

Half-sandwich Niobium(III) Nitrene (Imido) Complexes containing Carbonyl, Alkene and Acetylene Ligands

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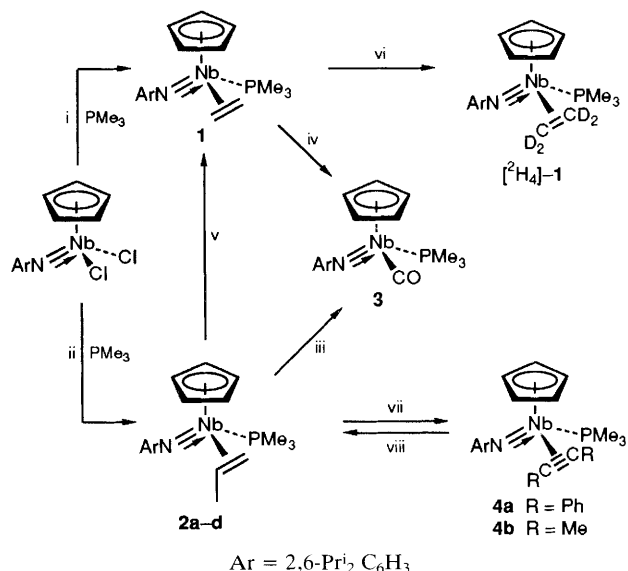
The chiral-at-metal niobium nitrene compounds $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)(\text{PMe}_3)(\text{L})]$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6$ and $\text{RC}\equiv\text{CR}$) have been prepared *via* the dichloride $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{N-2,6-Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$ and the molecular structure of the propene derivative has been determined.

There is considerable interest in the chemistry of complexes combining multiply bonded nitrene (or imido) ligands and neutral organic molecules at a single metal centre owing to their relevance to a number of important catalytic processes including ammoxidation, amination and oxyamination.¹ For

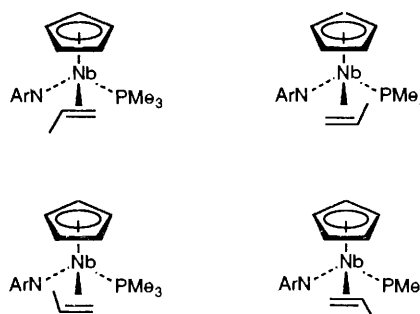
the Group 5 metals, such combinations are rare, presently being restricted to tantalum complexes of the type $[\text{Ta}(\text{NPh})\text{Cl}(\text{PMe}_3)_3(\text{RCH}=\text{CH}_2)]^2$ and $[\text{Ta}(\text{NAr})\text{X}(\text{py})_2(\text{RC}\equiv\text{CR})]$ ($\text{Ar} = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$; $\text{X} = \text{Cl}, \text{O-2,6-Pr}_2\text{C}_6\text{H}_3$; $\text{py} = \text{pyridine}$)³. Here, we report a series of imido-carbonyl,

-acetylene and -alkene complexes which represent the first examples of these ligand combinations for niobium. The chemistry is summarised in Scheme 1.

The yellow ethylene and propene complexes **1** and **2**[†] are prepared by treatment of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$ ⁴ with two equivalents of ethyl and *n*-propyl Grignard reagent, respectively, in the presence of PMe_3 . Propane is generated during the formation of **2** (by mass spec.) indicating that this reaction proceeds *via* β -hydride elimination and loss of alkane from a dialkyl intermediate. Owing to the prochiral nature of the propene ligand in **2**, four isomers may be observed, corresponding to the four possible propene binding orientations shown below. One of the isomers can be crystallised selectively from a saturated pentane solution at -78°C , and a molecular structure determination[‡] (Fig. 1) shows it to be the isomer in which the methyl substituent of the propene ligand is directed away from the PMe_3 and C_5H_5 ligands and towards the arylimido group, being accommodated in a relatively unhindered environment by a twisting of the 2,6-diisopropyl-



Scheme 1 Reagents and conditions: i, EtMgCl , 2 equiv., Et_2O , 12 h, room temp.; ii, Pr^nMgCl , 2 equiv., Et_2O , 12 h, room temp.; iii, CO (g), 1 atm, *n*-pentane, 15 min; iv, CO (g), 1 atm, *n*-pentane, 5 days; v, C_2H_4 , 4 equiv., benzene, 24 h, 60°C ; vi, C_2D_4 , 4 equiv., benzene, 10 days; vii, $\text{RC}\equiv\text{CR}$ (R = Me, Ph), 1 equiv. benzene, room temp.; viii, CH_2CHMe , 1 equiv., benzene, room temp.



