Ansa-bis(cyclopentadienyl) complexes of niobium(III) and niobium(IV); X-ray structures of [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(η^2-BH$_4$)] and [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(H)PMe$_3$]

Nigel J. Bailey [a], Malcolm L.H. Green [a,*], Michael A. Leech [b], John F. Saunders [b], Helen M. Tidswell [a]

[a] Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK
[b] Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, UK

Abstract

The new compounds [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)Cl$_2$], [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(η^2-BH$_4$)]*, [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(H)PR$_3$] (R = Me*, Ph) and [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(SPh)$_2$] have been prepared. An asterisk indicates that the X-ray crystal structure has been determined.

Keywords: Ansa; Cyclopentadienyl; Niobium; Group 5

1. Introduction

Interest in the development of new homogeneous catalyst systems for olefin polymerization has led to the recognition of stereo-rigid ansa-bridged complexes as an important class of compounds for study. For example, in 1985 Kaminsky et al. [1] reported that rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride with methylaluminoxane is a highly active catalyst for propene polymerization, producing polymer with a high degree of isotacticity, a high molecular weight and a narrow molecular weight distribution. ansa-Bridged metallocenes of the Group 4 metals have been studied intensively, and synthesised with a range of bridging groups [2]. Recently we have described ansa-bridged complexes of Group 6 metals and found them to exhibit markedly different reactivities to their unbridged analogues [3]. We are interested in finding further examples of the 'ansa-effect' on reactivity and in extending the investigation to the Group 5 metals.

Although it has long been known that vanadocene complexes are capable of polymerizing olefins [4,5], there have been few studies of ansa-bridged complexes of Group 5. An ansa-vanadocene complex has been

reported [6] and ansa-compounds of niobium with a backbone of two or three bridging atoms are known [7]. Also, an ansa-bridged η^5:η^1-biscyclopentadienyl niobium complex containing a CMe$_2$ bridging group was described [8]. A bridged monocyclopentadienyl-amidoniobium system has been reported [9]. Recently the first ansa-bridged η^5:η^5-biscyclopentadienyl complexes of niobium were reported [10]. Here we describe new ansa-η:η-biscyclopentadienyl niobium derivatives.
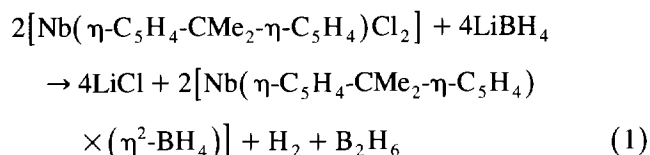
2. Results and discussion

The reaction between [K(C$_5$H$_4$)CMe$_2$(C$_5$H$_4$)K] and NbCl$_4$ · 2THF in equimolar ratio in THF at room temperature produced a purple–brown solution from which, after removal of the solvent and Soxhlet extraction into dichloromethane, purple crystals of [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)Cl$_2$] (1) were isolated. The compound 1 slowly decomposes in air and is only slightly soluble in dichloromethane and tetrahydrofuran and is insoluble in toluene. Analytical and spectroscopic data are listed in Table 1 for this and the other new complexes described in this work. This synthetic route for 1 is analogous to that used for ansa-tungstenocene and -molybdenocene dichlorides [3]. As is observed for the molybdenum and

* Corresponding author.

tungsten compounds, the reaction appears to be heterogenous and, in addition to the desired product, gives an amount of insoluble material which is presumed to be oligomeric in nature. The yield obtained for compound **1** is ca. 57% which is comparable to that reported for the analogous silicon-bridged complex [Nb(η-C_5H_4-SiMe$_2$-η-C_5H_4)Cl$_2$] [10]. Attempts to prepare compound **1** from the dilithium reagent of 2,2-*bis*-cyclopentadienylpropane resulted in lower yields and poor reproducibility. Compound **1** was found to sublime at 180 °C under a reduced pressure of 10^{-3} mmHg, but involatile decomposition products were also formed and thus sublimation is not an efficient method for purification of the material. The EPR spectrum of compound **1** shows 10 lines, as expected for an unpaired electron coupled to the ^{93}Nb ($I = 9/2$) nucleus, with a value of $g_{iso} = 1.992$ and a hyperfine splitting $|a|_{iso} = 90.5$ G, analogous to data reported for unbridged niobocene dichloride [11]. The electron impact ionization mass spectrum shows a peak assignable to the parent ion. The IR spectrum of compound **1** was assigned by comparison with the spectrum of [Ti(η-C_5H_5)$_2$Cl$_2$]. A strong band at 3106 cm^{-1} is assigned to the C–H stretches of the η-cyclopentadienyl rings; bands occurring between 2978 and 2731 cm^{-1}, which do not correspond to bands in the spectrum of [Ti(η-C_5H_5)$_2$Cl$_2$], are assigned to the backbone methyl C–H stretches. The Nb–Cl

stretches, expected below 400 cm^{-1}, are assigned by analogy to the spectrum of [NbMe$_3$Cl$_2$] [12]. In [NbMe$_3$Cl$_2$] the antisymmetric Nb–Cl stretching band occurs at 377 cm^{-1} in the IR spectrum and the symmetric stretching band at 328 cm^{-1} in the Raman spectrum. Therefore, bands at 352 and 338 cm^{-1} in the spectrum of compound **1** are tentatively assigned as the antisymmetric and symmetric Nb–Cl stretching modes respectively.

