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Synthesis of η-cyclopentadienylidene-4-imidopropylniobium derivatives $[Nb(\eta:\sigma\text{-}C_5H_4(CH_2)_3N)Cl_2]$ and $[Nb(\eta:\sigma\text{-}C_5H_4(CH_2)_3N)(PMe_3)Cl_2]$

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Abstract

The compound $[Nb(\eta:\sigma\text{-}C_5H_4(CH_2)_3N)Cl_2]$ is formed in a one-pot reaction between $NbCl_5$ and $C_5H_4(SiMe_3)(CH_2)_3N(SiMe_3)_2$: the crystal structure of the compound $[Nb(\eta:\sigma\text{-}C_5H_4(CH_2)_3N)(PMe_3)Cl_2]$ has been determined.

The imido ligand =NR can act as a 4-electron donor and yet it subtends a very small angle to the metal centre. Further, the imido ligand although unsaturated is often relatively inert and can behave as a 'spectator ligand' during reactions at the metal centre [1]. The η-cyclopentadienyl ligand is also normally inert during the reactions at the metal centre of η-cyclopentadienyl-metal derivatives. There is a very extensive chemistry of bent bis-η-cyclopentadienyltransition metal compounds in the general class $[M(\eta\text{-}C_5R_5)_2L_lX_x]$ where L is a 2 electron donor ligand and X is a one electron ligand, and l or x may be 0–3. We have been interested in exploring the chemistry of η-cyclopentadienylimidometal compounds [*i.e.* containing the moiety $M(\eta\text{-}C_5R_5)(=NR)$]. In this fragment the ligands contribute nine electrons to the metal centre yet occupy a relatively small part of the metal surface. It is anticipated that such compounds will have an extensive chemistry but with substantially differing reactivities from the analogous bent-bis-η-cyclopentadienylmetal compounds. In particular, the metal centre in the group $M(\eta\text{-}C_5R_5)(=NR)$ will have greater positive charge and should be sterically less crowded than for the fragment $M(\eta\text{-}C_5R_5)_2$. For example, it would be of interest to compare the chemistry of the compounds $[M(\eta\text{-}C_5R_5)(NR)X_2]$, M = V, Nb, Ta, Mo, W, and Re with their corresponding isoelectronic counterparts $[M(\eta\text{-}C_5R_5)_2X_2]$, where M = Ti, Zr, Hf, Nb, Ta, and W, respectively.

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Already there have been reports of η-cyclopentadienylimidometal compounds of Ti [2], V [3], Nb [4], Ta [5], Cr [6], Mo [7], W [8], Re [9] and Ir [10]. Here we describe the synthesis of a new class of compounds containing the moiety M(η-C_5R_5)(=NR), namely derivatives of the *ansa*-bridged η-4-cyclopentadienylidene-4-imidopropyl ligand, ($\eta:\sigma$-$C_5H_4(CH_2)_3N$) in which the imido moiety is tethered to the Cp group by an n-propyl chain.

Treatment of the commercially available *N*-(3-bromopropyl)phthalimide (**1**) with sodium cyclopentadienide gives *N*-(3-cyclopentadienylpropyl)phthalimide (**2**). This reacts with hydrazine to give the amine 3-cyclopentadienylpropylamine (**3**). The yield of this step was variable. Treatment of **3** with $CF_3SO_3SiMe_3$ and NEt_3 gives *N*,*N*-bis-trimethylsilyl-3-cyclopentadienyl propylamine (**4**) from which the ligand precursor *N*,*N*-bis-trimethylsilyl-3-(trimethylsilylcyclopentadienyl)propylamine (**5**) was prepared by treatment with lithiumbistrimethylsilyl followed by Me_3SiCl. Typically, **5** could be prepared on a 5–20 gram scale.

In a simple one-pot reaction, treatment of niobium pentachloride with **5** in dichloromethane gave light yellow crystals of [Nb($\eta:\sigma$-$C_5H_4(CH_2)_3N$)Cl_2] (**6**) in 38% yield on a scale of *ca.* 2.0 gram. Treatment of **6** with PMe_3 gave white crystals of the mono phosphine adduct [Nb($\eta:\sigma$-$C_5H_4(CH_2)_3N$)(PMe_3)Cl_2] (**7**). This was recrystallised from hot toluene.

