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Preliminary communication

METHYLDIPLATINUM(I) COMPLEXES

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Summary

Methyldiplatinum(I) complexes of general formula $[Pt_2MeL(\mu\text{-dppm})_2]^+ [X]^-$ (dppm = $Ph_2PCH_2PPh_2$), have been prepared by oxidative addition of methyl iodide to $[Pt_2(\mu\text{-dppm})_3]$ or by reaction of $[Pt_2HMe(\mu\text{-H})(\mu\text{-dppm})_2] [SbF_6]$ with the ligand L.

Well characterised methyldiplatinum(III) complexes are known [1], as well as innumerable examples of methylplatinum-(II) and -(IV) complexes, but methylplatinum(I) complexes are apparently unknown. Attempts to prepare such compounds by treatment of the diplatinum(I) complex $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [2] (dppm = $Ph_2PCH_2PPh_2$), with methylating agents such as methyllithium were unsuccessful, giving only $[PtMe_2(dppm)]$ and the dimer $[Pt_2Me_4(\mu\text{-dppm})_2]$ [3] as isolable products. Several other methyldiplatinum(II) complexes containing the grouping $Pt_2(\mu\text{-dppm})_2$ are also known [4]. However, two routes to methyldiplatinum(I) complexes, one involving oxidation of a platinum(0) precursor and the other reduction of a platinum(II) precursor, have now been developed and the methyldiplatinum(I) complexes, once isolated, are shown to possess good thermal stability.

The simplest route involves oxidative addition of methyl iodide to $[Pt_2(\mu\text{-dppm})_3]$ [5], prepared in situ by treatment of $[Pt(PPh_3)_4]$ with 2 molar proportions of dppm in benzene solution. Even in the presence of excess of methyl iodide, only one mole reacts with the diplatinum complex under the conditions used, namely benzene at room temperature and the reaction is described by eq. 1.

Oxidative addition of MeI to $[Pd_2(dppm)_3]$ has been demonstrated earlier [6], but that reaction gave the palladium(II) complex cation $[Pd_2(\mu\text{-I})Me_2\text{-}$

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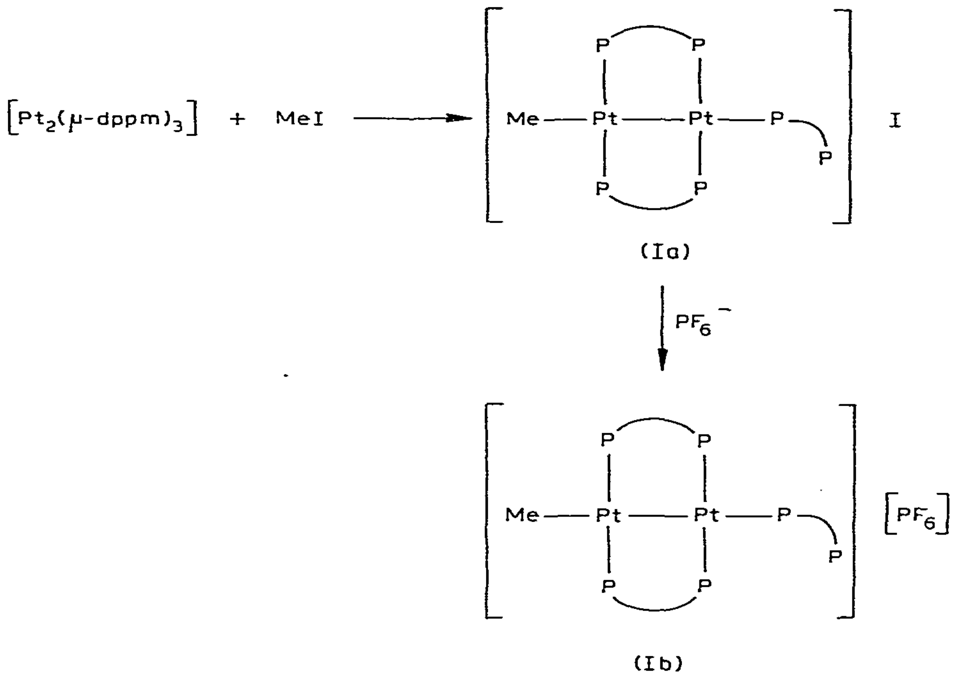
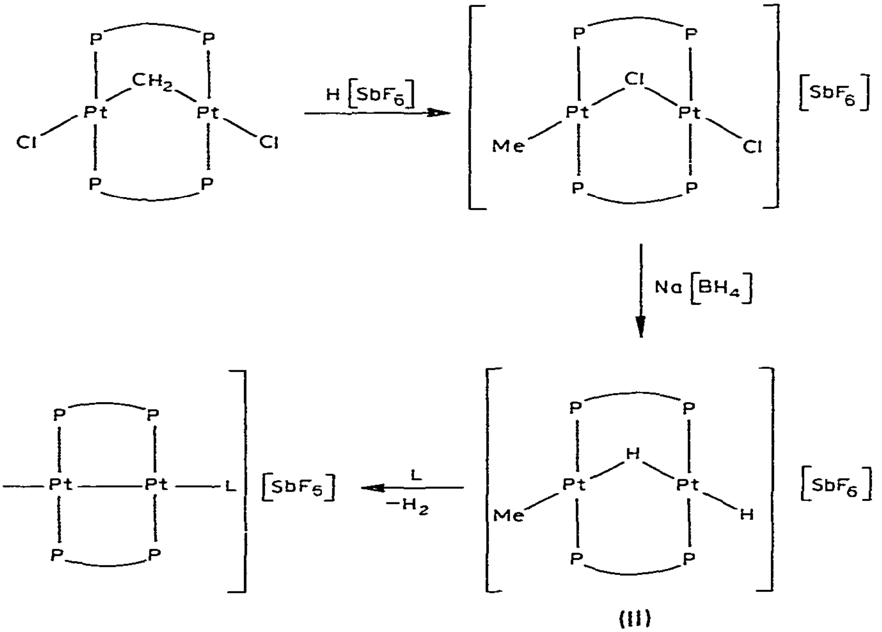


