyl)imido derivatives of Group 5 and 6 transition metals; crystal structures of $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NR)X]$ (M = Nb, R = $SiMe_3$, X = Cl; R = Bu^t, X = Cl, Br or I; M = Ta, R = Bu^t, X = Cl)†

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The new half-sandwich mono(cyclopentadienyl)tungsten compounds $[W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_3]$ and $[W(\eta\text{-}C_5H_4Me)(NBu^t)(L)Cl]$ (L = $\eta\text{-}C_2H_4$ or $\eta\text{-}MeC_2Me$) have been synthesized. In addition, the *ansa*-bis(cyclopentadienyl) Group 5 compounds $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NR)X]$ (M = V, R = Bu^t, X = Cl; M = Nb, R = $SiMe_3$, X = Cl;* R = Bu^t, X = Cl,* Br,* I* or Me; M = Ta, R = Bu^t, X = Cl* or Me) are reported. An asterisk indicates that the compound has been structurally characterized. Attempts to prepare the related dichloride compounds by replacement of the imido functionality in $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Cl]$ (M = V, Nb or Ta) using HCl led to decomposition, suggestive of a labilising of the cyclopentadienyl rings by the strongly bonding imido ligand.

The present work was carried out with two broad objectives. First, the organoimido ligand is unique since it can contribute a total of four electrons through a single ligating nitrogen atom, forms strong and frequently chemically inert bonds to transition metals and, by virtue of the organo R group, its steric and electronic properties are readily modified. Thus, it seems likely that the combination of the cyclopentadienyl ligand and the organoimido ligand may lead to a rich chemistry with potential applications in catalysis and organic synthesis. The first part of this work, therefore, is concerned with half-sandwich mono(cyclopentadienyl)imidotungsten derivatives, which are analogous to previously described molybdenum compounds.[1,2] Similar related half-sandwich compounds of Group 5 metals containing ancilliary imido ligands are known.[3]

Secondly, recent work has shown that *ansa*-bis(cyclopentadienyl) compounds can have reactivities which differ markedly from those of their non-*ansa* analogues.[4] This is attributed to the presence of the *ansa* bridge which prevents the $M(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)$ fragment from adopting a parallel ring sandwich structure and consequently raises the energy of the transition state in reactions such as reductive elimination. In order to achieve further insight into the structure–reactivity relationships in *ansa*-metallocene derivatives of the early transition metals it was decided to explore synthetic routes towards *ansa*-metallocenes of the Group 5 elements, in particular niobium and tantalum. Previous work in this area has included the preparation of *ansa*-bridged $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$.[5] However, the synthesis of this compound is laborious and we report here convenient preparations of *ansa* compounds containing ancillary imido ligands. The starting point for this work is based on the report by Schmidt and Sundermeyer[6] of the synthesis of the bis(cyclopentadienyl) *tert*-butylimido derivatives $[M(\eta^5\text{-}C_5H_5)_2(NBu^t)Cl]$ (M = Nb or Ta). During the course of this study an alternative synthetic route to *ansa*-bis(cyclopentadienyl)imido-niobium and -tantalum derivatives has been reported.[7] *ansa*-Metallocenes of vanadium have also been described.[8]

Results and Discussion

Treatment of the compound $[W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2]$ with chlorine gas gives the corresponding trichloride $[W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_3]$ **1** as a green microcrystalline solid. The analytical and spectroscopic data characterising this species and the other new compounds are given in Table 1 and will not be discussed unless their interpretation is not straightforward. The ^1H NMR spectrum of the compound **1** shows two virtual triplets assignable to the ring protons of the $\eta\text{-}C_5H_4Me$ group, indicating that on the NMR time-scale the molecule possesses a plane of symmetry. Reduction of the compound $[W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2]$ with potassium–graphite under 1 atm of ethene or with sodium amalgam in the presence of an excess of but-2-yne affords the tungsten(IV) compounds $[W(\eta\text{-}C_5H_4Me)(NBu^t)(L)Cl]$ (L = $\eta\text{-}C_2H_4$ **2** or $\eta\text{-}MeC_2Me$ **3**) respectively as golden-brown microcrystalline solids, in a manner analogous to that previously reported for the molybdenum complexes.[1] The ^1H NMR spectroscopic data for compound **2** show four distinct signals for the η-ethene ligand suggesting a high energy barrier to alkene rotation. This is rationalized by considering the nature of the frontier orbitals of the $\{W(\eta\text{-}C_5H_4Me)(NBu^t)\}$ fragment which, by isolobal analogy, may be proposed to have metallocene-like characteristics. This leads us to expect the alkene to be constrained to the 'inter-ligand wedge' defined by the methylcyclopentadienyl ring, the chiral tungsten centre and the *tert*-butylimido group. Similarly for the η^2-but-2-yne compound **3** the presence of two resonances due to the methyl groups of the alkyne indicates a structure which is static on the NMR time-scale.

The niobium trimethylsilylimido derivative $[Nb(NSiMe_3)(py)_2Cl_3]$ (py = pyridine) is readily prepared by the method of Doherty and co-workers.[9] Treatment of this compound with the dipotassium salt of 2,2-bis(cyclopentadienyl)propane gives yellow crystals of the diamagnetic *ansa*-metallocene $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NSiMe_3)Cl]$ **4**. We and other workers have noted that lower yields are obtained when the dilithium salt is employed in this system.[5,10] The crystal structure of compound **4** has been determined and its molecular structure, with atomic numbering scheme, is shown in Fig. 1. Selected

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† *Non-SI units employed:* mmHg = 133.322 Pa, atm = 101 325 Pa.