Treatment of the compound **1** with lithium borohydride in 1,2-dimethoxyethane at room temperature, according to Eq. (1) [13] gave green, air sensitive crystals of the borohydride compound [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)BH$_4$] (**2**).

$$2[Nb(\eta\text{-}C_5H_4\text{-}CMe_2\text{-}\eta\text{-}C_5H_4)Cl_2] + 4LiBH_4$$

$$\rightarrow 4LiCl + 2[Nb(\eta\text{-}C_5H_4\text{-}CMe_2\text{-}\eta\text{-}C_5H_4)$$

$$\times(\eta^2\text{-}BH_4)] + H_2 + B_2H_6 \qquad (1)$$

The IR spectrum of compound **2** contains two bands in the terminal B–H region, at 2461 and 2419 cm^{-1}, consistent with an η^2 bidentate binding mode for the borohydride ligand [14,15]. The ^{1}H NMR (C_6D_6) spectrum of compound **2** shows two multiplet resonances for the eight C_5H_4 hydrogens, as inferred by the existence of two planes of symmetry in the molecule, a singlet

Table 1
Analytical and spectroscopic data

Complex [a]	Spectroscopic data [b]
1 [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)Cl$_2$]	EPR: 10 lines, $g_{iso} = 1.992$, $|a|_{iso} = 90.5$ G
C, 46.6 (46.7); H, 4.2 (4.2); Cl, 22.0 (21.2)	Mass: [d] m/z 336 [26, M$^+$], 305 [5, M$^+$ − 2CH$_3$], 272 [8, M$^+$ − C$_2$H$_2$ − Cl], 269 [5, M$^+$ − 2CH$_3$ − Cl], 209 [21, M$^+$ − 2C$_2$H$_2$ − 2Cl], 194 [11, M$^+$ − 2C$_2$H$_2$ − 2Cl − CH$_3$], 144 [7, (CH$_3$)$_2$C(C$_5$H$_4$)(C$_3$H$_2$)$^+$, 129 [24, (CH$_3$)C(C$_5$H$_4$)(C$_3$H$_2$)$^+$], 114 [7, C(C$_5$H$_4$)(C$_3$H$_2$)$^+$]
2 [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)(η^2-BH$_4$)]	^{1}H: 5.67 [4H, t, J 2.5 Hz, C$_5$H$_4$], 4.56 [4H, t, J 2.5 Hz, C$_5$H$_4$], 0.01 [6H, s, CH$_3$], −3.24 [4H, br d, J 85 Hz, BH$_4$]
C, 55.1 (56.2); H, 6.6 (6.5)	^{13}C: 106.3 [s, C$_5$H$_4$], 81.8 [s, C$_5$H$_4$, C$_{ipso}$], 79.6 [s, C$_5$H$_4$], 32.2 [s, CMe$_2$], 20.9 [s, CMe_2]
	^{11}B: 23.1 [quintet, J 90 Hz]
	Mass: [e] the characteristic isotope pattern was observed, data given for ^{11}B, m/z 280 [100, M$^+$ + 2]
3 [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)(H)PMe$_3$]	^{1}H: [c] 5.24 [2H, m, C$_5$H$_4$], 4.49 [4H, m, C$_5$H$_4$], 4.37 [2H, m, C$_5$H$_4$], 0.82 [9H, d, J 7 Hz, PMe$_3$], 0.71 [3H, s, CH$_3$], 0.64 [3H, s, CH$_3$], −5.03 [1H, d, J 39 Hz, NbH]
C, 56.7 (56.4); H, 7.1 (7.1)	^{13}C: 97.1 [s, C$_5$H$_4$], 92.2 [s, C$_5$H$_4$], 71.8 [s, C$_5$H$_4$], 69.6 [s, C$_5$H$_4$], 61.6 [s, C$_5$H$_4$, C$_{ipso}$], 33.2 [s, CMe$_2$], 23.1 [d, J 20 Hz, PMe$_3$], 22.8 [s, CH$_3$], 22.4 [s, CH$_3$]
	^{31}P: 3.9 [s, PMe$_3$]
4 [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)(H)PPh$_3$]	^{1}H: 7.72–7.68 [6H, m, PPh$_3$], 7.01–6.93 [9H, m, PPh$_3$], 5.37 [2H, m, C$_5$H$_4$], 4.62 [2H, m, C$_5$H$_4$], 4.17 [2H, m, C$_5$H$_4$], 4.14 [2H, m, C$_5$H$_4$], 0.68 [6H, s, CH$_3$], −4.11 [1H, d, J 34 Hz, NbH]
C, 70.0 (70.7); H 5.7 (5.7)	^{13}C: 139.4 [d, J 29 Hz, PPh$_3$], 133.6 [d, J 11 Hz, PPh$_3$], 128.6 [m, PPh$_3$], 100.9 [s, C$_5$H$_4$], 94.3 [s, C$_5$H$_4$], 74.2 [s, C$_5$H$_4$], 73.0 [s, C$_5$H$_4$], 63.9 [s, C$_5$H$_4$, C$_{ipso}$], 33.1 [s, CMe$_2$], 22.7 [s, CH$_3$], 22.1 [s, CH$_3$]
	^{31}P: 66.8 [s, PPh$_3$]
5 [Nb(η-C_5H_4-CMe$_2$-η-C_5H_4)(SPh)$_2$]	EPR: 10 lines, $g_{iso} = 1.978$, $|a|_{iso} = 115$ G
C, 62.0 (62.4); H, 5.0 (5.0): S, 13.4 (13.3)	Mass: [d] m/z 218 [100, (SPh)$_2^+$], 186 [5, SPh$_2^+$], 154 [15, Ph$_2^+$], 109 [68, SPh$^+$], 77 [16, Ph$^+$]

[a] Analytical data given as Found (Calc.) in %.