The compounds **2–7** have been characterised by their ^1H NMR spectra and by microanalysis (for **4–7**) [11*]. The crystal structure of **7** has been determined [12*] and two views of the molecular structure are shown in Fig. 1 together with selected bond lengths and angles.

The structure of **7** is largely similar to that of the non-*ansa* bridged analogue [Nb(η-C_5H_5)(NMe)(PMe_3)Cl_2] (2 crystallographically independent molecules in the asymmetric unit) [5a]. The Nb atom in **7** is in a pseudo-square-based pyramidal environment with the PMe_3 ligand lying *cis* to a Cl ligand [Cl(1)] and the imido nitrogen atom [N(1)] and *trans* to a second chloride ligand [Cl(2)]. The angle for the Nb(1)–N(1)–C(1) linkage [150.6(6)°] deviates substantially from 180° (the value expected for a rigorously linear imido ligand) but this bending does not appear to adversely influence the metal–nitrogen bond length. Thus the corresponding Nb–N bond distances and Nb–N–Me angles for the two molecules of [Nb(η-C_5H_5)(NMe)(PMe_3)Cl_2] are 1.772(4) and 1.782(4) Å and 170.1(4) and 167.9(4)° respectively [5a]. Moreover, the Cp_{cent}–Nb(1)–N(1) angle (111.0°) in **7** is substantially more acute than the corresponding angle for [Nb(η-C_5H_5)(NMe)(PMe_3)Cl_2] (119.2 and 118.9°), presumably reflecting restraints imposed by the closed $(CH_2)_3$ linkage. The angles subtended at the three carbons of the $(CH_2)_3$ linkage (see Fig. 1) are all larger than those anticipated for formally sp^3 hybridised C atoms, an observation also indicative of some strain in the $(CH_2)_3$ linkage of the Nb($\eta:\sigma$-$C_5H_4(CH_2)_3N$) fragment. The value for C_5(centroid)–metal–C_5Entroid) angle in *ansa*-metallocenes is typically in the range 119–130° [13] and is therefore larger than the corresponding angle [Cp_{cent}–Nb(1)–N(1)] in **7**.

The new chemistry is shown in Scheme 1. We anticipate that the ligand precursor **5** will give rise to an extensive chemistry of the *ansa*-bridged η-cyclopentadienylidene-4-imidopropylmetal compounds [M($\eta:\sigma$-$C_5H_4(CH_2)_3N$)L_lX_x].

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* Reference number with asterisk indicates a note in the list of references.

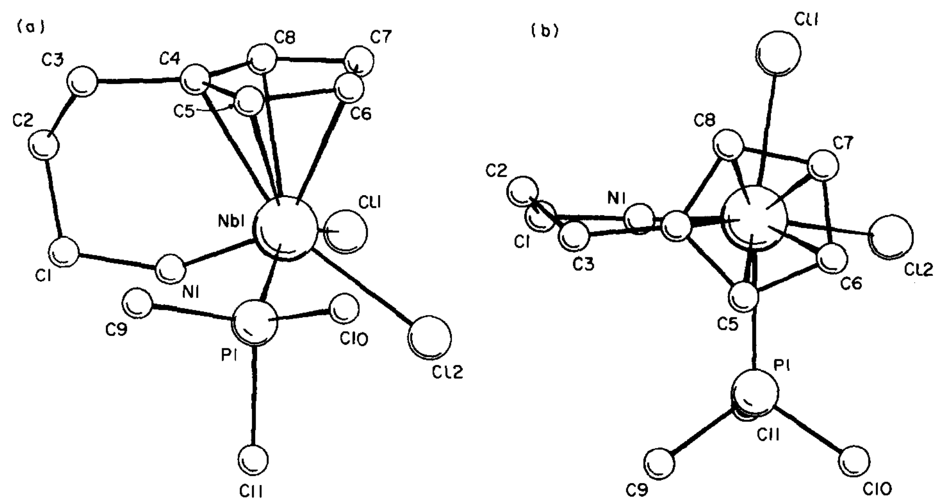
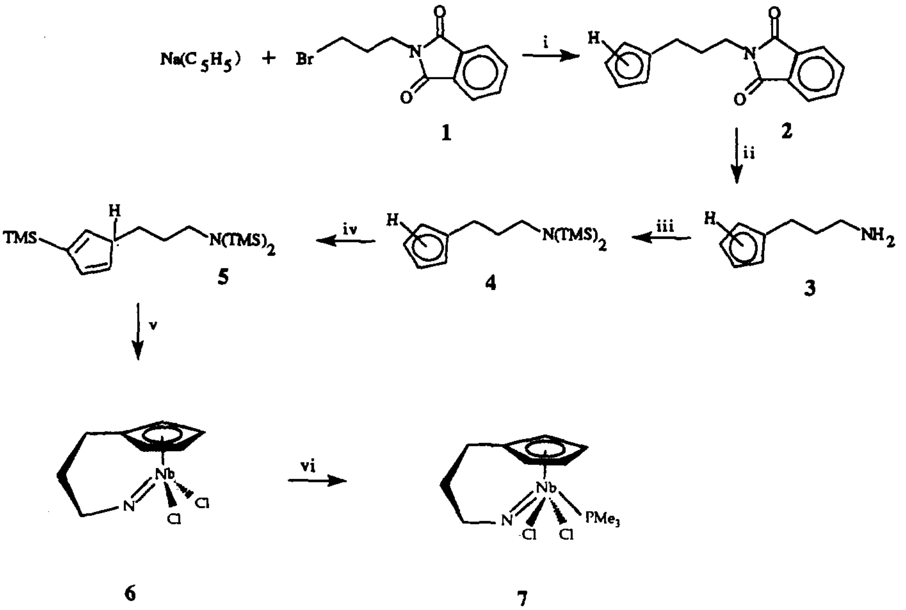