Table 1 Analytical and spectroscopic data

Complex[a]	Spectroscopic data[b]
1 $[W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_3]$ Green C, 27.3 (27.3); H, 3.4 (3.6); N, 3.0 (3.2)	IR (CsI disc): ν(W−Cl) 340, 310, 285 ^{1}H (300 MHz):[c] 6.48 (2 H, t, *J* 2.5, $C_5\mathit{H}_4$Me), 6.25 (2 H, t, *J* 2.5, $C_5\mathit{H}_4$Me), 2.55 (3 H, s, C_5H_4*Me*), 1.49 (9 H, s, CMe_3)
2 $[W(\eta\text{-}C_5H_4Me)(NBu^t)(\eta\text{-}C_2H_4)Cl]$ Yellow-brown C, 36.0 (36.3); H, 5.0 (5.1); N, 3.5 (3.5)	IR (CsI disc): ν(W−Cl) 290 ^{1}H (300 MHz): 5.43 (2 H, br m, $C_5\mathit{H}_4$Me), 5.23 (1 H, br m, $C_5\mathit{H}_4$Me), 4.61 (1 H, br m, $C_5\mathit{H}_4$Me), 2.65 (2 H, m, C_2H_4), 2.22 (1 H, m, C_2H_4), 1.73 (3 H, s, C_5H_4*Me*), 1.53 (1 H, m, C_2H_4), 0.96 (9 H, s, CMe_3) ^{13}C-{^{1}H} (75 MHz):[d] 104.3 (s, *C*$_5$H$_4$Me), 100.4 (s, *C*$_5$H$_4$Me), 97.1 (s, *C*$_5$H$_4$Me), 96.1 (s, *C*$_5$H$_4$Me), 40.7 (s, C_2H_4), 32.8 (s, C_2H_4), 29.2 (s, C*Me*$_3$), 14.2 (s, C_5H_4*Me*)
3 $[W(\eta\text{-}C_5H_4Me)(NBu^t)(\eta\text{-}MeCCMe)Cl]$ Yellow-brown C, 39.0 (39.7); H, 5.0 (4.6); N, 3.3 (3.3)	IR (CsI disc): ν(alkyne CC) 1802 ^{1}H (300 MHz): 5.72 (1 H, q, *J* 2.5, $C_5\mathit{H}_4$Me), 5.59 (1 H, q, *J* 2.5, $C_5\mathit{H}_4$Me), 5.51 (1 H, br q, $C_5\mathit{H}_4$Me), 4.93 (1 H, br q, $C_5\mathit{H}_4$Me), 2.76 (3 H, s, MeCCMe), 2.53 (3 H, s, MeCCMe), 1.80 (3 H, s, C_5H_4*Me*), 0.99 (9 H, s, CMe_3) ^{13}C-{^{1}H} (75 MHz): 146.0 (s, Me*C*CMe), 144.6 (s, MeC*C*Me), 123.6 (s, *C*$_5$H$_4$Me, C_{ipso}), 106.1 (s, *C*$_5$H$_4$Me), 104.1 (s, *C*$_5$H$_4$Me), 101.5 (s, *C*$_5$H$_4$Me), 98.1 (s, *C*$_5$H$_4$Me), 69.0 (s, *C*Me$_3$), 30.3 (s, NC*Me*$_3$), 21.3 (s, *Me*CCMe), 14.2 (s, C_5H_4*Me*), 12.7 (s, MeCC*Me*)
4 $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NSiMe_3)Cl]$ Yellow C, 49.6, (49.8); H, 6.1 (6.0); N, 3.7 (3.6)	IR (KBr disc): ν(Nb−Cl) 317 ^{1}H (500 MHz): 6.50 (2 H, m, C_5H_4), 5.94 (4 H, m, C_5H_4), 5.20 (2 H, m, C_5H_4), 1.28 (3 H, s, CH_3), 0.99 (3 H, s, CH_3), 0.06 (9 H, s, $SiMe_3$) ^{13}C-{^{1}H} (125 MHz): 137.9 (s, C_5H_4, C_{ipso}), 120.6 (s, C_5H_4), 115.5 (s, C_5H_4), 103.4 (s, C_5H_4), 95.0 (s, C_5H_4), 36.2 (s, *C*Me$_2$), 24.0 (s, C*Me*$_2$), 22.5 (s, C*Me*$_2$), 0.9 (s, $SiMe_3$) Mass (^{35}Cl): *m/z* 387 [M^+], 372 [$M^+ - CH_3$], 357 [$M^+ - 2CH_3$], 352 [$M^+ - Cl$], 342 [$M^+ - 3CH_3$], 300 [$M^+ - NSiMe_3$], 263 [$Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}^+$]
5 $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Cl]$ Yellow C, 54.9 (55.2); H, 6.8 (6.3); N, 3.9 (3.8)	^{1}H (500 MHz):[c] 6.41 (2 H, q, *J* 3, C_5H_4), 6.35 (2 H, q, *J* 3, C_5H_4), 6.03 (2 H, q, *J* 3, C_5H_4), 5.57 (2 H, q, *J* 3, C_5H_4), 1.80 (3 H, s, CH_3), 1.52 (3 H, s, CH_3), 1.07 (9 H, s, CMe_3) ^{13}C-{^{1}H} (75 MHz):[c] 143.8 (s, C_5H_4, C_{ipso}), 120.4 (s, C_5H_4), 111.2 (s, C_5H_4), 104.0 (s, C_5H_4), 94.4 (s, C_5H_4), 69.6 (s, N*C*Me$_3$), 36.8 (s, *C*Me$_2$), 30.4 (s, C*Me*$_3$), 24.2 (s, C*Me*$_2$), 23.2 (s, C*Me*$_2$) Mass (^{35}Cl): *m/z* 369 [M^+], 354 [$M^+ - CH_3$], 334 [$M^+ - Cl$], 319 [$M^+ - CH_3 - Cl$], 298 [$M^+ - NBu^t$], 263 [$Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}^+$], 57 [$Bu^{t+}$]
