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Preliminary communication

CYCLOPENTADIENYL-NIOBIUM AND -TANTALUM CHEMISTRY; X-RAY STRUCTURES OF $\{(\eta\text{-}C_5H_5)NbCl_3[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]\}$, $C_6H_5CH_3$ AND $\{[\eta\text{-}C_5H_4CH_3)NbCl_3OH]_2\text{-}\mu\text{-}O\}$

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Summary

A new convenient route to $[Ta(\eta\text{-}C_5H_5)_2Cl_2]$ is described. The compound $[Ta(\eta\text{-}C_5H_5)_2(SCH_3)_2]$ and hence $\{[Ta(\eta\text{-}C_5H_5)_2(SCH_3)_2Pt(SCH_3)_2Ta(\eta\text{-}C_5H_5)_2]\text{-}(PF_6)_2\}$ are derived from it. Monocyclopentadienylniobium halides are shown to be precursors of the new derivatives given in the title.

Convenient synthetic routes to monocyclopentadienyl halides of niobium and tantalum have been described recently [1, 2]. Further study of these compounds shows them to be precursors to a variety of new compounds of these metals.

Treatment of a toluene suspension of $[Nb(\eta\text{-}C_5H_5)Cl_4]$ (I) with $EtAlCl_2$ in the presence of dppe (1,2-bisdiphenylphosphinoethane) gives deep violet crystals (II). Compound II is paramagnetic and the crystal structure has been determined.

Crystal data: $\{(\eta\text{-}C_5H_5)NbCl_3[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]\}, C_6H_5CH_3$; triclinic, a 9.112(3), b 11.996(3), c 17.113(5) Å, α 70.40(2), β 87.41(2), γ 80.32(2)°, space group $P\bar{1}$, $Z = 2$, D_{calc} 2.26 g cm^{-3}, 6188 independent reflections were measured by four circle diffractometry using Mo-K_α radiation (λ 0.71069 cm^{-1}). The structure was solved by the heavy atom method and refined by "large" block least-squares. The positions of the hydrogen atoms were found from difference Fourier syntheses. The conventional agreement index, R, is now 0.088.

The unit cell contains two molecules with the structure shown in Fig. 1, together with two disordered solvent molecules of toluene. The niobium atom is at the centre of a distorted coordination octahedron. The three chlorine and the phosphorus atoms (P(1) and P(2)) are at distances 2.479, 2.460, 2.473, 2.679 and 2.789 Å respectively from the niobium which is 0.622 Å above the plane defined by the first four atoms. The Nb—C distances lie in the range 2.389 to 2.466 Å and the normal to the ring at the Nb atom is 2.092 Å.

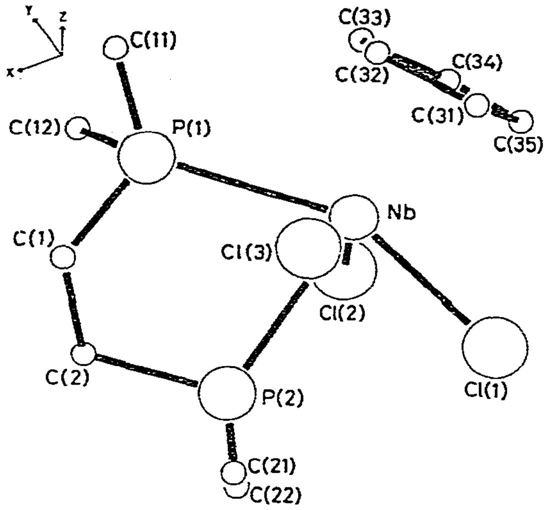

Fig. 1. Structure of $[(\eta\text{-}C_5H_5)NbCl_3(dppe)]$ projected onto the Nb, P(1), P(2) plane: phenyl carbon atoms omitted for clarity.

