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Preliminary Communication

Redox reactions of vanadium(0) and niobium(0) bis(mesitylene) (mes) derivatives with metal carbonyl halides of Group 7. The crystal and molecular structure of $[\mathrm{mes(CO)_2Nb(\mu\text{-}I)_2Re(CO)_3}]$, a metal–metal bonded heterobimetallic complex *

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Abstract

Redox reactions of $[\mathrm{M(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2}]$, $[\mathrm{Mmes_2}]$, (M = V or Nb) with $[\mathrm{MX(CO)_5}]$ (M = Mn, X = Cl, Br, or I; M = Re, X = Br or I) leading to oxidation of the organometallic of Group 5 have been investigated. The crystal structure of $[\mathrm{mes(CO)_2Nb(\mu\text{-}I)_2Re(CO)_3}]$ **1b**, has been solved by X-ray diffraction methods; the organometallic derivative can best be described as containing rhenium(0) and niobium(II) centres of d^7 and d^3 configurations, respectively, with a Nb-Re distance (average) of 2.921(4) Å.

Convenient (Nb) and high-yield (V) syntheses of $[\mathrm{Vmes_2}]$ [1] and $[\mathrm{Nbmes_2}]$ [2] have recently been reported. These zerovalent compounds are oxidized by $[\mathrm{V(CO)_6}]$, $[\mathrm{Co_2(CO)_8}]$, $[\mathrm{FeCp_2}]^+$, or by *N*,*N*′-dimethyl-4,4′-dipyridine cation [2,3]. In this communication we present some preliminary data on the redox reactions of $[\mathrm{Vmes_2}]$ and $[\mathrm{Nbmes_2}]$ with organometallic compounds of Group 7. This paper is a contribution to the rapidly increasing field of redox reactions between organometallic complexes in non-aqueous systems [4].

From the reaction of $[\mathrm{Vmes_2}]$ with $[\mathrm{MnX(CO)_5}]$ various products have been isolated, depending on the nature of the halide and/or the solvent (see eqns. (1) (2)).

$$[\mathrm{Vmes_2}] + [\mathrm{MnI(CO)_5}] \xrightarrow{\text{toluene}} [\mathrm{Vmes_2}]\mathrm{I} + 1/2[\mathrm{Mn_2(CO)_{10}}] \quad (1)$$

$$[\mathrm{Vmes_2}] + 2[\mathrm{MnBr(CO)_5}] \xrightarrow{\text{dme}} [\mathrm{VBr_2(dme)_2}] + [\mathrm{Mn_2(CO)_{10}}] \quad (2)$$

The products of reaction (2) are dependent on the stability of $[\mathrm{Vmes_2}]\mathrm{Br}$, which is assumed to be the intermediate: we have recently reported [5] that $[\mathrm{Vmes_2}]\mathrm{Br}$, formed in the initial stage of the reaction of $[\mathrm{Vmes_2}]$ with $\mathrm{CPh_3Br}$, readily disproportionates to $[\mathrm{Vmes_2}]$ and $[\mathrm{VBr_2(dme)_2}]$ in the presence of dme.

In the reaction with $[\mathrm{MnX(CO)_5}]$, $[\mathrm{Nbmes_2}]$ is oxidized to $\mathrm{Nb^I}$ (see eqn. (3)).

$$[\mathrm{Nbmes_2}] + [\mathrm{MnX(CO)_5}] \xrightarrow[\text{X = Cl or I}]{} [\mathrm{Nbmes_2X}] + 1/2[\mathrm{Mn_2(CO)_{10}}] \quad (3)$$

No response was observed in the reaction of $[\mathrm{Vmes_2}]$ with $[\mathrm{ReX(CO)_5}]$ even in boiling THF, whereas the niobium compound rapidly reacted with $[\mathrm{ReX(CO)_5}]$ in toluene giving a green solid which was recrystallized from toluene as green-black crystals of **1** [6] see reaction sequence (4)).

$$[\mathrm{Nbmes_2}] \xrightarrow[\text{X = Br or I}]{[\mathrm{ReX(CO)_5}]} [\mathrm{mes(CO)_2Nb(\mu\text{-}X)_2Re(CO)_3}]$$
$$(\mathbf{1a}, \mathrm{X = Br};\ \mathbf{1b}, \mathrm{X = I}) \quad (4)$$

The yield of the reaction never exceeded 50%: one oxidizing equivalent of rhenium is presumably reduced to give unidentified rhenium(0) products, thus accounting for the X/Re molar ratio of 2 in **1**. $[\mathrm{Nbmes_2I}]$ is likely to be an intermediate in the formation of **1b**; yields as high as 75% of **1b** were accordingly obtained by reaction of $[\mathrm{Nbmes_2I}]$ with $[\mathrm{ReI(CO)_5}]$ (eqn. (5)).

$$[\mathrm{Nbmes_2I}] + [\mathrm{ReI(CO)_5}] \longrightarrow \mathbf{1b} + \mathrm{mes} \quad (5)$$

Compound **1b** was studied by X-ray diffraction methods [7] and the molecular structure is shown in Fig. 1. It is a heterobimetallic complex with two iodide bridges, and can be best described as containing niobium(II) and rhenium(0) metal centres of d^3 and d^7 configurations, respectively. The geometry around the niobium atom is distorted square pyramidal, the