6 $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Br]$ Yellow C, 49.6 (49.3); H, 6.0 (5.6); N, 3.5 (3.4)	^{1}H (500 MHz): 6.53 (2 H, q, *J* 2.5, C_5H_4), 6.02 (2 H, q, *J* 2.5, C_5H_4), 5.75 (2 H, q, *J* 2.5, C_5H_4), 5.39 (2 H, q, *J* 2.5, C_5H_4), 1.30 (3 H, s, CH_3), 1.03 (3 H, s, CH_3), 1.00 (9 H, s, CMe_3) ^{13}C-{^{1}H} (125 MHz): 143.5 (s, C_5H_4, C_{ipso}), 119.1 (s, C_5H_4), 110.7 (s, C_5H_4), 104.0 (s, C_5H_4), 93.5 (s, C_5H_4), 36.1 (s, *C*Me$_2$), 30.1 (s, C*Me*$_3$), 23.9 (s, C*Me*$_2$), 22.6 (s, C*Me*$_2$), N*C*Me$_3$ not located Mass (^{81}Br): *m/z* 414 [M^+], 399 [$M^+ - CH_3$], 343 [$M^+ - NBu^t$]
7 $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)I]$ Orange C, 43.2 (44.2); H, 5.0 (5.0); N, 3.0 (3.0)	^{1}H (500 MHz): 6.66 (2 H, m, C_5H_4), 6.17 (2 H, m, C_5H_4), 5.55 (2 H, m, C_5H_4), 5.34 (2 H, m, C_5H_4), 1.29 (3 H, s, CH_3), 1.01 (9 H, s, CMe_3), 0.93 (3 H, s, CH_3) ^{13}C-{^{1}H} (125 MHz): 142.9 (s, C_5H_4, C_{ipso}), 116.5 (s, C_5H_4), 110.1 (s, C_5H_4), 103.5 (s, C_5H_4), 93.5 (s, C_5H_4), 69.7 (s, N*C*Me$_3$), 35.9 (s, *C*Me$_2$), 30.0 (s, C*Me*$_3$), 23.8 (s, C*Me*$_2$), 22.3 (s, C*Me*$_2$) Mass: *m/z* 460 [M^+], 445 [$M^+ - CH_3$], 389 [$M^+ - NBu^t$], 263 [$Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}^+$], 127 [$I^+$], 71 [$NBu^{t+}$], 57 [$Bu^{t+}$]
8 $[V\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Cl]$[e] Yellow-brown	^{1}H (300 MHz):[c] 6.72 (2 H, m, C_5H_4), 6.55 (2 H, m, C_5H_4), 6.42 (2 H, m, C_5H_4), 6.31 (2 H, m, C_5H_4), 1.51 (3 H, s, CH_3), 1.40 (3 H, s, CH_3), 1.31 (9 H, s, CMe_3) ^{51}V (131 MHz):[c] −667 (s, f.w.h.h. = 790 Hz)[f]
9 $[Ta\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Cl]$ Orange C, 45.0 (44.1); H, 5.6 (5.1); N, 3.1 (3.1)	^{1}H (300 MHz):[c] 6.25 (2 H, q, *J* 3, C_5H_4), 6.21 (2 H, q, *J* 3, C_5H_4), 6.09 (2 H, q, *J* 3, C_5H_4), 5.71 (2 H, q, *J* 3, C_5H_4), 1.78 (3 H, s, CH_3), 1.57 (3 H, s, CH_3), 1.07 (9 H, s, CMe_3) ^{13}C-{^{1}H} (75 MHz):[c] 142.7 (s, C_5H_4, C_{ipso}), 118.6 (s, C_5H_4), 111.1 (s, C_5H_4), 103.1 (s, C_5H_4), 91.7 (s, C_5H_4), 66.3 (s, N*C*Me$_3$), 36.5 (s, *C*Me$_2$), 31.9 (s, C*Me*$_3$), 24.2 (s, C*Me*$_2$), 23.4 (s, C*Me*$_2$)
10 $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Me]$ Yellow C, 61.5 (61.9); H, 7.5 (7.5); N, 3.8 (4.0)	^{1}H (500 MHz):[c] 6.61 (4 H, q, *J* 2.5, C_5H_4), 5.84 (2 H, q, *J* 3, C_5H_4), 5.56 (2 H, q, *J* 2, C_5H_4), 1.73 (3 H, s, CH_3), 1.37 (3 H, s, CH_3), 0.97 (9 H, s, CMe_3), 0.76 (3 H, s, NbMe) ^{13}C-{^{1}H} (75 MHz):[c] 139.7 (s, C_5H_4, C_{ipso}), 111.9 (s, C_5H_4), 107.5 (s, C_5H_4), 103.0 (s, C_5H_4), 93.0 (s, C_5H_4), 66.1 (s, N*C*Me$_3$), 36.1 (s, *C*Me$_2$), 31.1 (s, C*Me*$_3$), 24.0 (s, C*Me*$_2$), 23.3 (s, C*Me*$_2$), 2.3 (br s, NbMe) Mass: *m/z* 349 [M^+], 334 [$M^+ - CH_3$], 319 [$M^+ - 2CH_3$], 278 [$M^+ - NBu^t$], 263 [$Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}^+$]
11 $[Ta\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Me]$ Yellow C, 49.3 (49.4); H, 5.0 (5.0); N, 3.0 (3.2)	^{1}H (300 MHz):[c] 6.53 (2 H, m, C_5H_4), 5.84 (2 H, m, C_5H_4), 5.58 (2 H, m, C_5H_4), 5.41 (2 H, m, C_5H_4), 1.73 (3 H, s, CH_3), 1.41 (3 H, s, CH_3), 0.96 (9 H, s, CMe_3), 0.69 (3 H, s, TaMe) ^{13}C-{^{1}H} (75 MHz):[c] 139.5 (s, C_5H_4, C_{ipso}), 111.4 (s, C_5H_4), 107.5 (s, C_5H_4), 102.8 (s, C_5H_4), 91.7 (s, C_5H_4), 64.6 (s, N*C*Me$_3$), 36.1. (s, *C*Me$_2$), 32.4 (s, C*Me*$_3$), 24.2 (s, C*Me*$_2$), 23.7 (s, C*Me*$_2$), 2.2 (br s, TaMe) Mass (^{35}Cl): *m/z* 437 [M^+], 424 [$M^+ - CH_3$], 366 [$M^+ - NBu^t$]