[b] NMR data (C_6D_6, 198 K) given as chemical shift (δ) [relative intensity, multiplicity (J in Hz), assignment]. EPR data (CH$_2$Cl$_2$) recorded at 298 K. Mass spectra data given as m/z [intensity (%), assignment].

[c] Assignment was confirmed by a ^{1}H/^{13}C correlation experiment.

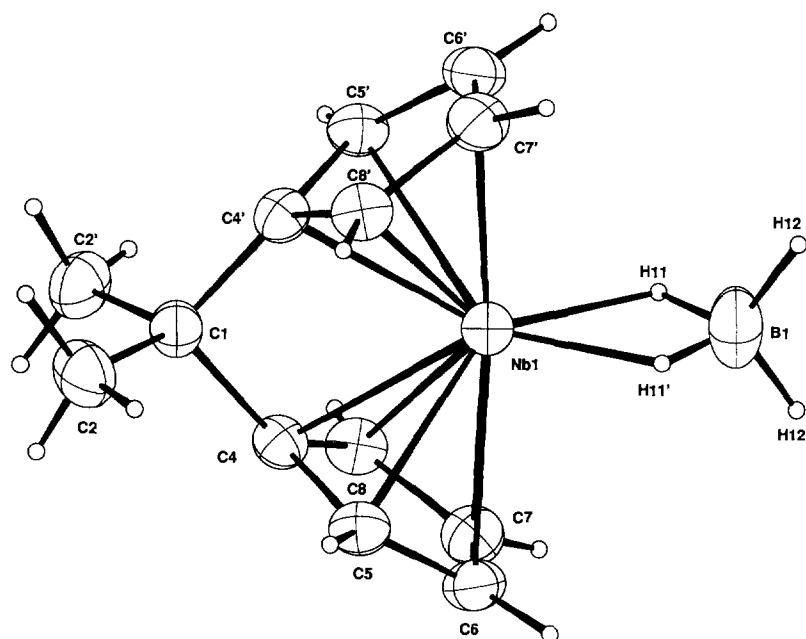[d] Electron impact.

[e] Fast atom bombardment (NOBA matrix).

Fig. 1. Molecular structure of [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)(η^2-BH$_4$)] (2) showing atom labelling scheme. Atoms labelled with a prime are generated from their counterparts by the symmetry operation $\bar{x}, y, \bar{z} + 1/2$. Hydrogen atom labels on the ansa-ligand are omitted for clarity.

assignable to the two bridging methyl groups and a very broad resonance (FWHH = 300 Hz) centred at δ −3.2 ppm (J = 85 Hz) corresponding to the BH$_4$ group and suggesting that it is fluxional on the NMR timescale. As is observed for the analogous unbridged compound [14], the fluxionality is too rapid to be slowed on the NMR timescale; no further fine structure could be observed for this resonance on cooling a toluene-d$_8$ solution to −90 °C. The proton-decoupled ^{13}C NMR (C$_6$D$_6$) spectrum of compound 2 contains three singlets in the Cp region, a singlet at δ 32.2 ppm assignable to the bridging quaternary carbon and a singlet at δ 20.9 ppm assignable to the bridging methyl groups. A binomial quintet centred at δ 23.1 ppm (J = 90 Hz) is observed in the coupled ^{11}B NMR spectrum as expected for the BH$_4$ group, which we have already noted to be fluxional. The fast atom bombardment mass spectrum (NOBA matrix) of compound 2 contains a peak at m/z = 280 (base peak) with an envelope in agreement with the correct isotope pattern calculated for M + 2.

The X-ray crystal structure of compound 2 was determined and confirms the assignment of η^2 binding to the borohydride ligand. The molecular structure is shown, with atomic numbering scheme, in Fig. 1. Selected bond distances, angles and other data are given in Tables 2–5. The X-ray crystal structure of the unbridged analogue, [Nb(η-C$_5$H$_5$)$_2$(η^2-BH$_4$)], has been published [16], although the quality of the structure determination was low (R = 12.8%) and thus a meaningful structural comparison with compound 2 cannot be made. However, we note that the angle subtended by the two ring centroid to niobium vectors in ansa-bridged compound 2 is 125° compared to 130° given for unbridged [Nb(η-C$_5$H$_5$)$_2$(η^2-BH$_4$)].