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

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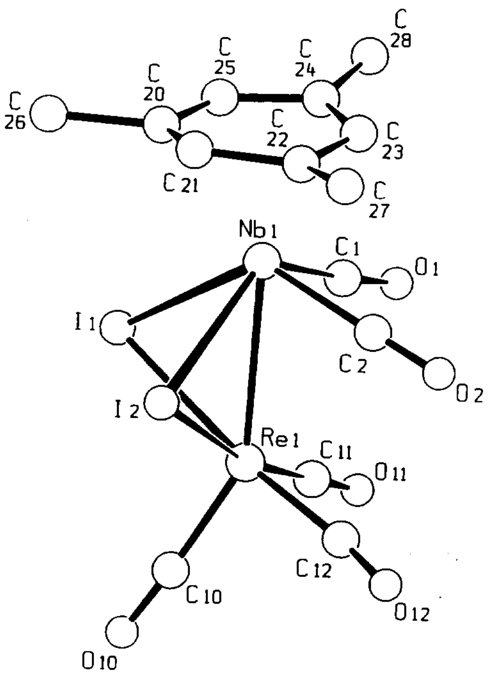

Fig. 1. A SCHAKAL plot of the molecular structure of **1b**. Selected bond distances (Å) and angles (degrees) are: Nb1–C (arene, mean value): 2.41(5); Nb1–C (carbonyl, mean value): 2.03(5); Nb1–I (mean value): 2.903(5); Re1–I (mean value): 2.802(4); Re1–C (mean value): 1.86(5); C–O (mean value): 1.16(5); Nb1–C–O (mean value): 175(4); Re1–C–O (mean value): 171 (5); Nb1–I1–Re1: 62.0(2); Nb1–I2–Re1: 62.0(2).

mesitylene occupying the apical position. The diamagnetism of the complex suggests the presence of a niobium-rhenium single bond. The mean Nb–Re distance (averaged over three independent molecules in the unit cell) of 2.921(4) Å compares well with the value of 2.90 Å calculated from the sum of the Re^0 and Nb^{II} covalent radii obtained from the Re–Re [3.041(1) Å] and Nb–Nb [2.761(2) Å] distances in $[Re_2(CO)_{10}]$ [10] and $[(\eta^6\text{-}C_6Me_6)_2Nb_2(\mu\text{-}Br)_4]$ [2], respectively. Compounds **1** represent a new addition to the class of metal–metal bonded heterobimetallic systems [4b].

Further studies on the oxidation of bis(arene) metal(0) complexes of Group 5, aimed at comparing the relative reactivities of the 3d system with respect to their 4d congeners [11] are being carried out and will be reported later.

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6 A solution of $[ReI(CO)_5]$ (0.39 g, 0.86 mmol) in toluene (50 ml; $\tilde{\nu}_{CO}$; 2146w, 2041vs, 1984s cm^{-1}) was treated with $[Nbmes_2]$ (0.29 g, 0.87 mmol). After 15 h stirring at room temperature $[ReI(CO)_5]$ had disappeared (IR of the supernatant solution). The brown green solid was filtered and the solution was cooled to *ca.* −30°C for some days: black-green crystals of $[mes(CO)_2Nb(\mu\text{-}I)_2Re(CO)_3]$, stable in air for short periods of time, were collected by filtration and dried *in vacuo* (0.15 g). Anal. Found: C, 21.1, H, 1.5, I, 31.7; calcd for $C_{14}H_{12}I_2NbO_5Re$: C, 21.2, H, 1.5, I, 32.0%. IR spectrum (toluene): 2027vs, 1965m, 1950w and 1928m cm^{-1}; (THF): 2023vs, 1994w, 1964m, 1925vs cm^{-1}. ^1H-NMR [THF-d_8, δ values in ppm referred to TMS as internal standard): 6.17 (3 H, s), 2.26 (9 H, s). Another crop of 0.15 g of **1b** (44% total yield based on the rhenium complex used) was obtained by extraction of the solid from the filtration of the crude reaction mixture with toluene.

7 Enraf-Nonius CAD4; Cu-Kα radiation ($\lambda = 1.5418$ Å), graphite monochromator, empirical absorption correction (DIFABS [8]); intensity data collected with the ω-scan method at room temperature. Crystal data: $C_{14}H_{12}I_2NbO_5Re$, orthorhombic, space group $P2_12_12_1$ (No. 19); $a = 10.294(1)$, $b = 15.139(1)$, $c = 36.960(3)$ Å, $V = 5760(1)$ Å^3, $Z = 12$, $\rho_{calc.} = 2.744$ g cm^{-3}, μ(Cu-Kα) = 424.35 cm^{-1}; $F(000) = 4296$; 7293 reflections in the scan range $5 < \theta < 65°$, 3229 with $I > 3\sigma(I)$, 3000 independent reflections with $I > 3\sigma(I)$ in structure solution and refinement [9] for 336 parameters. $R = 0.062$; $R_w = 0.063$; $w^{-1} = 1/\sigma^2(F_0)$, GOF = 1.265; the extinction coefficient $g = 0.256 \times 10^{-7}$ was refined and the calculated structure factors were corrected for the secondary extinction. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (UK). Any request should be accompanied by a full literature citation for this communication.

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