[a] Analytical data given as found (calculated) in %. [b] Infrared (cm^{-1}) given where a confident assignment was possible, NMR (298 K) given as chemical shift (δ) (relative intensity, multiplicity, coupling constant *J*/Hz, assignment). The NMR spectra were recorded in C_6D_6 unless otherwise stated. Electron-impact mass spectra data given as *m/z* (assignment). The expected isotope pattern was observed in all cases. Machine calibration accurate to 1%. [c] In CD_2Cl_2. [d] Distortionless enhancement of polarisation transfer sequence. [e] Satisfactory elemental analysis data were not obtained (see text). [f] f.w.h.h. = full width at half-height.

interatomic distances and angles for compound **4** and for the other new structures reported here appear in Table 2 along with selected structural data for the related unbridged compound $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ for comparison.[11] The Nb−N−Si linkage in compound **4** deviates noticeably from linearity [Nb−N−Si(14) 167.71(7)°], presumably a result of the steric requirements imposed by the bulky trimethylsilyl group. The angle subtended by the two ring centroid to niobium vectors in this and the other new *ansa* compounds is smaller than the same angle measured in $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$. This suggests that the *ansa* bridge is pulling the η-cyclopentadienyl rings away from the region occupied by the co-ligands.

Since compound **4** could only be prepared in low yield, we decided to use the niobium compound $[Nb(NBu^t)(py)_2Cl_3]$[12] as an alternative starting point for the synthesis of new complexes. Treatment of $[Nb(NBu^t)(py)_2Cl_3]$ with the dipotassium salt of

Table 2 Comparison of selected interatomic distances (Å) and angles (°) for the complexes **4**–**7**, **9** and [Nb(η-C_5H_5)$_2$(NBu^t)Cl][a] with estimated standard deviations in parentheses

	4	**5**	**6**	**7**	**9**	[Nb(η-C_5H_5)$_2$(NBu^t)Cl]
M−X	2.4387(4)	2.446(1)	2.6022(4)	2.8400(3)	2.434(5)	2.462(2), 2.453(2)
M−N	1.777(1)	1.762(3)	1.765(2)	1.770(2)	1.78(2)	1.789(4), 1.737(6)
N−Si/N−C	1.737(1)	1.438(5)	1.448(3)	1.440(3)	1.43(2)	not reported
M−Cp^1_{cent}	2.174	2.189	2.181	2.176	2.179	2.214, 2.205
M−Cp^2_{cent}	2.187	—	—	2.180	—	2.205, 2.211
M−Cp^1 range	2.396(1)–2.536(1)	2.401(3)–2.557(3)	2.395(2)–2.551(2)	2.397(2)–2.528(2)	2.40(1)–2.55(1)	2.426(7)–2.612(7), 2.438(8)–2.57(1)
M−Cp^1 average	2.484	2.495	2.490	2.486	2.492	2.505, 2.488
M−Cp^2 range	2.402(1)–2.549(1)	—	—	2.386(2)–2.551(2)	—	2.399(9)–2.558(8), 2.438(9)–2.596(9)
M−Cp^2 average	2.496	—	—	2.490	—	2.488, 2.499
M−N−Si/M−N−C	167.71(7)	178.4(3)	178.3(2)	171.8(2)	179.6(13)	173.6(4), 179.4(5)
N−M−X	98.21(4)	95.3(1)	93.77(8)	98.91(6)	94.9(5)	93.6(1), 95.1(2)
C(4)−C(1)−C(4′)	98.89(9)[b]	99.3(3)	99.1(2)	99.4(2)[b]	100.5(14)	—
C(2)−C(1)−C(3)	109.9(1)	112.2(2)	110.1(3)	109.4(2)	106.9(16)	—
Cp_{cent}−M−Cp_{cent}	114.2	113.3	113.4	114.2	113.7	122.7, 124.0

Cp^1 = Ring C(4)–C(8), Cp^2 = ring C(9)–C(13) for compounds **4** and **7**. [a] Given for comparison.[11] The asymmetric unit contains two crystallographically independent molecules. [b] C(4)−C(1)−C(9).