Table 2
Selected bond distances (Å) for compound 2

Nb(1)–C(4)	2.262(4)	C(1)–C(4)	1.514(6)
Nb(1)–C(5)	2.308(5)	C(4)–C(5)	1.440(6)
Nb(1)–C(6)	2.419(5)	C(5)–C(6)	1.402(8)
Nb(1)–C(7)	2.418(5)	C(6)–C(7)	1.387(8)
Nb(1)–C(8)	2.302(5)	C(7)–C(8)	1.401(8)
Nb(1)–B(1)	2.36(1)	C(8)–C(4)	1.431(6)
Nb(1)–H(11)	1.94(7)	B(1)–H(11)	1.25(7)
C(1)–C(2)	1.518(7)	B(1)–H(12)	1.07(6)

Table 3
Comparison of selected structural data for complexes 2 and 3

Compound	2	3
Nb–Cp1(cent)	2.01	2.01
Nb–Cp2(cent)	—	2.01
Nb–Cp1 range	2.262–2.419	2.273–2.437
Nb–Cp1 average	2.342	2.347
Nb–Cp2 range	—	2.272–2.434
Nb–Cp2 average	—	2.351
Cp(cent)–Nb–Cp(cent)	125.0	126.1
Bending angle θ	114.1	117.3
Cp–Cbr–Cp	96.9(5)	98.5(6)

Distances in Å. Angles in degrees. Cp1 = ring C(4–8) in complexes 2 and 3. Cp2 = ring C(9–13) in complex 3. The bending angle is defined as the angle between the lines from the metal centre normal to the planes of the η-cyclopentadienyl rings. Cp–Cbr–Cp = C(4)–C(1)–C(4′) for complex 2, C(4)–C(1)–C(9) for complex 3.

Table 4

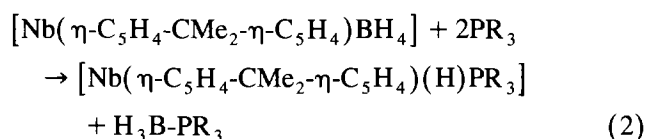Crystal data, data collection and processing parameters for complexes 2 and 3

Compound	2	3
Molecular formula	$C_{13}H_{18}BNb$	$C_{16}H_{24}NbP$
Formula weight (AMU)	278.00	340.25
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pbca$
a (Å)	10.565(6)	12.205(2)
b (Å)	12.648(7)	15.330(3)
c (Å)	9.802(6)	17.175(2)
β (°)	107.03(4)	
Unit-cell volume (Å³)	1252.3	3213.5
Formula units per cell, Z	4	8
ρ_{calc} (g cm⁻³)	1.48	1.42
μ (mm⁻¹)	0.89	0.80
Crystal size (mm³)	0.1×0.15×0.3	0.2×0.2×0.3
θ_{max} (°)	24	26
Radiation	Mo-Kα	Mo-Kα
	$\lambda = 0.71069$ Å	$\lambda = 0.71069$ Å
Scan type	$2\theta/\Omega$	Ω (image plate)
No. of reflections:		
total	2755	18079
unique	985	3958
in refinement [$I > 3\sigma(I)$]	800	1538
R_{merge}	0.043	0.083
No. of variables	97	163
Residual electron density: min, max (e Å⁻³)	−0.61, 1.11	−0.56, 0.45
R	0.034	0.056
R_w	0.039	0.032
Temperature (K)	293	298

Table 5

Selected fractional atomic coordinates for compound 2

Atom	x	y	z
Nb(1)	0.0000	0.22147(5)	0.2500
C(1)	0.0000	0.4556(5)	0.2500
C(2)	0.1200(6)	0.5258(5)	0.3103(7)
C(4)	−0.0206(4)	0.3763(3)	0.3571(5)
C(5)	0.0842(5)	0.3185(4)	0.4561(5)
C(6)	0.0268(5)	0.2312(4)	0.5034(5)
C(7)	−0.1082(5)	0.2306(4)	0.4356(5)
C(8)	−0.1396(5)	0.3179(4)	0.3437(5)
B(1)	0.0000	0.0347(8)	0.2500
H(11)	−0.100(7)	0.091(6)	0.201(7)
H(12)	0.031(6)	−0.012(5)	0.174(6)

The reactions between compound 2 and two equivalents of a tertiary phosphine PR_3 (R = Me, Ph) gave the phosphine-hydride complexes [Nb(η-C_5H_4-CMe_2-η-

C_5H_4)(H)PR_3] (R = Me (3), R = Ph (4)) according to Eq. (2) [13].

$$[Nb(\text{η-}C_5H_4\text{-}CMe_2\text{-η-}C_5H_4)BH_4] + 2PR_3$$
$$\rightarrow [Nb(\text{η-}C_5H_4\text{-}CMe_2\text{-η-}C_5H_4)(H)PR_3]$$
$$+ H_3B\text{-}PR_3 \qquad (2)$$