Fig. 1. Molecular structure of $[Nb(\eta:\sigma\text{-}C_5H_4(CH_2)_3N)(PMe_3)Cl_2]$ (7). (a) General view. (b) Viewed perpendicular to the C_5H_4 plane [11*]. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) as follows: Nb(1)–N(1) 1.759(5), Nb(1)–P(1) 2.627(2), Nb(1)–Cl(1), 2.487(2), Nb(1)–Cl(2) 2.495(2), Nb(1)–Cp_{cent} 2.11, Nb(1)–N(1)–C(1) 150.6(6), N(1)–C(1)–C(2) 111.2(7), C(1)–C(2)–C(3) 119.3(10), C(2)–C(3)–C(4) 117.1(8), N(1)–Nb(1)–P(1) 85.0(2), N(1)–Nb(1)–Cl(1) 92.9(2), N(1)–Nb(1)–Cl(2) 123.7(2), P(1)–Nb(1)–Cl(1) 148.35(6), P(1)–Nb(1)–Cl(2) 74.62(6), Cl(1)–Nb(1)–Cl(2) 80.40(7), N(1)–Nb(1)–Cp_{cent} 111.0 where Cp_{cent} refers to the computed C_5H_4 ring centroid.



Scheme 1. (i) In THF at 0°C for 1 h then 14 h at r.t., 71%. (ii) Hydrazine mono-hydrate in MeOH at 65°C for 15 h, 20–44%. (iii) $CF_3SO_3SiMe_3$ and NEt_3, in Et_2O for 3.5 h, 83%. (iv) $Li[N(TMS)_2]$ in THF at −78°C for 15 min, the TMSCl for 15 h at r.t., 84%. (b) $NbCl_5$ in CH_2Cl_2 at −78°C for 5 h, then r.t., for 48 h, 38%. (vi) Excess of PMe_3 in CH_2Cl_2, 77%.

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11 Analytical and spectroscopic data. For **2**: M.S. showed a peak at 253 amu corresponding to the molecular ion of $C_{16}H_{15}NO_2$. ^{1}H-NMR ($CDCl_3$): δ 7.83 (s, 2H, phenyl), 7.81 (s, 2H, phenyl), 6.40–6.01 (3H, CH of Cp), 3.68 (t, 2H, CH_2), 2.81 (s, 2H, CH_2 of Cp), 2.42 (m, 2H, CH_2), 1.83 (m, 2H, CH_2), mixture of isomers.

For **3**: IR: KBr pellet. ν(N–H) 3053 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.46–5.93 (3H, CH of Cp), 2.91 (d, 2H, CH_2 of Cp), 2.69 (t, 2H, CH_2), 2.38 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.39 (s, 2H, NH_2), mixture of isomers.