The four possible orientations of the propene ligand in **2**

phenyl substituent relative to its orientation in $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NAr})\text{Cl}_2]$.⁴ The metal–nitrogen distance, at 1.793(11) Å, is at the long end of the range observed for Nb–N(imido) bond lengths,⁵ and compares with a metal–nitrogen distance of 1.761(6) Å⁴ in the starting dichloride; the slight increase in Nb–N bond length for **2** is attributed to its lower formal metal oxidation state. The metal–carbon distances for the methylene and methine carbons are 2.39(3) and 2.28(3) Å, respectively, with a C–C distance of 1.58(4) Å. Caution is required in the interpretation of these bond parameters owing to disorder in the propene ligand.[‡]

However, of considerable interest is the orientation of the propene group, since in recent work⁴ we have noted a close similarity between the frontier orbitals of the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})]$ fragment with those of bent metallocenes. Pseudo-metallocene character would require the C(21)–C(22) bond of the propene ligand to lie coplanar with the phosphine bond to allow favourable overlap with the metallocene-like frontier orbitals of the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{NR})]$ fragment; we find that the Nb–P bond lies only 7.1° out of the Nb–C(21)–C(22) plane which does indeed lend further support to the metallocene analogy.

The ethylene ligand of **1** is not displaced by substituted alkenes but will exchange slowly with C_2D_4 and carbon monoxide to give the deuterio-ethylene complex $[\text{H}_2\text{D}_2]$ -**1** and the carbonyl compound **3**, respectively. The propene deriva-

[†] Satisfactory elemental analyses have been obtained. *Selected spectroscopic data* for **1**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.00 (s, 5H, C_5H_5), 0.98, 1.00 (d, 12H, $^3J_{\text{HH}}$ 7.0 Hz, CHMe_2), 4.20 (sept, 2H, $^3J_{\text{HH}}$ 7.0 Hz, CHMe_2), 0.96 (unresolved, 9H, PMe_3), 0.58, 1.40, 1.64 (m, 4H, C_2H_4), 6.88 (t, 1H, $^3J_{\text{HH}}$ 7.0 Hz, *p*- C_6H_3) and 7.02 (d, 2H, $^3J_{\text{HH}}$ 7.0 Hz, *m*- C_6H_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz, 298 K): δ 17.0 (s, PMe_3), 24.0 (s, CHMe_2), 24.5 (s, C_2H_4), 27.5 (s, CHMe_2), 28.2 (s, C_2H_4), 100.6 (s, C_5H_5), 121.7, 122.4, 143.5, 152.2 (s, ArC). For **2a**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.48 (d, 5H, $^3J_{\text{PH}}$ 1.2 Hz, C_5H_5), 1.16, 1.22 (d, 12H, $^3J_{\text{HH}}$ 7.2 Hz, CHMe_2), 3.51 (sept, 2H, $^3J_{\text{HH}}$ 7.2 Hz, CHMe_2), 0.96 (d, 9H, $^2J_{\text{PH}}$ 7.2 Hz, PMe_3), 1.53 (d, 3H, $^3J_{\text{HH}}$ 6.4 Hz, CH_2CHMe) and 6.90–7.01 (m, 3H, C_6H_3). For **2b**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.43 (d, 5H, $^3J_{\text{PH}}$ 1.2 Hz, C_5H_5), 1.20, 1.26 (d, 12H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 3.68 (sept, 2H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 0.90 (d, 9H, $^2J_{\text{PH}}$ 7.2 Hz, PMe_3), 2.02 (d, 3H, $^3J_{\text{HH}}$ 6.4 Hz, CH_2CHMe) and 6.90–7.01 (m, 3H, C_6H_3). For **2c**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.40 (d, 5H, $^3J_{\text{PH}}$ 1.2 Hz, C_5H_5), 1.17, 1.23 (d, 12H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 3.90 (sept, 2H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 0.95 (d, 9H, $^2J_{\text{PH}}$ 7.2 Hz, PMe_3), 2.24 (d, 3H, $^3J_{\text{HH}}$ 6.4 Hz, CH_2CHMe) and 6.90–7.01 (m, 3H, C_6H_3). For **2d**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.35 (d, 5H, $^3J_{\text{PH}}$ 1.2 Hz, C_5H_5), 1.23, 1.29 (d, 12H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 4.02 (sept, 2H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 1.01 (d, 9H, $^2J_{\text{PH}}$ 7.2 Hz, PMe_3), 2.06 (d, 3H, $^3J_{\text{HH}}$ 6.4 Hz, CH_2CHMe) and 6.90–7.01 (m, 3H, C_6H_3), the methine and methylene signals of the propene ligand are unresolved and partially obscured. For **3**: ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 5.22 (s, 5H, C_5H_5), 1.32 (d, 12H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 4.06 (sept, 2H, $^3J_{\text{HH}}$ 6.8 Hz, CHMe_2), 0.85 (d, 9H, $^2J_{\text{PH}}$ 7.2 Hz, PMe_3), 7.01 (t, 1H, $^3J_{\text{HH}}$ 7.2 Hz, *o*- C_6H_3) and 7.11 (d, 2H, $^3J_{\text{HH}}$ 7.2 Hz, *m*- C_6H_3); ^{13}C NMR (C_6D_6 , 100.6 MHz, 298 K): δ 20.6 (s, PMe_3), 23.6 (s, CHMe_2), 28.1 (s, CHMe_2), 95.6 (s, C_5H_5), 122.0, 122.4, 141.5, 152.2 (s, ArC); IR (Nujol, CsI , cm^{-1}): 1870 [$\nu(\text{CO})$].