These complexes were isolated as red crystals in ca. 40% yield. The ^{1}H NMR (C_6D_6) data for compounds 3 and 4 are consistent with their formulation as phosphine hydrides. Well resolved doublets are observed for the Nb–H resonances at δ −5.03 and −4.11 ppm respectively. The ^{31}P NMR (C_7D_8) spectra each show a broad singlet at room temperature which sharpens considerably on cooling, as expected for the phosphorus nucleus bound to the quadrupolar niobium nucleus. The IR spectra of 3 and 4 are complex and it is not possible to assign unambiguously the Nb–H stretching frequencies. Despite repeated attempts by both the electron impact
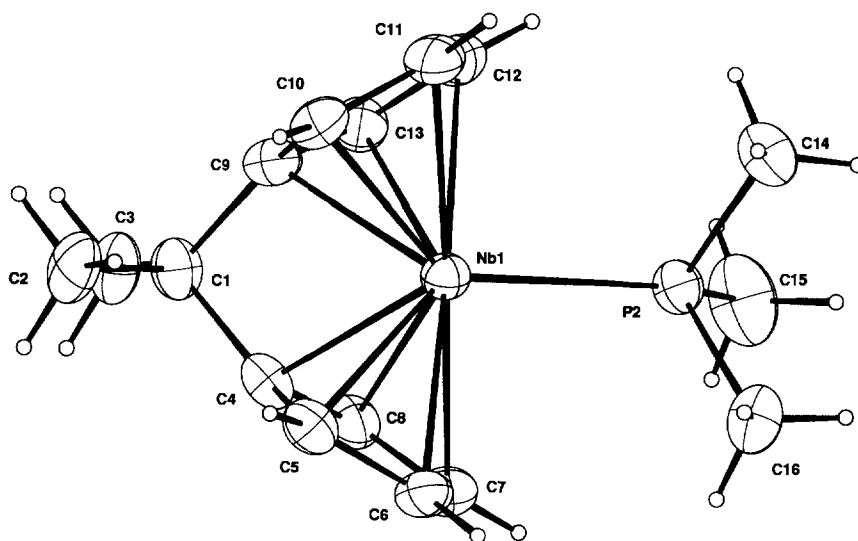

Fig. 2. Molecular structure of [Nb(η-C_5H_4-CMe_2-η-C_5H_4)(H)PMe_3] (3) showing atom labelling scheme. Hydrogen atom labels are omitted for clarity.

Table 6
Selected bond distances (Å) for compound 3

Nb(1)–C(4)	2.273(7)	C(1)–C(2)	1.54(1)
Nb(1)–C(5)	2.294(6)	C(1)–C(3)	1.53(1)
Nb(1)–C(6)	2.382(7)	C(1)–C(4)	1.54(1)
Nb(1)–C(7)	2.437(8)	C(1)–C(9)	1.54(1)
Nb(1)–C(8)	2.347(6)	C(4)–C(5)	1.44(1)
Nb(1)–C(9)	2.272(9)	C(5)–C(6)	1.43(1)
Nb(1)–C(10)	2.295(8)	C(6)–C(7)	1.40(1)
Nb(1)–C(11)	2.388(8)	C(7)–C(8)	1.39(1)
Nb(1)–C(12)	2.434(7)	C(8)–C(4)	1.41(1)
Nb(1)–C(13)	2.366(9)	C(9)–C(10)	1.45(1)
Nb(1)–P(2)	2.553(2)	C(10)–C(11)	1.43(1)
P(2)–C(14)	1.828(8)	C(11)–C(12)	1.38(1)
P(2)–C(15)	1.82(1)	C(12)–C(13)	1.43(1)
P(2)–C(16)	1.82(1)	C(13)–C(9)	1.44(1)

Table 7
Selected fractional atomic coordinates for compound 3

| Atom	x	y	z
Nb(1)	0.35475(5)	−0.13626(3)	−0.22842(4)
P(2)	0.3336(2)	−0.2297(1)	−0.1063(1)
C(1)	0.2821(7)	−0.0397(5)	−0.3681(6)
C(2)	0.3617(8)	0.0132(5)	−0.4193(5)
C(3)	0.1661(7)	−0.0318(5)	−0.4008(5)
C(4)	0.2861(6)	−0.0121(4)	−0.2819(6)
C(5)	0.3866(7)	0.0104(4)	−0.2424(6)
C(6)	0.3661(8)	−0.0008(4)	−0.1610(5)
C(7)	0.2573(9)	−0.0277(5)	−0.1513(6)
C(8)	0.2096(6)	−0.0360(4)	−0.2244(6)
C(9)	0.3207(6)	−0.1350(4)	−0.3585(5)
C(10)	0.4340(7)	−0.1607(5)	−0.3476(5)
C(11)	0.4308(8)	−0.2452(5)	−0.3119(6)
C(12)	0.3231(8)	−0.2704(5)	−0.3009(5)
C(13)	0.2514(8)	−0.2034(4)	−0.3284(6)
C(14)	0.4120(8)	−0.3312(5)	−0.1083(7)
C(15)	0.2016(9)	−0.2680(6)	−0.0699(8)
C(16)	0.3870(9)	−0.1774(5)	−0.0188(6)

and fast atom bombardment techniques, meaningful mass spectra could not be obtained. The X-ray crystal structure of compound 3 was determined and is shown, with atomic numbering scheme, in Fig. 2. Selected bond distances, angles and other data are given in Tables 3, 4, 6 and 7. The dominance of the niobium atom in the electron density map precluded direct location of the hydride but its presence may be inferred from the non-linear phosphorus–niobium-bridging carbon angle, C(1)–Nb(1)–P(2) = 156°.

