Mono-η-cyclopentadienylchloro Derivatives of Niobium and Tantalum and Improved Routes to Mono-η-cyclopentadienyl-chloro, -oxochloro, and -oxo Derivatives of Molybdenum

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Summary Simple synthetic routes are described for the compounds $[M(\eta\text{-}C_5H_4R)Cl_4]_n$ (M=Nb or Ta, R=H, Me), $[Nb(\eta\text{-}C_5H_4Me)_2Cl_2]$, $[Mo(\eta\text{-}C_5H_4R)Cl_4]_n$, $[Mo(\eta\text{-}C_5H_4R)Cl_2O]$, and $[(\eta\text{-}C_5H_4R(O)Mo(\mu\text{-}O)_2Mo(O)(\eta\text{-}C_5H_4R)]$.

Abel has shown that trialkyl(cyclopentadienyl)tin compounds with certain transition metal carbonyl halides give η-cyclopentadienylmetal–carbonyl compounds.[1] Tri-n-butyl tin chloride (I) is inexpensive and the compounds $[Bu^n_3Sn(C_5H_4R)]$ (II, R=Me or Bu^n), may be prepared in *ca.* 80% yield from (I) and $[NaC_5H_4R]$ in the manner described for (II, R=H).[2] Also, $[Bu^n_3Sn(C_5Me_4Et)]$ (III) is formed from (I) and $[LiC_5Me_4Et]$. The compounds (II) and (III) are pale yellow liquids which slowly decompose in moist air.

Treatment at room temperature of saturated solutions of niobium pentachloride in toluene or dichloromethane with (II, R=H) (1 mol. equiv.) gave, after 10 min, and upon concentration, excellent red microcrystals of stoicheiometry $[Nb(\eta\text{-}C_5H_4R)Cl_4]_n$ (IV, R=H) in 85% yield.† The compound (IV, R=Me) is prepared with similar ease, *ca.* 70%.†

Treatment of $NbCl_5$ with (II R=Bu^n) followed by addition of moist HCl gas gave excellent large crystals of $[Nb(\eta\text{-}C_5H_4Bu^n)Cl_3(OH)].CH_2Cl_2$ (V).† Tantalum pentachloride similarly reacted with (II, R=H or Me) giving crystalline $[Ta(\eta\text{-}C_5H_4R)Cl_4]_n$ (VI, R=H or Me).† The compounds (IV) and (VI) were moderately soluble in toluene and CH_2Cl_2 but steady decomposition precluded the determination of molecular weights and ^1H n.m.r. spectra. The i.r. spectra of (IV)–(VI) showed bands typical for $\eta\text{-}C_5H_4R$ ligands and the spectra, where R=H, strongly resembled that of the compound $[Mo(\eta\text{-}C_5H_4R)Cl_4]_n$.[3] The mass spectra of (IV, R=Me) and (VI, R=Me) showed the highest bands at m/e = 277 and 351, respectively, corresponding to the ions $[M(\eta\text{-}C_5H_4Me)Cl_3]^+$, where M=Nb or Ta.

Treatment of $NbCl_5$ with (II, R=Me) (2 mol. equiv.) gave, after 3 h, the known compound $[Nb(\eta\text{-}C_5H_4Me)_2Cl_2]$ in *ca.* 80% yield. Therefore this represents a very convenient route to this compound.

The homogeneous reaction between (III) and iron(II) chloride gave $[Fe(C_5Me_4Et)_2]$ in essentially quantitative yield.

The unusual compounds $[Mo(\eta\text{-}C_5H_4R)Cl_4]_n$ (VII, R=H), $[Mo(\eta\text{-}C_5H_4R)Cl_2O]$ (VIII, R=H), and $[(\eta\text{-}C_5H_4R)(O)\text{-}Mo(\mu\text{-}O)_2Mo(O)(\eta\text{-}C_5H_4R)]$ (IX, R=H) have been previously synthesised but in low yield.[3] Treatment of $[MoOCl_3]_n$ with TlC_5H_4R (R=H or Me) in tetrahydrofuran, followed by addition of HCl to the filtrate of the reaction mixture gave red crystalline (VII, R=H or Me) in *ca.* 40% yield. Treatment of (VII) with propylene oxide gave (VIII) quantitatively. Finally, slow hydrolysis of (VII) in water gave (IX) in *ca.* 50% yield.

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† Satisfactory elemental analyses were obtained for all new compounds.

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