[‡] *Crystal data* for $\text{C}_{23}\text{H}_{37}\text{NPNb}$: $M = 451.4$, monoclinic, $P2_1/m$, $a = 8.543(4)$, $b = 16.069(4)$, $c = 8.551(3)$ Å, $\beta = 94.35(4)^\circ$, $U = 1170.5$ Å³, $Z = 2$, $D_c = 1.281$ g cm^{-3} , $\lambda(\text{Cu-K}\alpha) = 1.54184$ Å, $\mu = 4.97$ mm^{-1} , $F(000) = 476$, $T = 180$ K. The structure was determined by Patterson and difference syntheses, with blocked-cascade least-squares refinement on F . Intensities were measured by an on-line profile fitting method.⁶ SHELXTL⁷ and locally written computer programs were employed, and atomic scattering factors were taken from ref. 8. The weighting scheme was $w^{-1} = \sigma^2(F_o) = \sigma_c^2(F_o) + 20 + 53G + 5G^2 - 42H + 37H^2 - 155GH$, where $G = F_o/F_{\text{max}}$ and $H = \sin\theta/\sin\theta_{\text{max}}$; the coefficients were derived from analysis of the data.⁹ Anisotropic thermal parameters for Nb and all non-H atoms of imido and phosphine ligands, ideal rigid pentagons for Cp with C–C 1.420 Å, H atoms constrained [C–H 0.96 Å, H–C–H 109.5°], Cp H on ring angle bisectors, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, but not included for the alkene ligand. Extinction effects were insignificant. The Cp and alkene ligands are disordered, superimposing on each other across the mirror plane through Nb, N and P atoms. The final $R = 0.0660$, $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.0472$, $S = 1.05$ for 115 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

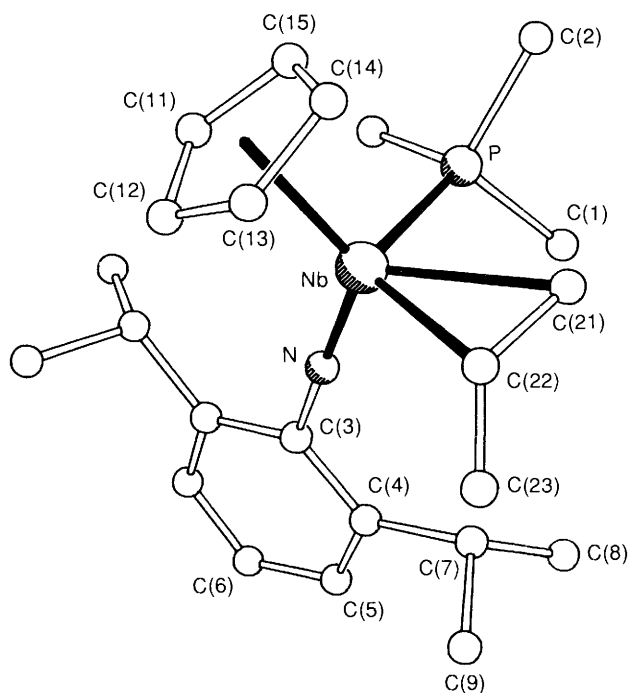


Fig. 1 Crystal structure of one of the isomers of complex **2**

tive **2** is carbonylated more rapidly, and also reacts with ethylene at 60 °C in benzene to give **1**. This is attributed to the greater lability of the monosubstituted alkene of **2** compared with the ethylene ligand in **1**. For the same reason, **2** is also less stable than **1**, decomposing *via* loss of alkene at room temperature to give black hydrocarbon-soluble paramagnetic products which, to date, have not been identified. Disubsti-

tuted acetylene complexes are also accessible *via* treatment of **2** with one equivalent of diphenylacetylene or but-2-yne, leading to equilibrium mixtures of **2** with **4a** and **b**, respectively. Thermochemical and kinetic studies on these transformations are currently in progress.

BP Chemicals and the SERC are gratefully acknowledged for financial support. V. C. G. is the recipient of a BP Chemicals Young University Lecturer Award.

Received, 14th October 1991; Com. 1105214D

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