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Preliminary Communication

Niobium and tantalum methyl complexes containing imido and cyclopentadienyl ligands. Crystal structure of $[\mathrm{Nb}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{N^tBu})(\mathrm{Me})(\mathrm{Cl})]$ *

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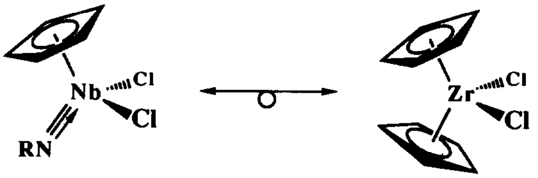
Abstract

Mono- and di-methyl complexes of the type $(\eta\text{-}\mathrm{C_5H_5})\mathrm{Nb}(\mathrm{NR})(\mathrm{Me})(\mathrm{Cl})$ ($\mathrm{R} = {}^t\mathrm{Bu}$, 2,6-$^i\mathrm{Pr_2C_6H_3}$) and $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{M}(\mathrm{N\text{-}2,6\text{-}{}^iPr_2C_6H_3})(\mathrm{Me})_2$ (M = Nb, Ta) have been prepared by treatment of $(\eta\text{-}\mathrm{C_5R'_5})\mathrm{M}(\mathrm{NR})(\mathrm{Cl_2})$ with one or two equivalents of methylmagnesium chloride respectively. Trimethylphosphine adducts are readily formed from the mono-methyl but not from the dimethyl compounds. The molecular structure of $(\eta\text{-}\mathrm{C_5H_5})\mathrm{Nb}(\mathrm{N^tBu})(\mathrm{Me})(\mathrm{Cl})$ is reported.

We recently described a series of half-sandwich imido compounds of niobium and tantalum of general formula $(\eta\text{-}\mathrm{C_5R'_5})\mathrm{M}(\mathrm{NR})\mathrm{X_2}$ (M = Nb, Ta) [1]. These are of considerable interest since they may be regarded as being pseudo-isoelectronic with bent metallocenes of the type $(\eta\text{-}\mathrm{C_5R_5})_2\mathrm{MX_2}$ (M = Ti, Zr, Hf) (illustrated below for Nb and Zr). Moreover, calculations indicate that the frontier orbitals of the [CpM(NR)] and $[\mathrm{Cp_2M}]$ fragments possess remarkably similar characteristics [1,2]. This relationship is derived from the similarities between the symmetries of the frontier orbitals of the imido fragment $[\mathrm{NR}]^{2-}$ and those of the cyclopentadienyl anion $[\mathrm{C_5H_5}]^-$, both of which bond to a metal through a combination of one σ and two π symmetry orbitals. We have thus embarked upon a programme of study to evaluate the similarities and differences between the chemistries of these systems.



Alkyl derivatives of titanocene and zirconocene are important both as stoichiometric and as catalytic reagents for a variety of organic transformations [3] and have attracted much renewed interest due to their role in Ziegler-type polymerizations of α-olefins [4]. We describe below the synthesis and characterisation ** of a series of mono- and dimethyl complexes of the half-sandwich imido system as a prelude to

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

** Selected spectroscopic data: NMR data (^{1}H NMR, 400 MHz; ^{13}C NMR, 100.5 MHz as δ (ppm) relative to [^{1}H] impurities in the deuterated solvent, ^{a} in [$^2\mathrm{H_6}$] benzene, ^{b} in [^{2}H] chloroform. Satisfactory microanalyses have been obtained for all the new compounds.

