Pentamethyl- and Hexamethyl-platinate(IV)

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Summary Reactions of tetramethylbis(methyldiphenylphosphine)platinum(IV) or trimethylplatinum iodide with methyl-lithium in diethyl ether yield lithium hexamethyl platinate(IV); in the former case, pentamethyl(methyldiphenylphosphine)platinate(IV) is observed as an intermediate.

RECENTLY considerable success has been achieved in the synthesis of binary methyl derivatives and anionic permethyl complexes of the early transition metals.¹ The recent identification of Li[Me₄Au] in solution by spectroscopic techniques² and the isolation of thermally stable tetramethylaurate(III) compounds³ suggested that a number of co-ordinatively saturated methyl complexes of the later transition elements should exist.

We have observed a ready reaction between etherinsoluble $[(Me_3PtI)_4]$ and MeLi in Et₂O which yields quantitatively hexamethylplatinate(IV). Thus, $[(Me_3PtI)_4]$ dissolves in a solution of MeLi in Et₂O during 4 h at room temperature to yield a colourless, homogeneous solution. This result is in contrast to a report⁴ that $[(Me_aPtI)_4]$ and MeLi do not react in the poor donor solvent hexane.

The ¹H n.m.r. spectrum exhibits a singlet at τ 10.55 with singlet satellites ${}^{2}J({}^{195}\text{Pt-H}) 40.0 \text{ Hz} \{cf. \tau 8.27, J 76 \text{ Hz for}$ $[(Me_3PtI)_4]$ in CDCl₃ solution}. When the reaction is carried out in $(C_2D_5)_2O$ in the presence of 1 mol of PPh₃ per mol of [(Me₃PtI)₄], the ¹H n.m.r. spectrum initially shows two doublets at τ 10.32, ${}^{3}J({}^{31}P-H)$ 5.4 Hz, and 9.53, ${}^{3}J({}^{31}P-H)$ H) 6.7 Hz, intensity ratio of ca. 4:1; doublet satellites indicate ${}^{2}J({}^{195}\text{Pt-H})$ 41.4 Hz for the τ 10.32 resonance and 55.0 Hz for the τ 9.53 signal. These data indicate the formation of Li[Me₅PtPPh₃]. After 2 days, the τ 10.32 and 9.53 resonances had disappeared, and only the singlet at τ 10.55 was observed. Integration of this signal and its satellites relative to the PPh3 resonance shows that the τ 10.55 signal is due to 6 equivalent methyl groups per platinum.

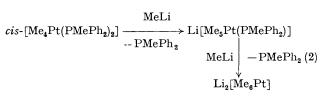
$$12 MeLi$$

$$[Me_{3}PtI]_{4} \longrightarrow 4 LiI + 4 Li_{2}[Me_{6}Pt]$$

$$8 MeLi \qquad 4 PPh_{3} \qquad (1)$$

$$4 Li[Me_{5}PtPh_{3}] + 4 LiI \longrightarrow 4 Li_{2}[Me_{6}Pt] + 4 PPh_{3}$$

When $[Me_4Pt(PMePh_2)_2]$ is treated with halide-free MeLi in Et₂O for 5 days, the ether-insoluble complex gradually dissolves, and the ¹H n.m.r. spectrum exhibits a doublet, τ 10.38, ${}^{3}J({}^{31}P-H)$ 6 Hz, with doublet satellites, ${}^{2}J({}^{195}Pt-H)$ 42 Hz; the resonance of the unique methyl is obscured by the intense Et₂O resonance centred at τ 8.88. If this solution is maintained at 50 °C in the presence of excess of MeLi, the doublet at τ 10.38 is replaced gradually by a singlet τ 10.52, ²J(¹⁹⁵Pt-H) 40 Hz. The absence of coupling to phosphorus indicates the formation of Li₂[Me₆Pt]. Observation of a separate MeLi resonance indicates that exchange between MeLi and the platinate(IV) species is slow.



These reactions are analogous to those used to produce Li[Me₄Au] by reaction of [Me₃AuPPh₃] or [KAuCl₄] with MeLi in Et₂O.^{2,3}

The high-field methyl resonance, τ 10.55, is characteristic of a completely methylated species, and the low coupling constant, ${}^{2}J({}^{195}\text{Pt-H}) 40.0 \text{ Hz}$, is to be expected for a complex with mutually trans methyl groups. Smith and his co-workers⁵ observed that the coupling depended mainly on the trans ligand, and the value for coupling to the mutually trans methyl groups of [Me₄Pt(PMePh₂)₂] is 43.1 Hz.

Raman spectra of solutions prepared from $[(Me_3PtI)_4]$ and MeLi are consistent with the presence of essentially octahedral Me₆Pt²⁻. The δ_s (Me) vibrations transform as $A_{1g} + E_g$, and bands are observed at 1250 pol., 1205 depol. The v(Pt-C) co-ordinates transform according to the same representation. An intense, polarized band is observed at 508 cm^{-1} , and a depolarized band at 505 cm^{-1} is almost accidentally degenerate with it. Coupling should be minimal because of the massive platinum atom. Consequently, these (Pt-C) stretches would be expected to occur at frequencies similar to those for the vibrations of the mutually trans methyl groups of [Me₄Pt(PMePh₂)₂]. This compound exhibits intense scattering at 503 cm^{-1} which can be assigned to in-phase stretching of the trans methyl groups.

Trimethylplatinum(IV) compounds were first reported⁶ in 1907, and tetramethylplatinum(IV) complexes were described in 1967,7 but the penta- and hexa-methylplatinate (IV) compounds had eluded detection so far.

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