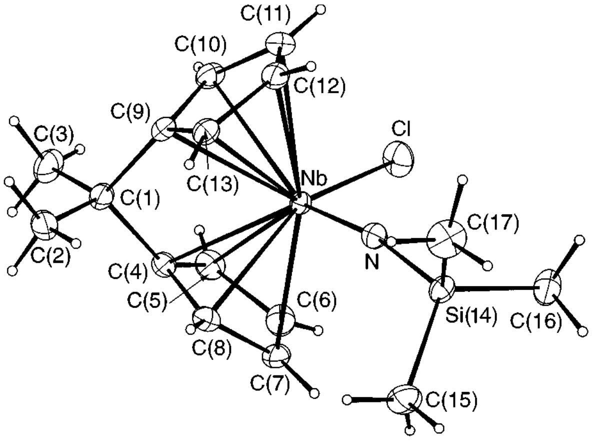


Fig. 1 Molecular structure of [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NSiMe_3)Cl] **4** showing the atom numbering scheme. Hydrogen atom labels are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level

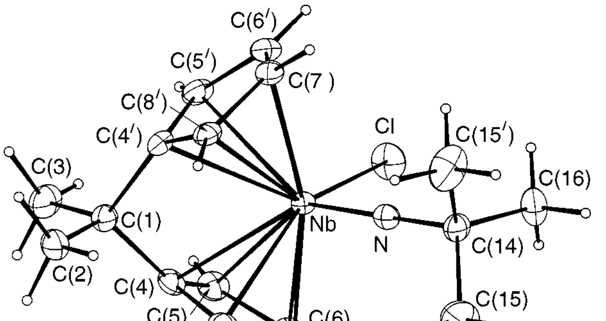
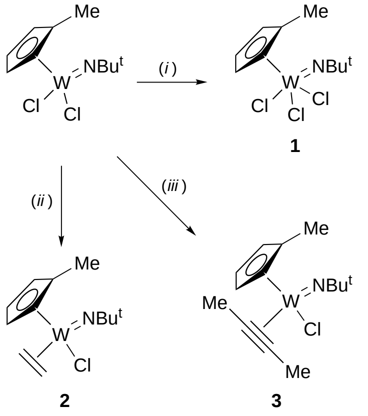


Fig. 2 Molecular structure of [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)Cl] **5** showing atom numbering scheme. Atoms labelled with a prime are generated from their counterparts by the symmetry operation $x, \frac{1}{2} - y, z$. Hydrogen atom labels are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level

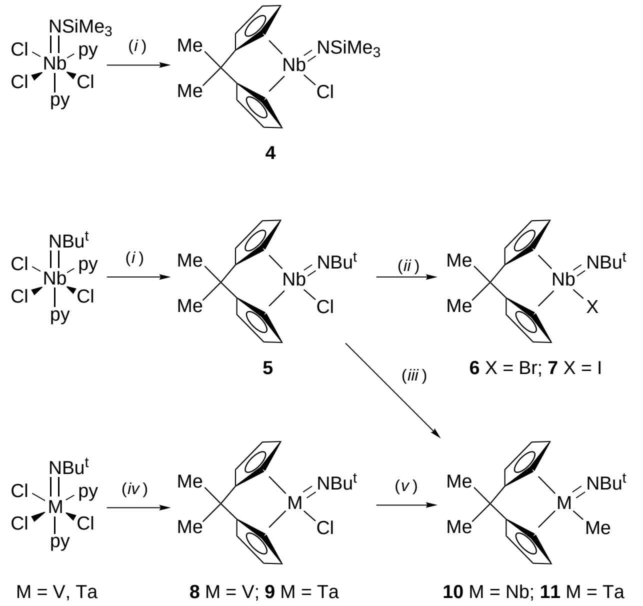
2,2-bis(cyclopentadienyl)propane gives the corresponding *tert*-butylimido complex [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)Cl] **5** in 77% yield. The crystal structure of **5** has been determined and the molecular structure is shown in Fig. 2. In contrast with compound **4**, the imido group in **5** is almost linear [Nb−N−C(14) 178.4(3)°].

The compound **5** readily undergoes halide exchange on treatment with trimethylsilyl bromide or iodide. The compounds [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)Br] **6** and [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)I] **7** have been synthesized and fully characterized. Their molecular structures are similar to that of **5** and display no surprising structural features. The atom numbering schemes employed for compounds **6** and **7** are the same as for **5** and **4** respectively. Note that bending of the imido group away from the iodide is observed in compound **7** [Nb−N−C(14) 171.8(2)°]. Treatment of the compound **5** with methyllithium in diethyl ether gives the corresponding methyl derivative [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)Me] **10** as a yellow powder in 64% yield.



Scheme 1 (*i*) Chlorine gas for 1 min in dichloromethane at room temperature (r.t.), yield 16%; (*ii*) potassium–graphite (KC_8) in tetrahydrofuran with ethene (1 atm) at r.t., 50%; (*iii*) Na/Hg in tetrahydrofuran with but-2-yne at r.t., 33%

The vanadium and tantalum analogues of compound **5** may be prepared by treatment of [M(NBu^t)(py)$_2$$Cl_3$] (M = V[13] or Ta[12]) with the dilithium salt [Li(C_5H_4)CMe_2(C_5H_4)Li], giving the complexes [M{(η-C_5H_4)CMe_2(η-C_5H_4)}(NBu^t)Cl] (M = V **8** or Ta **9**) respectively. The synthesis of the vanadium complex **8** is hampered by the redox lability of vanadium(v) in the presence of the reduced cyclopentadienyl ligand. Nevertheless, spectroscopic data consistent with the proposed structure have been obtained. The ^{1}H NMR data for compound **8** show significant deshielding of the cyclopentadienyl ring protons compared to those of the analogous niobium and tantalum compounds. The crystal structure of the tantalum compound **9** has been determined and its molecular geometry is close to that of its niobium analogue **5**. The atom numbering scheme used for **9** corresponds to that for compound **5**.