When compound 1 was treated with two equivalents of NaSPh in THF at reflux for 16 h the corresponding dithiolate, [Nb(η-C_5H_4-CMe_2-η-C_5H_4)(SPh)$_2$] (5), was

eventually obtained as purple–black crystals which slowly decomposed if exposed to air. The EPR spectrum of compound 5 shows 10 lines, a value of g_{iso} = 1.978 comparable to the unbridged analogue [17] and a hyperfine splitting $|a|_{iso}$ = 115 G. Electron impact ionisation mass spectrometry showed only peaks due to decomposition products, the base peak being m/z = 218, corresponding to [(SPh)$_2$]$^+$, the formation of which
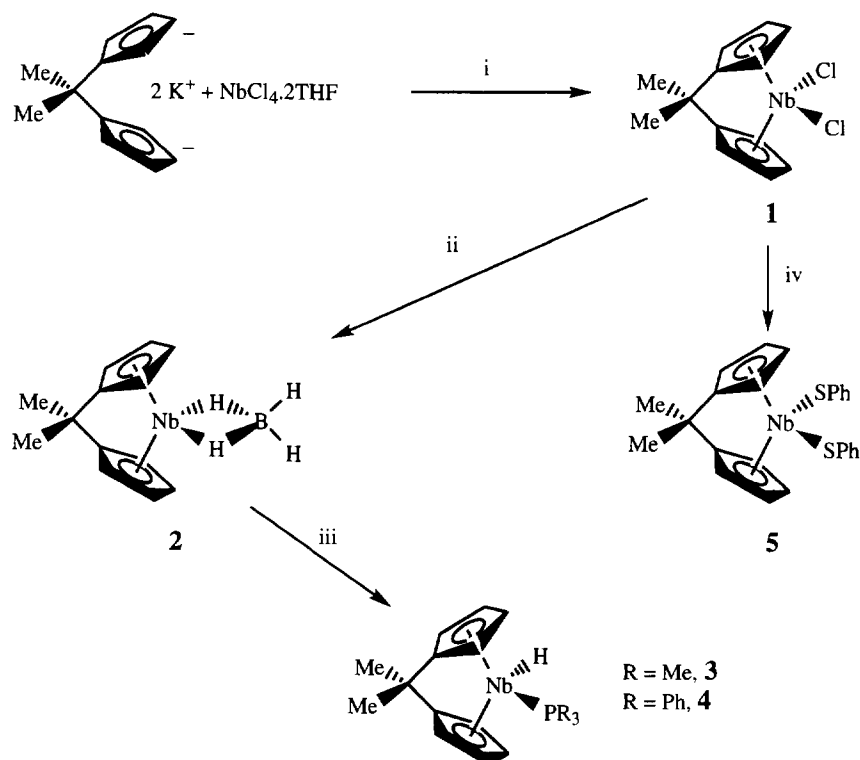
Scheme 1. Reagents and conditions: (i) in tetrahydrofuran at RT; (ii) LiBH$_4$ in 1,2-dimethoxyethane at RT; (iii) PR$_3$ in benzene at RT; (iv) NaSPh in tetrahydrofuran at reflux.

requires neighbouring SPh groups. The IR spectrum shows bands assignable to the Nb–S stretches at 484 cm^{-1} (antisymmetric) and 385 cm^{-1} (symmetric).

Treatment of compound 1 with two equivalents of methyl magnesium bromide gave an orange crystalline solid which shows a peak in the mass spectrum assignable to the cation [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)Me$_2$]$^+$ and the EPR spectrum shows 10 lines (g_{iso} = 2.0205, $|a|_{iso}$ = 73 G). However, the compound was extremely air sensitive and satisfactory elemental analysis data could not be obtained. Other methylating reagents (MeLi and Me$_2$Zn) gave intractable mixtures of products.

Treatment of compound 1 with LiEt$_3$BH, LiAlH$_4$ or NaAlH$_2$(OCH$_2$CH$_2$OMe)$_2$ gave mixtures of products from which no pure compound could be isolated. In the case of reaction with NaAlH$_2$(OCH$_2$CH$_2$OMe)$_2$ the ^{1}H NMR spectrum of the crude reaction mixture contained a broad (FWHH = 30 Hz) weak resonance centred at δ − 12.95 ppm, suggesting that a niobium hydride species had been formed. A method successful for the conversion of [Nb(η-C$_5$Me$_5$)$_2$(η^2-BH$_4$)] to the corresponding trihydride was investigated as an alternative route to [Nb(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)H$_3$]. A solution of compound 2 in toluene was treated with pyridine under an atmosphere of hydrogen [18] but this gave only an intractable brown oil. Thus it appears that the *ansa*-niobium metallocene system of 1 is less conducive to ligand substitution reactions than the non-*ansa* analogues.

The new chemistry outlined above is summarised in Scheme 1.

3. Experimental

All experiments were performed under dry dinitrogen using standard Schlenk line techniques or an inert atmosphere dry box containing dinitrogen. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from Na/K alloy (petroleum ether b.p. 40–60 °C, diethyl ether and pentane), from sodium (1,2-dimethoxyethane, petroleum ether b.p. 100–120 °C and toluene), from potassium (tetrahydrofuran and benzene) or from phosphorus pentoxide (dichloromethane) under a slow continuous stream of dinitrogen. Solvents were thoroughly degassed by the pump fill technique followed by re-admission of dinitrogen or by purging with dinitrogen for 15 min prior to use. Deuterated NMR solvents were dried (benzene and toluene over sodium benzophenone ketyl, dichloromethane over calcium hydride), distilled and degassed by the freeze–pump–thaw technique prior to use.