Treatment of a suspension in toluene of $[Ta(\eta\text{-}C_5H_5)Cl_4]$ (III) with $[EtAlCl_2]_2$ followed by the addition at 0°C of ethanol precipitates brown crystals of the dichloride $[Ta(\eta\text{-}C_5H_5)_2Cl_2]$ (IV) (ca. 40% yield). Since the preparation of III is straightforward [1, 2] the above reaction represents a very direct and convenient synthesis of IV. Treatment of IV in dry ethanol with sodium methanethiolate gives purple crystals of $[Ta(\eta\text{-}C_5H_5)_2(SCH_3)_2]$ (V). This in dichloromethane reacts rapidly with $[Pt(PhCN)_2Cl_2]$ giving the trinuclear mixed-metal compound $[(\eta\text{-}C_5H_5)_2Ta(\mu\text{-}SCH_3)_2Pt(\mu\text{-}SCH_3)_2Ta(\eta\text{-}C_5H_5)_2]A_2$, where A may be Cl^- or PF_6^-. (^{1}H NMR in $(CD_3)_2CO$, $A = PF_6$: τ 3.72 ppm, 20, s, $(\eta\text{-}C_5H_5)_4$; τ 6.92 ppm, 12, triplet (1:4:1), J(Pt,Me) 41 Hz, $[(Me)_4]$). Finally partial hydrolysis of $[Nb(\eta\text{-}C_5H_4CH_3)Cl_4]$ (VI) gives a red crystalline derivative of which the crystal structure showed to be binuclear.

Crystal data: $\{[(\eta\text{-}C_5H_4CH_3)NbCl_3OH]_2\text{-}\mu\text{-}O\}$ (VII); triclinic, a 7.352(1), b 11.094(2), c 12.973(1) Å, α 75.12(1), β 75.50(1), γ 86.28(1)°, space group $P\bar{1}$, D_{calc} 2.03 g cm^{-3}, $Z = 2$. Four circle diffractometry data; 4974 independent reflections. The structure was solved as described above. Hydrogen atoms were located from difference Fourier syntheses. The R value is now 0.048.

Each part of this dimer (Fig. 2) has a similar geometry to compound II. The Nb—O—Nb bridge is significantly non linear (172°). The Nb—O(1) distances 1.908 and 1.919 Å may be compared with that of 1.876 Å found for $\{[(\eta\text{-}C_5H_5)_2NbCl_2]_2O\}(BF_4)_2$ [3]. The torsional angle between planes C1(11),C1(12),C1(13),O(1) and C1(21), C1(22), C1(23),O(1), respectively, is 94.8°. The other Nb—O distances 2.192 and 2.198 Å are those expected for a hydroxy group. Hydrogen bonds O(11)—H(1)···C1(21) and O(21)—H(2)···C1(11) make a further link between the two parts of this dimer (average values: O—H, 0.95 Å; H···Cl, 2.14 Å; angle O—H···Cl 160°).

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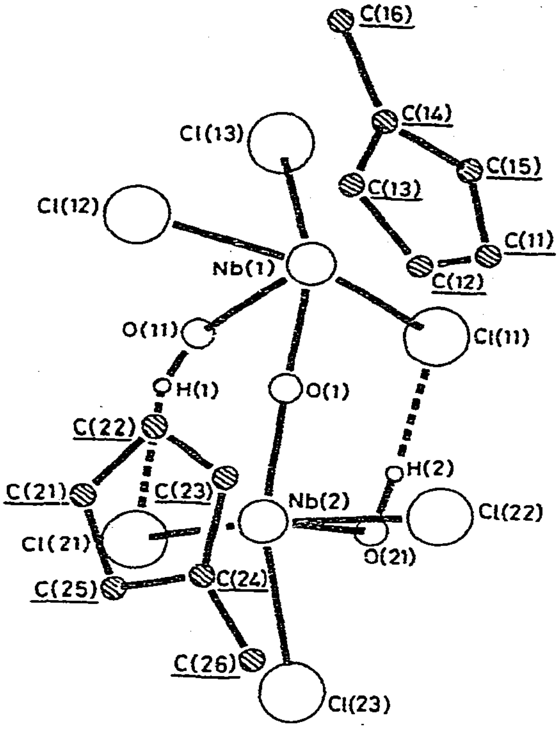

Fig. 2. View of the $\{[(\eta\text{-}C_5H_5)NbCl_3OH]_2\text{-}\mu\text{-}O\}$ molecule projected on the O(11),C1(11),O(21),C1(21) best plane.

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