Scheme 2 (*i*) [$K(C_5H_4)CMe_2(C_5H_4)K$] in tetrahydrofuran at r.t., compound **4,** yield 12% or **5**, 77%; (*ii*) $SiMe_3X$ in light petroleum at r.t., X = Br, 63%, or I, 63%; (*iii*) M = Nb, LiMe in diethyl ether at 0 °C, 64%; (*iv*) [$Li(C_5H_4)CMe_2(C_5H_4)Li$] in tetrahydrofuran at r.t., M = V, 62%, or Ta, 45%; (*v*) M = Ta, LiMe in diethyl ether at r.t., 46%

In a transformation analogous to that achieved for the niobium system, treatment of the tantalum complex **9** with methyllithium affords the corresponding tantalum methyl derivative [$Ta\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NBu^t)Me$] **11**.

It was hoped that compounds **5**, **8** and **9** would provide a convenient source of d^1 Group 5 *ansa*-metallocene dihalide compounds analogous to the non-*ansa* [$M(\eta\text{-}C_5H_5)_2Cl_2$]. However, attempts to replace the *tert*-butylimido ligand in **5**, **8** or **9** by treatment with HCl resulted only in the formation of intractable mixtures. The kinetic stability of bis(cyclopentadienyl)niobium dichloride is well established; for example, it can be heated to reflux in concentrated hydrochloric acid almost indefinitely.[14] The reactivity of the *ansa*-metallocenes may be associated with the labilising effect which the strongly bonding *tert*-butylimido group has on the cyclopentadienyl rings, as has been noted in related, apparently 20-electron, compounds.[15] In addition, it may be considered that the presence of the *ansa* bridge leads to some ‘pulling away’ of the cyclopentadienyl rings.

The new compounds and reactions are summarized in Schemes 1 and 2.

Experimental

General

Unless otherwise stated experiments were performed under dry dinitrogen using standard Schlenk-line techniques or in an inert-atmosphere dry-box containing dinitrogen. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from Na/K alloy (light petroleum, diethyl ether and pentane), from sodium (light petroleum, b.p. 100–120 °C, and toluene), from potassium (tetrahydrofuran) or from phosphorus pentaoxide (dichloromethane) under a slow continuous stream of dinitrogen. Light petroleum refers to the b.p. 40–60 °C fraction. Solvents were thoroughly degassed by the pump-fill technique followed by readmission of dinitrogen or by purging with dinitrogen for 15 min prior to use. Deuteriated NMR solvents were dried (C_6D_6 over sodium–benzophenone, [$^2H_2$]dichloromethane over calcium hydride), distilled and degassed by the freeze–pump–thaw technique prior to use. Celite® filtration aid was from Fluka Chemie and oven-dried at 100 °C prior to use.

Instrumentation

The NMR experiments were carried out on a Varian UnityPlus 500 (^1H, ^{13}C and ^{51}V at 499.868, 125.703 and 131.403 MHz respectively) or on a Bruker AM 300 spectrometer (^1H and ^{13}C at 300.13 and 75.5 MHz respectively). The spectra were referenced internally relative to the residual protiosolvent (^1H) and solvent (^{13}C) resonances relative to $SiMe_4$ (^1H, ^{13}C; δ 0) or externally to $VOCl_3$ (^{51}V, δ 0). Electron impact ionisation mass spectra were recorded on an AEI MS 302 spectrometer upgraded with a data-handling system supplied by Mass Spectrometry Services Ltd. Infrared spectra were recorded on a Mattson Polaris FTIR or a Perkin-Elmer 1710 FTIR spectrometer. Samples were prepared as pressed CsI or KBr discs. Elemental analysis data were obtained from the microanalysis department of this laboratory or from Analytische Laboratorien, Gummersbach, Germany.

Starting materials

The compounds [$W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2$],[1] [$Nb(NSiMe_3)(py)_2Cl_3$],[9] [$M(NBu^t)(py)_2Cl_3$] (M = V,[13] Nb or Ta[12]) and ($C_5H_5)CMe_2(C_5H_5$)[16] were prepared by published procedures. The alkali-metal salts [$Li(C_5H_4)CMe_2(C_5H_4)Li$] and [$K(C_5H_4)CMe_2(C_5H_4)K$] were prepared from the protio ligand by treatment with *n*-butyllithium in cold light petroleum or potassium hydride in tetrahydrofuran respectively. Potassium–graphite (KC_8) was prepared by heating graphite with 0.125 equivalents of freshly cut potassium metal under argon at 130 °C. All other reagents were used as supplied.

Preparations

[$W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_3$] 1. Chlorine gas was passed through a solution of [$W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2$] (0.295 g, 0.7 mmol) in dichloromethane (50 cm^3) for 1 min. The solution rapidly turned yellow. The volatiles were removed under reduced pressure and the orange residue was extracted into toluene (25 cm^3) and filtered. On cooling to −25 °C the filtrate afforded compound **1** as a green microcrystalline solid. Yield, 49 mg, 16%.

[$W(\eta\text{-}C_5H_4Me)(NBu^t)(\eta\text{-}C_2H_4)Cl$] 2. A three-necked round-bottomed flask (1 l) was charged with a solution of [$W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2$] (0.95 g, 23 mmol) in tetrahydrofuran (200 cm^3) under an atmosphere of ethene. The flask was cooled to −40 °C and KC_8 (0.30 g, 22 mmol) was added *via* a solid-addition funnel over the course of 15 min. The reaction mixture was allowed to warm to room temperature (upon which the KC_8 was observed to lose its bronze colour) and filtered through Celite. The volatiles were removed under reduced pressure and the resulting solid was extracted with light petroleum (3 × 20 cm^3). The extracts were combined and concentrated to 10 cm^3. Cooling of this solution to −80 °C gave compound **2** as a brown crystalline solid which was washed with cold light petroleum (3 × 2 cm^3) and dried *in vacuo* at −25 °C for 24 h and at room temperature for 24 h. Yield, 0.47 g, 50%.