NMR experiments were carried out on a Varian UnityPlus 500 spectrometer (^{1}H, ^{13}C, ^{11}B, ^{31}P NMR spectra were recorded at 499.868, 125.703, 160.380 and 202.345 MHz respectively). The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances relative to TMS (^{1}H, ^{13}C; δ = 0 ppm) or externally to BF$_3$ · Et$_2$O (^{11}B; δ = 0 ppm) or 85% H$_3$PO$_4$ (^{31}P; δ = 0 ppm). Chemical shifts (δ) are expressed in ppm, coupling constants (J) in Hz. EPR spectra were recorded on a Varian E 109 instrument and referenced to DPPH.

Electron impact ionization mass spectra were recorded on an AEI MS 302 mass spectrometer upgraded with a data handling system supplied by Mass Spectrometry Services Ltd. Fast atom bombardment mass spectra were recorded by the EPSRC Mass Spectrometry Service at the University College of Swansea under the supervision of Dr. J.A. Ballantine. IR spectra were recorded on a Mattson Polaris FTIR spectrometer or a Perkin–Elmer 1710 FTIR spectrometer. Samples were prepared as pressed KBr discs. Data are quoted in cm^{-1}. Elemental analysis data was obtained from the microanalysis department of the Inorganic Chemistry Laboratory.

NbCl$_4$ · 2THF [19], (C$_5$H$_5$)CMe$_2$(C$_5$H$_5$) [20] and trimethylphosphine [21] were prepared by the published procedures. [K(C$_5$H$_4$)CMe$_2$(C$_5$H$_4$)K] was prepared by the action of potassium hydride on the protio-ligand in THF. Sodium thiophenoxide was prepared by the reaction between sodium sand and thiophenol in toluene. Lithium borohydride and triphenylphosphine were purchased from Aldrich Chemical Co. and used as supplied.

3.1. Synthesis of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)Cl₂] (1)

The compound NbCl$_4$ · 2THF (16.9 g, 44.6 mmol) was suspended in THF (100 ml) and stirred at room temperature. A suspension of [K(C$_5$H$_4$)CMe$_2$(C$_5$H$_4$)K] in THF (100 ml) was added dropwise over a period of 1 h. This brown reaction mixture was stirred for 24 h and the volatiles removed under reduced pressure to give a purple–brown solid. Soxhlet extraction of this solid with dichloromethane gave a saturated purple solution. The mother liquor of the extract was decanted off leaving the product 1 as purple crystals which were dried in vacuo. Further product was obtained from the mother liquor by removal of all volatiles under reduced pressure. Yield 8.6 g (57% based on NbCl$_4$ · 2THF).

3.2. Synthesis of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(η²-BH₄)] (2)

A mixture of the compound 1 (750 mg, 2.21 mmol) and LiBH$_4$ (145 mg, 6.63 mmol) was suspended in 1,2-dimethoxyethane (40 ml) and stirred at room temperature. Effervescence was observed on addition of the solvent. After 24 h the volatiles were removed from the brown reaction mixture under reduced pressure and the

resulting solid was extracted with petroleum ether (2 × 50 ml). This dark green solution was concentrated to 30 ml and cooled to −80 °C yielding the product **2** as dark green crystals. Yield 470 mg (75% based on compound **1**). Crystals of compound **2** suitable for X-ray diffraction were obtained by cooling a solution in petroleum ether (b.p. 100–120 °C) to −80 °C.

3.3. Synthesis of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(H)PMe₃] (3)

The compound **2** (80 mg, 0.29 mmol) in benzene (30 ml) was treated with trimethylphosphine (0.1 ml, 73 mg, 1 mmol) at room temperature. The solution turned immediately from green to red on addition of the phosphine. This solution was stirred for 3 h and the volatiles removed in vacuo to give a red solid. The product was extracted into pentane (30 ml) to remove it from the phosphine borane adduct. Removal of the volatiles from this pentane solution under reduced pressure gave the compound **3** as a red microcrystalline solid which was purified by recrystallization from pentane at −80 °C. Yield 40 mg (42% based on compound **2**). Crystals suitable for X-ray diffraction studies were obtained from a solution of compound **3** in pentane by slow cooling to −80 °C.

3.4. Synthesis of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(H)PPh₃] (4)

A mixture of the compound **2** (80 mg, 0.29 mmol) and triphenylphosphine (148 mg, 0.57 mmol) was dissolved in benzene (30 ml) and stirred at room temperature for 3 h. During this time the reaction mixture changed from green to deep red. The volatiles were removed under reduced pressure and the resulting red solid extracted with pentane (50 ml) giving a dark red solution. Removal of volatiles from this solution under reduced pressure gave the compound **4** as a red solid which was purified by recrystallization from pentane at −80 °C. Yield 55 mg (37% based on compound **2**).

3.5. Synthesis of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(SPh)₂] (5)

A colourless solution of NaSPh (400 mg, 3.0 mmol) in THF (100 ml) was added dropwise at room temperature to a stirred suspension of compound **1** (500 mg, 1.5 mmol) in THF (100 ml) over a period of 20 min. A homogeneous red–violet solution resulted after a further 30 min stirring at room temperature. This solution was transferred to a Rotaflo® ampoule and heated at 80 °C under reduced pressure for 16 h. The volatiles were then removed under reduced pressure and the resulting brown solid extracted into toluene (150 ml) and filtered. The volatiles were removed from this violet solution under

reduced pressure and the resulting purple oil extracted into diethyl ether (60 ml). Cooling of this diethyl ether solution to −80 °C yielded the product **5** as purple–black crystals. Yield 108 mg (15% based on compound **1**).