2a: ^{1}H NMR: 5.69 [5H, s, $\mathrm{C_5H_5}$], 1.15 [3H, s, $\mathrm{CH_3}$], 1.13 [9H, s, $\mathrm{C(CH_3)_3}$]. ^{a} ^{13}C{^{1}H}: 108.6 [$\mathrm{C_5H_5}$], 66.7 [$\mathrm{CH_3}$], 65.6 [$\mathit{C}\mathrm{(CH_3)_3}$], 31.3 [$\mathrm{C}(\mathit{C}\mathrm{H_3})_3$]. ^{a}
2b: ^{1}H: 5.64 [5H, s, $\mathrm{C_5H_5}$], 1.34 [3H, s, $\mathrm{CH_3}$], 3.80 [2H, sept (J 7.5), $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 1.27 [12H, d ($J$ 7.5), $\mathrm{CH(C}\mathit{H}_3)_2$], 7.06 [2H, d ($J$ 5.0), m-$\mathrm{C_6H_3}$], 6.97 [1H, t (J 5.0), p-$\mathrm{C_6H_3}$]. ^{a} ^{13}C{^{1}H}: 110.0 [$\mathrm{C_5H_5}$], 40.4 [$\mathrm{CH_3}$], 28.5 [$\mathit{C}\mathrm{H(CH_3)_2}$], 24.4 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 152.2 [*ipso*-$\mathrm{C_6H_3}$], 144.6 [$o$-$\mathrm{C_6H_3}$], 122.7 [$m$-$\mathrm{C_6H_3}$], 125.2 [$p$-$\mathrm{C_6H_3}$]. ^{a}
3a: ^{1}H: 5.87 [5H, s, $\mathrm{C_5H_5}$], 0.67 [3H, s, $\mathrm{CH_3}$], 1.42 [9H, s, $\mathrm{C(CH_3)_3}$], 1.42 [9H, d (J 8), $\mathrm{P(CH_3)_3}$]. ^{b} ^{13}C{^{1}H}: 109.7 [$\mathrm{C_5H_5}$], not observed [$\mathrm{CH_3}$], 71.4 [$\mathit{C}\mathrm{(CH_3)_3}$], 30.8 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 16.2 [d ($J$ 26), $\mathrm{P(CH_3)_3}$]. ^{b}
3b: ^{1}H: 5.75 [5H, s, $\mathrm{C_5H_5}$], 1.44 [3H, s, $\mathrm{CH_3}$], 3.91 [2H, sept (J 7.0), $\mathrm{C}\mathit{H}$ $\mathrm{(CH_3)_2}$], 1.19, 1.30 [12H, d (J 7.0), $\mathrm{CH(C}\mathit{H}_3)_2$], 0.83 [9H, d ($J$ 3.0), $\mathrm{P(CH_3)_3}$], 7.15 [2H, d (J 7.0), m-$\mathrm{C_6H_3}$)], 6.92 [1H, t (J 7.0), p-$\mathrm{C_6H_3}$]. ^{a} ^{13}C{^{1}H}: 108.2 [$\mathrm{C_5H_5}$], 32.4 [$\mathrm{CH_3}$], 27.6 [$\mathit{C}\mathrm{H(CH_3)_2}$], 24.3, 24.8 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 15.0 [$\mathrm{P(CH_3)}$], 151.2 [*ipso*-$\mathrm{C_6H_3}$], 144.9 [$o$-$\mathrm{C_6H_3}$], 123.0 [$m$-$\mathrm{C_6H_3}$], 124.7 [$p$-$\mathrm{C_6H_3}$]. ^{a}
5a: ^{1}H: 1.67 [15H, s, $\mathrm{C_5(CH_3)_5}$], 0.53 [6H, s, $\mathrm{CH_3}$], 3.75 [2H, sept (J 7.0), $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 1.35 [12H, d ($J$ 7.0), $\mathrm{CH(C}\mathit{H})_3)_2$], 7.14 [2H, d ($J$ 7.6), m-$\mathrm{C_6H_3}$], 7.00 [1H, t (J 7.6), p-$\mathrm{C_6H_3}$]. ^{a} ^{13}C{^{1}H}: 116.0 [$\mathit{C}_5\mathrm{(CH_3)_5}$], 10.8 [$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$], 41.0 [$\mathrm{CH_3}$], 28.3 [$\mathit{C}\mathrm{H(CH_3)_2}$], 24.2 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 150.6 [*ipso*-$\mathrm{C_6H_3}$], 144.6 [$o$-$\mathrm{C_6H_3}$], 122.4 [$m$-$\mathrm{C_6H_3}$], 123.4 [$p$-$\mathrm{C_6H_3}$]. ^{a}
5b: ^{1}H: 1.71 [15H, s, $\mathrm{C_5(CH_3)_5}$], 0.30 [6H, s, $\mathrm{CH_3}$], 3.69 [2H, sept (J 6.8), $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 1.37 [12H, d ($J$ 6.8), $\mathrm{CH(C}\mathit{H}_3)_2$], 7.23 [2H, d ($J$ 7.6), m-$\mathrm{C_6H_3}$], 6.98 [1H, t (J 7.6), p-$\mathrm{C_6H_3}$]. ^{a} ^{13}C{^{1}H}: 116.0 [$\mathit{C}_5\mathrm{(CH_3)_5}$], 10.6 [$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$], 48.4 [$\mathrm{CH_3}$], 28.1 [$\mathit{C}\mathrm{H(CH_3)_2}$], 24.3 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 151.5 [*ipso*-$\mathrm{C_6H_3}$], 144.1 [$o$-$\mathrm{C_6H_3}$], 122.2 [$m$-$\mathrm{C_6H_3}$], 122.5 [$p$-$\mathrm{C_6H_3}$]. ^{a}

