Homoleptic Methyl Compounds of Rhodium and Iridium(III). *X*-Ray Crystal Structures of Tetramethylethylenediamine Lithium Hexamethyl-rhodate(III) and -iridate(III)

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The interaction of tetrahydrothiophen (tht) complexes, $MCl_3(tht)_3$, M = Rh, Ir, with methyl-lithium in Et_2O followed by addition of tetramethylethylenediamine (tmed) gives $[Li(tmed)]_3[M(Me)_6]$ as thermally and air sensitive crystals; the isostructural compounds have a slightly distorted octahedral MMe_6 core with three pairs of *cis*-methyl groups bridged by Li(tmed) units *via* $Li \cdots H_3C$ interactions; the symmetry of the MMe_6 core is lowered from O_h to D_3 by interaction of the MMe_6 core with the Li(tmed) units.

The first homoleptic alkyl species of the platinum group (8,9,10) metals, namely the tetramethylplatinate(II) and hexamethylplatinate(IV) species have been known for some time.[1] These very air and thermally sensitive species were characterised in solution by n.m.r., i.r., and Raman spectra, but no structural studies were made, although what was considered to be a pentamethylenediethylenetriamine (pmdt) complex, $[Li(pmdt)]_2[PtMe_6]$, was obtained as a solid. More recently pentahalogeno aryl anions of both Pd and Pt in oxidation states II and III have been well characterised by Usón and co-workers,[2] while the similar rhodium(III) pentafluorophenyl anion, $[Rh(C_6F_5)_5]^{2-}$, has been made and found to have a square pyramidal structure in the $[Ph_3P(CH_2Ph)]^+$ salt.[3]

We have synthesised the hexamethyl anions of rhodium and iridium, $[MMe_6]^{3-}$, as the tetramethylethylenediamine (tmed) lithium compounds and have determined their structures. Relatively few compounds having $[MMe_6]^{n-}$ units have been structurally characterised; *viz* $[Li(dioxan)]_3[Cr^{III}Me_6]$,[4] $[Li(tmed)]_3[Er^{III}Me_6]$,[5] $[Li(tmed)]_2[Mn^{IV}Me_6]$,[6] and $[Li(tmed)]_2[Zr^{IV}Me_6]$;[7] with the exception of the zirconium compound, which has a trigonal prismatic $ZrMe_6$ unit, the others have octahedral MMe_6 groups.

These rhodium and iridium compounds were made by the interaction of the tetrahydrothiophen (tht) complexes, $MCl_3(tht)_3$,[8] with six equivalents of methyl-lithium in diethyl ether at −78 °C; after warming to 0 °C the solution was filtered, then an excess of tmed added; reduction in volume

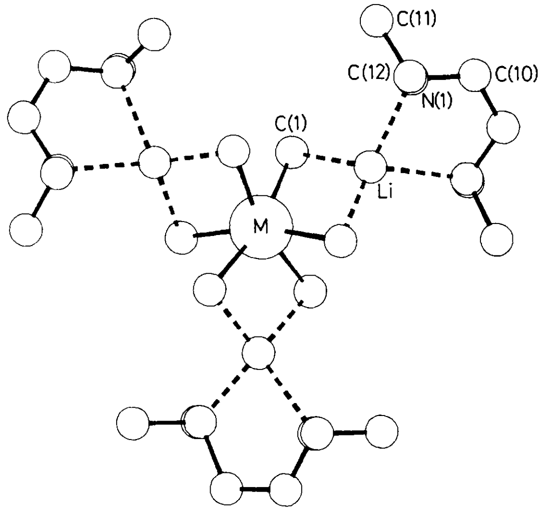

Figure 1. Molecular structure of $[\mathrm{Li(tmed)}]_3[\mathrm{MMe_6}]$, M = Rh, Ir.

and cooling to −30 °C gave high yields (*ca.* 92%) of the crystalline compound. Both compounds are very air sensitive and thermally unstable at temperatures above *ca.* 20 °C; it was not possible to obtain microanalyses.

The rhodium and iridium compounds, which are the first homoleptic alkyls of these elements, are isostructural[†] and comprise a slightly distorted $\mathrm{MMe_6}$ unit with three pairs of *cis* methyl groups bridged, as in similar species,[5—7] by Li(tmed) units *via* $\mathrm{Li \cdots H_3C}$ interactions (see Figure 1). The complete system has D_3 symmetry; the bridged Me–M–Me angles are 104.3(4)° (Rh) and 105.6(5)° (Ir), the M–C distances are 2.190(7) Å (Rh) and 2.164(10) Å (Ir) and the $\mathrm{Li \cdots C}$ distances are 2.13(1) Å (Rh) and 2.16(2) Å (Ir). The structure is analogous to that of the erbium complex[5] and comparable to that of $[\mathrm{Li(dioxan)}]_3[\mathrm{CrMe_6}]$[4] except that in the latter the Li co-ordination involves bridging dioxan molecules rather than chelating (tmed) ligands, as here.

A similar ruthenium complex has been obtained from $\mathrm{RuCl_3(tht)_3}$,[‡] and attempts are also being made to obtain structural data on the platinum and palladium compounds.[1] Reactions of the Rh, Ir, and Ru compounds will be described subsequently, but it may be noted that the rhodium compound with carbon monoxide gives the unusual octahedral rhodium(III) carbonyl *fac*-$\mathrm{Me_3Rh(CO)(tmed)}$, whose *X*-ray structure has been determined.

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8 E. A. Allen and W. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 613. Note that $\mathrm{RhCl_3(tht)_3}$ appears to be regarded as a new compound in ref. 3 where a similar preparation is reported.

[†] *Crystal data*: $\mathrm{C_{24}H_{66}Li_3N_6M}$, rhombohedral, space group $R\bar{3}c$, $Z = 6$. M = Rh; $M_r = 562.55$, $a = b = 16.303(3)$, $c = 24.590(4)$ Å, $U = 5660.1$ Å^3, $D_x = 0.99$ g cm^{-3}, $F(000) = 1104$, $\mu(\text{Mo-}K_\alpha) = 53.3$ cm^{-1}. M = Ir; $M_r = 651.85$, $a = b = 16.548(3)$, $c = 24.790(4)$ Å, $U = 5878.9$ Å^3, $D_x = 1.10$ g cm^{-3}, $F(000) = 1153$, $\mu(\text{Mo-}K_\alpha) = 43.6$ cm^{-1}. Intensity data were collected at 220 K using an Enraf Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) and an $\omega/2\theta$ scan. Structure solution was *via* the heavy atom method and refinement by least squares. Details are: M = Rh 726/1111 data $[F > 6\sigma(F)]$, $R = 0.044$, $R_w = 0.044$, weight $= [\sigma^2(F_o) + 0.001F_o^2]^{-1}$, 105 parameters. M = Ir 672/1153 data, $[F_o > 6\sigma(F_o)]$, $R = 0.032$, $R_w = 0.032$, 105 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] This new compound has correct analyses.