[$W(\eta\text{-}C_5H_4Me)(NBu^t)(\eta\text{-}MeCCMe)Cl$] 3. An excess of but-2-yne (0.1 cm^3) was added to a solution of [$W(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2$] (0.58 g, 1.4 mmol) in tetrahydrofuran (50 cm^3) and the mixture stirred at 0 °C. Sodium amalgam (33 mg Na in 2 cm^3 Hg, 1 equivalent) was added over 15 min. The reaction mixture was allowed to warm to room temperature, stirred for 3 h and filtered through Celite. The volatiles were removed under reduced pressure to give a dark brown oil, which was extracted with light petroleum (3 × 20 cm^3). The extracts were combined, concentrated to 10 cm^3 under reduced pressure and cooled to −80 °C to afford compound **3** as a brown low-melting solid which was washed with cold light petroleum (3 × 2 cm^3) and dried *in vacuo*. Yield, 0.195 g, 33%.

[$Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NSiMe_3)Cl$] 4. A solution of the ligand salt [K(C_5H_4)CMe$_2$(C_5H_4)K] (0.60 g, 2.4 mmol) in tetrahydrofuran (50 cm^3) was added dropwise to a solution of [Nb(NSiMe$_3$)(py)$_2$Cl$_3$] (1.00 g, 2.3 mmol) in tetrahydrofuran (100 cm^3) at room temperature over the course of 30 min. The reaction mixture was stirred for 1 h and the volatiles then removed under reduced pressure giving a green-black oily solid. This was extracted with pentane (2 × 30 cm^3) and filtered to give an orange solution and an unidentified black microcrystalline residue. Removal of the solvent from the filtrate under reduced pressure gave compound **4** as a spectroscopically pure pale green powder. Yield 100 mg, 12%. An analytically pure sample was obtained as yellow needles by recrystallization from pentane at −80 °C. Crystals suitable for structure determination were grown by slow evaporation of a solution in light petroleum (b.p. 100–120 °C).

[Nb{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Cl] 5. In a typical preparation a solution of [Nb(NBu^t)(py)$_2$Cl$_3$] (1.0 g, 2.3 mmol) in tetrahydrofuran (30 cm^3) was treated dropwise with a solution of [K(C_5H_4)CMe$_2$(C_5H_4)K] (0.58 g, 2.3 mmol) in tetrahydrofuran (30 cm^3) over 1 h at room temperature. The mixture was stirred for 24 h. The resulting red solution was filtered and the solvent removed under reduced pressure affording compound **5** as a brown solid in sufficient purity for subsequent studies. Yield, 0.66 g, 77%. An analytically pure sample was obtained as yellow needles by cooling a pentane solution to −80 °C. Crystals of sufficient quality for X-ray crystallographic studies were obtained by slow cooling of a solution in diethyl ether to −80 °C.

[Nb{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Br] 6 and [Nb{(η-C_5H_4)-CMe$_2$(η-C_5H_4)}(NBu^t)I] 7. To a solution of compound **5** (100 mg, 0.3 mmol) in light petroleum (30 cm^3) was added SiMe$_3$Br (0.5 cm^3, 0.6 g, 3.9 mmol) with stirring and a small amount of gelatinous orange precipitate formed. After 1 h the volatiles were removed under reduced pressure and the orange solid residue was extracted with light petroleum (2 × 30 cm^3) and filtered. The solvent was removed from the yellow filtrate under reduced pressure to give compound **6** as a yellow solid, which was recrystallized from pentane to give yellow needles. Yield, 70 mg, 63%. Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a solution in light petroleum (b.p. 100–120 °C).

In an analogous procedure a solution of compound **5** (100 mg, 0.3 mmol) was treated with SiMe$_3$I (0.5 cm^3, 0.7 g, 3.5 mmol) yielding **7** as an orange microcrystalline solid. Yield, 80 mg, 63%. Crystals suitable for X-ray diffraction studies were obtained by slow cooling of a solution in diethyl ether to −80 °C.

[V{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Cl] 8. A solution of [V(NBu^t)(py)$_2$Cl$_3$] (1.85 g, 4.8 mmol) in tetrahydrofuran (100 cm^3) was added to a solution of [Li(C_5H_4)CMe$_2$(C_5H_4)Li] (0.88 g, 4.8 mmol) in tetrahydrofuran (50 cm^3) at room temperature over 30 min with stirring. The colour changed from green to green with red dichroism. After 16 h the solvent was removed under reduced pressure and the residue extracted with dichloromethane (80 cm^3). After filtration and removal of the solvent under reduced pressure the resulting brown solid was washed with pentane (3 × 50 cm^3) and dried *in vacuo.* Yield, 0.94 g, 62%.

[Ta{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Cl] 9. A suspension of [Li(C_5H_4)CMe$_2$(C_5H_4)Li] (2.91 g, 15.8 mmol) in tetrahydrofuran (75 cm^3) was added *via* a wide-bore transfer tube to a stirred solution of [Ta(NBu^t)(py)$_2$Cl$_3$] (8.03 g, 15.6 mmol) in tetrahydrofuran (75 cm^3) at −78 °C. The solution changed from orange to red-purple over 10 min. It was allowed to warm to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure and the oily residue was dried *in vacuo* for 1 h, then extracted with dichloromethane (150 cm^3) and filtered to remove LiCl. The solvent was removed under reduced pressure and the oily brown residue washed with pentane (4 × 50 cm^3) and dried *in vacuo* to give compound **9** as a brown powder. Yield, 3.77 g, 45%. Crystals suitable for X-ray diffraction studies were obtained by cooling a solution in dichloromethane–light petroleum (b.p. 100–120 °C) to −80 °C.