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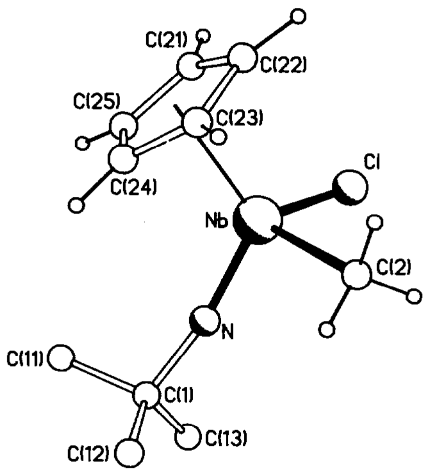
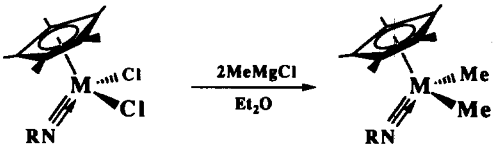


Fig. 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (degrees): Nb–Cl 2.365(2), Nb–N 1.740(4), Nb–C(2) 2.193(5), N–C(1) 1.456(6), Cl–Nb–N 107.1(1), Cl–Nb–C(2) 104.3(2), N–Nb–C(2) 98.1(2), Nb–N–C(1) 169.2(3). Only one component of the disordered tert-butyl group is shown.

investigations of their stoichiometric and catalytic reactivity.

The dichlorides **1** react with one molar equivalent of MeMgCl in diethyl ether to give the orange crystalline methyl complexes **2** according to eqn. (1). Both **2a** and **2b** can be isolated as large orange cubes upon prolonged storage of saturated pentane solutions at −20°C. The crystal structure *** of **2a** is shown in Fig. 1, and important bond distances and angles are included in the caption. The Nb–N and Nb–Cl distances (1.740(4) Å and 2.365(2) Å, respectively) are unexceptional, being close to those found for the dichloride **1a** [1].

Treatment of **2** with a further equivalent of MeMgCl afforded an intractable oil. However, the pentamethylcyclopentadienyl derivatives **4** reacted in a straightforward manner with an excess of MeMgCl to give the dimethyl derivatives **5**, which were isolated as yellow crystalline solids in good yield (eqn. (2)).



(2)

4a M = Nb
4b M = Ta

5a M = Nb
5b M = Ta

R = 2,6-i-$Pr_2C_6H_3$

The mono-methyl derivatives **2** were found to react with trimethylphosphine to give the PMe_3 adducts **3**. It is to be expected that the phosphine will bind within (or close to) the Cl–Nb–C(Me) plane, *cf.* the Cl–Nb–Cl plane in $CpNb(N^tBu)Cl_2(PMe_3)$ [1], and similarly in a lateral position as opposed to a site bisecting the two chloro ligands; this would be consistent with the directional properties of the LUMO of the $[CpNb(NR)X_2]$ fragment [1]. It is not possible to distinguish which of the lateral sites (*i.e.* adjacent to the chloro or methyl substituents) the PMe_3 occupies from the available spectroscopic data, but consideration of the available space favours coordination at the position adjacent to the chloro ligand, as illustrated in eqn. (1). By contrast, the sterically hindered dimethyl derivatives **5** do not form adducts with PMe_3, although we note that a t-butylimido tantalum derivative has been prepared [5].

The methyl complexes described here, and their closely related benzyl derivatives reported earlier [6], will provide useful entry points for explorations of the stoichiometric and catalytic reactivity of these pseudometallocene molecules.

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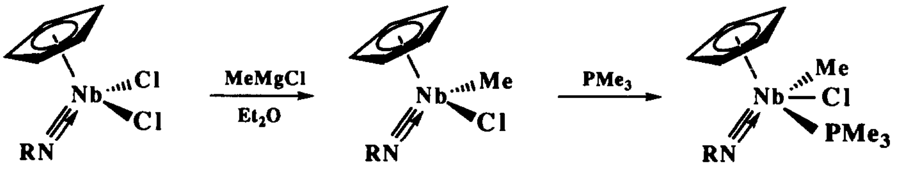

(1)

1a R = t-Bu
1b R = 2,6-i-$Pr_2C_6H_3$

2a R = t-Bu
2b R = 2,6-i-$Pr_2C_6H_3$

3a R = t-Bu
3b R = 2,6-i-$Pr_2C_6H_3$

*** Crystal data for $C_{10}H_{17}NClNb$: $M = 279.6$, monoclinic, $P2_1/n$, $a = 6.7361(5)$, $b = 14.0546(15)$, $c = 13.6760(20)$ Å, $\beta = 97.522(9)°$, $V = 1283.6$ Å^3, $Z = 4$, $D_c = 1.447$ g cm^{-3}, λ(Cu-Kα) = 1.54184 Å, $\mu = 9.48$ mm^{-1}, $F(000) = 568$, $T = 295$ K. The structure was solved and refined (least squares on F) from 1469 unique observed absorption-corrected reflections with $2\theta < 110°$, with anisotropic thermal parameters and constrained H atoms and with a disordered tert-butyl group (without H atoms), to a final $R = 0.0444$, $R' = 0.0372$. The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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