For **4**: Found; C, 61.21; H, 10.87; N, 5.20. $C_{14}H_{29}NSi_2$ calc.: C, 62.84; H, 10.83; N, 5.23%. M.S. showed a peak at 267 amu corresponding to the molecular ion of $C_{14}H_{29}NSi_2$. ^{1}H-NMR ($CDCl_3$): δ 6.48–5.97 (m, 3H, CH of Cp), 2.41 (d, 2H, CH_2 of Cp), 2.76 (m, 2H, CH_2), 2.28 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 0.06 (s, 18H, 2TMS), mixture of isomers.

For **5**: Found: C, 56.69; H, 11.34; N, 4.34. $C_{17}H_{37}NSi_3$ calc.: C, 60.10; H, 10.98; N, 4.12%. M.S. showed a peak at 339 amu for the molecular ion of $C_{17}H_{37}NSi_3$. ^{1}H-NMR($CDCl_3$): δ 6.71–6.08 (m, 3H, CH of Cp), 3.30–2.89 (m, 1H, CH of Cp), 2.78 (m, 2H, CH_2), 2.33 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 0.03 (s, 18H, $N(TMS)_2$), −0.07 (s, 9H, Me_3 of CpTMS), mixture of isomers.

For **6**: Found: C, 34.08; H, 4.11; N, 4.53; Cl, 24.27. $C_8H_{10}Cl_2NNb$ calc.: C, 33.83; H, 3.55; N, 4.93; Cl, 24.97%. ^{1}H-NMR (C_6D_6): δ 5.91 (br, s, 2H, CH of Cp), 5.03 (br, s, 2H, CH of Cp), 2.88 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 1.30 (m, 2H, CH_2).

For **7**: Found: C, 36.39; H, 5.60; N, 3.79; Cl, 20.11. $C_{11}H_{19}Cl_2NNbP$ calc.: C, 36.69; H, 5.32; N, 3.89; Cl, 19.69%. ^{1}H-NMR (CD_2Cl_2): δ 6.20 (br, s, 2H, CH of Cp), 6.07 (br, s, 1H, CH of Cp), 5.47 (br, m, 1H, CH of Cp), 3.82 (m, 1H, CH_2), 3.46 (m, 1H, CH_2), 2.88 (m, 1H, CH_2), 2.35 (br, m, 1H, CH_2), 2.16 (br, m, 2H, CH_2), 1.60 (br, d, 9H, PMe_3, ^2J(H–P) = 12 Hz). ^{31}P-NMR (CD_2Cl_2): δ −2.3 (br, m, $\Delta\nu_{1/2}$ = 725 Hz). ^{13}C-DEPT (CD_2Cl_2): δ 118.1 (CH), 110.0 (CH), 108.7 (CH), 100.2 (CH), 59.3 (CH_2), 30.8 (CH_2), 24.6 (CH_2), 15.1 (d, CH_3, ^1J(P–C) = 24 Hz).

12 Crystal data for **7**: $C_{11}H_{19}Cl_2NNbP$, $M = 360.06$, crystal size = *ca.* 0.20×0.40×0.60 mm, monoclinic, space group $P2_1/c$, $a = 9.347(3)$, $b = 12.958(5)$, $c = 12.846(5)$ Å, $\beta = 107.89(3)°$, $V = 1480.7$

Å^3, $Z = 4$, $D_c = 1.615$ g cm^{-3}, μ(Cu-K_α) = 110.5 cm^{-1}, $F(000) = 728$, scan type ω–2θ, $T = 293$ K, $2 < 2\theta < 120°$, total unique data 2199, no. of observations $[I > 3\sigma(I)]$ 1604, observations/variables 10.9, $R_{\mathrm{merge}} = 0.059$, $R = 0.045$, $R_w = 0.054$ (Chebyshev parameters 25.1, −16.2, 18.5), maximum peak in final Fourier difference synthesis 1.3 e Å^{-3}. Table of atom coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.
Data were collected on an Enraf–Nonius CAD4 diffractometer. An empirical absorption correction based on azimuthal scan data was applied and the data were corrected for Lp effects. Systematically absent reflections were rejected and equivalent reflections were merged. The niobium atom position was determined from a Patterson synthesis. Subsequent difference syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with isotropic thermal parameters 1.3 times that of the U_{eq} of the attached carbon atom. The non-hydrogen atoms were refined using full-matrix least-squares procedures with the hydrogen atoms 'riding' on their supporting carbon atoms. A Chebyshev weighting scheme was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction in the final stages of refinement. Crystallographic calculations were carried out using the CRYSTALS package [14] on a Micro Vax 3800 computer in the Chemical Crystallography Laboratory, Oxford.

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