[Nb{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Me] 10. A solution of compound **5** (0.98 g, 2.7 mmol) in diethyl ether (30 cm^3) was cooled to 0 °C and treated with LiMe (2 cm^3 of a 1.4 M solution in diethyl ether, 2.8 mmol) upon which an orange colour developed. The reaction mixture was stirred for 12 h and a white precipitate formed. The volatiles were removed under reduced pressure and the residue extracted with pentane (30 cm^3) and filtered through Celite. The residue was washed with further portions of pentane until the washings were colourless (3 × 30 cm^3). The extracts were combined and the solvent was removed under reduced pressure yielding compound **10** as a yellow microcrystalline solid which was purified by recrystallization from pentane. Yield, 0.60 g, 64%.

[Ta{(η-C_5H_4)CMe$_2$(η-C_5H_4)}(NBu^t)Me] 11. A solution of compound **9** (0.46 g, 1 mmol) in diethyl ether (100 cm^3) was treated with LiMe (0.75 cm^3 of a 1.4 M solution in diethyl ether, 1 mmol) at room temperature. No colour change was observed. After 2 h the volatiles were removed under reduced pressure and the residue was washed with pentane (2 × 50 cm^3). Compound **11** was sublimed at 80 °C (10^{-1} mmHg) onto a cold-finger at −78 °C as a white solid. Yield, 200 mg, 46%.

Crystallography

Crystal data, data collection and processing parameters are given in Table 3.

Data collection. For compounds **4**, **6** and **7** a crystal was mounted on a glass fibre using a drop of highly viscous perfluoropolyether to exclude air and prevent solvent loss. It was then plunged into a cold nitrogen stream (150 K) using an Oxford Cryosystems CRYOSTREAM cooling system. The data were collected on an Enraf-Nonius DIP2000 image-plate diffractometer and the images were processed using the DENZO and SCALEPACK programs.[17] For **5** and **9** a crystal was mounted in similar fashion and transferred to the goniometer head of a FAST area-detector diffractometer driven by the software package MADNES.[18] The data were collected by Dr. Simon Coles of the EPSRC X-Ray Crystallography Service at the University of Wales, Cardiff.

Data for all structures were corrected for Lorentz-polarization effects. A partial absorption correction is implied by multiframe scaling of the image-plate data using equivalent reflections.

Structure solution and refinement. The structures were solved by direct methods, SIR 92,[19] giving non-hydrogen atom positions. The structures were refined using full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. For compound **4** the hydrogen atoms were located in Fourier difference maps and refined isotropically. For **5** the hydrogen atoms were located in Fourier difference maps but not refined. For **6**, **7** and **9** the hydrogen atoms were placed in calculated positions during the final cycles of refinement. Three-parameter Chebychev weighting schemes[20] were applied to all structures. All crystallographic calculations were performed using the CRYSTALS package.[21] Neutral atom scattering factors were taken from ref. 22.

CCDC reference number 186/636.

Table 3 Crystal data, data collection and processing parameters for complexes **4**–**7** and **9***

	4	**5**	**6**	**7**	**9**
Molecular formula	$C_{16}H_{23}ClNNbSi$	$C_{17}H_{23}ClNNb$	$C_{17}H_{23}BrNNb$	$C_{17}H_{23}INNb$	$C_{17}H_{23}ClNTa$
M	385.81	369.73	414.19	461.19	457.78
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$	$P2_1/m$	$Pcab$	$P2_1/m$
a/Å	6.904(1)	6.862(1)	7.117(1)	13.062(1)	6.8831(7)
b/Å	25.236(1)	10.402(1)	10.239(1)	15.744(1)	10.403(1)
c/Å	9.820(1)	11.744(1)	11.746(1)	16.813(1)	11.773(3)
β/°	91.512(2)	98.73(1)	98.267(3)		98.774(9)
U/Å^3	1710.34	828.56	847.05	3457.56	833.17
Z	4	2	2	8	2
D_c/g cm^{-3}	1.50	1.48	1.62	1.77	1.82
F(000)	783.93	375.83	410.85	1784.44	441.69
h, k, l ranges	−7 to 8, 0–31, 0–12	−7 to 7, 0–11, 0–12	−8 to 8, 0–12, 0–14	0–26, 0–19, 0–45	−7 to 7, 0–12, 0–13
T/K	150	150	150	150	120
μ/mm^{-1}	0.89	0.85	3.01	2.43	6.67
Crystal size/mm	0.3 × 0.3 × 0.5	0.07 × 0.11 × 0.28	0.15 × 0.25 × 0.25	0.4 × 0.4 × 0.4	0.24 × 0.18 × 0.18
θ_{max}/°	26.5	26	26	26	25
No. reflections:					
total	9686	3648	3623	8066	3557
unique	3299	1349	1751	3479	1374
in refinement	3094	1104	1583	2889	1229
Observed criterion	$I > 5\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 5\sigma(I)$	$I > 3\sigma(I)$
R_{merge}	0.016	0.073	0.028	0.029	0.113
Number of variables	285	104	153	182	109
$\Delta\rho_{min,max}$/e Å^{-3}	−0.77, 0.81	−0.41, 0.55	−0.87, 0.46	−0.83, 1.01	−1.87, 1.36
R	0.020	0.028	0.027	0.025	0.043
R'	0.022	0.030	0.032	0.036	0.060

* Details in common: Mo-Kα radiation (0.710 69 Å); ω scans; $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

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