(1)



(2)

(Ic , L = η^1-dppm ;
Id , L = PPh_3 ;
Ie , L = PMe_2Pn ;
If , L = C_5H_5N)

(μ-dppm)$_2$]$^+$. In the present work, the complexes Ia and Ib were isolated in 94 and 68% overall yield respectively, as yellow crystalline solids. Reaction 1 was also carried out using pure recrystallised [Pt$_2$(μ-dppm)$_3$] and complex Ib was obtained in an overall yield of 76%.

The second route to methylplatinum(I) complexes is shown in eq. 2; it is considerably more lengthy but is of more general applicability than that of eq. 1.

The key step in this sequence is the binuclear reductive elimination of dihydrogen from complex II, which was prepared in two steps (eq. 2) from the known complex [Pt$_2$Cl$_2$(μ-CH$_2$)(μ-dppm)$_2$] [7]. The reactions with phosphine ligands to give complexes Ic—Ie occur thermally at room temperature, but pyridine does not induce the thermal reductive elimination so that complex If was prepared by the ready photolysis of complex II in pyridine solution. The reactions occur with reasonable selectivity as shown in eq. 2 but, in some cases, are complicated by a competing reaction leading to formation of CH$_4$ and the known hydridodiplatinum(I) complex cations [8] [Pt$_2$HL(μ-dppm)$_2$]$^+$. This complication was most prominent with the bulky ligand L = PPh$_3$, when about 20% of the hydridoplatinum complex was formed, but occurred to an extent of less than 10% in other cases. The thermal reactions to give Ic—Ie occur more slowly than the corresponding reactions of the complex [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$]$^+$, (III). Thus the second order rate constants for reaction of II and III with dppm in CH$_2$ClCH$_2$Cl were 0.22 l mol^{-1} s^{-1} (at 27°C) and 10.9 l mol^{-1} s^{-1} (at 21°C) respectively [9].

The new methyldiplatinum(I) complexes are yellow crystalline solids, which were characterised by elemental analysis and by the very characteristic ^{1}H and ^{31}P{^{1}H} NMR spectra. Details of characterisation will be given in our full paper, but it is worth noting here that the spectra are, in most respects, similar to those of the corresponding hydridodiplatinum(I) complexes [8], except that a methylplatinum signal replaces a hydridoplatinum signal (e.g. Ie in CD$_2$Cl$_2$: δ(MePt) −0.14 ppm, ^2J(PtH) 59, ^3J(PH) 6.4, ^4J(*H*—*P*Me$_2$Ph) 2.3 Hz; Id in CD$_2$Cl$_2$: δ(MePt) −0.05 ppm, ^2J(PtH) 59.6, ^3J(PH) 6.6, ^4J(*H*—*P*Ph$_3$) 2.4 Hz). In the ^{31}P{^{1}H} NMR spectrum of complex Ib at −80°C, separate signals due to the non-equivalent phosphorus atoms, PtP^A—P^B, of the η^1-dppm ligand were observed (δ(P^A) 23.4 ppm, ^1J(PtP) 2017, ^2J(PtP) 435, ^2J(P^{A}P^B) 90, ^2J(P^{A}Pdppm) 14 Hz; δ(P^B) −31.9 ppm) with a large coupling ^2J(P^{A}P^B) but in the room temperature spectrum this coupling was absent although the separate signals due to P^A and P^B were still observed. This loss of coupling is attributed to the onset of a fluxional process, possibly involving P^A for P^B exchange [8], and is similar to that observed also for [Pt$_2$H(η^1-dppm)(μ-dppm)$_2$]$^+$.

The chemistry of these, and related, alkyldiplatinum(I) complexes may be expected to model the chemistry of alkyl groups on a platinum metal surface during catalysis and is under active investigation.

Acknowledgments

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