3.6. X-ray structure determination of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(η²-BH₄)] (2)

Crystal data, data collection and processing parameters are given in Table 4. A crystal of compound **2** was mounted in a Lindemann glass capillary tube under N₂ and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. The data were collected and indexed as monoclinic with symmetry consistent with a C-centred cell. The structure was solved in the space group C2/c [22] using direct methods, SIR92, [23] and the CRYSTALS package [24]. Full-matrix least-squares refinement was performed on the structure and a Chebychev weighting scheme was applied [25]. Hydrogen atoms were located from Fourier difference maps and their positions refined, yielding a final R value of 3.43% (R_w = 3.88%).

3.7. X-ray structure determination of [Nb(η-C₅H₄-CMe₂-η-C₅H₄)(H)PMe₃] (3)

Crystal data, data collection and processing parameters are given in Table 4. A crystal of compound **3** was mounted in a Lindemann glass capillary tube under N₂. The data were collected on a DIP2000 image plate diffractometer and indexed as orthorhombic with systematic absences consistent with the space group Pbca [22] by the DENZO© program [26]. A list of F_obs was compiled by SCALEPACK© [27] and the structure solved by direct methods, SIR92, [23] using the CRYSTALS package [24]. Full-matrix least-squares refinement was performed on the structure and a Chebychev weighting scheme was applied [25]. Hydrogen atoms were placed on the ligand geometrically, producing a final R value of 5.58% (R_w = 3.21%).

References

[1] W. Kaminsky, K. Külper, H.H. Brintzinger and F.R.W.P. Wild, Angew. Chem., Int. Ed. Engl., 24 (1985) 507.
[2] R.L. Halterman, Chem. Rev., 92 (1992) 965.
[3] L. Labella, A. Chernega and M.L.H. Green, J. Chem. Soc., Dalton Trans., (1995) 395.
[4] D.S. Breslow, Chem. Abstr., 54 (1960) 11573.

[5] G.L. Karapinka and W.L. Carrick, *J. Polym. Sci.*, *55* (1961) 145.

[6] B. Dorer, J. Diebold, O. Weyand and H.H. Brintzinger, *J. Organomet. Chem.*, *427* (1992) 245.

[7] D.A. Lemenovskii, V.P. Fedin, A.V. Aleksandrov, Yu.L. Slovohotov and Yu.T. Struchkov, *J. Organomet. Chem.*, *201* (1980) 257.

[8] A.N. Chernega, M.L.H. Green and A.G. Suárez, *Can. J. Chem.*, *73* (1995) 1.

[9] W.A. Hermann and W. Baratta, *J. Organomet. Chem.*, *506* (1996) 357.

[10] A. Antiñolo, M. Martinez-Ripoll, Y. Mugnier, A. Otero, S. Prashar and A.M. Rodriguez, *Organometallics*, *15* (1996) 3241.

[11] I.H. Elson and J.K. Kochi, *J. Am. Chem. Soc.*, *97* (1975) 1262.

[12] G.S. McGrady, personal communication, 1995.

[13] C.R. Lucas, in F. Basolo (ed.), *Inorganic Syntheses*, Vol. 16, McGraw-Hill, New York, 1976, p. 107.

[14] T.J. Marks and W.J. Kennelly, *J. Am. Chem. Soc.*, *97* (1975) 1439.

[15] T.J. Marks and J.R. Kolt, *Chem. Rev.*, *77* (1977) 263.

[16] N.I. Kurillova, A.I. Gusev and Y.T. Struchkov, *Zh. Strukt. Khim.*, *15* (1974) 718.

[17] W.E. Douglas and M.L.H. Green, *J. Chem. Soc., Dalton Trans.*, (1972) 1796.

[18] R.A. Bell, S.A. Cohen, N.M. Doherty, R.S. Threlkel and J.E. Bercaw, *Organometallics*, *5* (1986) 972.

[19] L.E. Manzer, *Inorg. Chem.*, *16* (1977) 525.

[20] I.E. Nifant'ev, P.V. Ivchenko and M.V. Borzov, *J. Chem. Res.*, (1992) 162.

[21] R. Thomas and K. Eriks, in S.Y. Tyree, Jr. (ed.), *Inorganic Syntheses*, Vol. 9, McGraw-Hill, New York, 1967, p. 59.

[22] T. Hahn, *International Tables for Crystallography*, Reidel, Dordrecht, 1st edn., 1983.

[23] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, *27* (1994) 435.

[24] D.J. Watkin, J.R. Carruthers and P.W. Betteridge, CRYSTALS, Chemical Crystallography Laboratory, University of Oxford, Oxford, UK, 1996.

[25] J.R. Carruthers and D.J. Watkin, *Acta Crystallogr.*, *A35* (1979) 698.

[26] Z. Otwinowski, DENZO©, Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT, 1993.

[27] Z. Otwinowski, SCALEPACK©, Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT, 1993.