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Preliminary communication

Formation of unsymmetrical *cis*-dialkyls of platinum(II) from platinum(II) hydroxo-complexes

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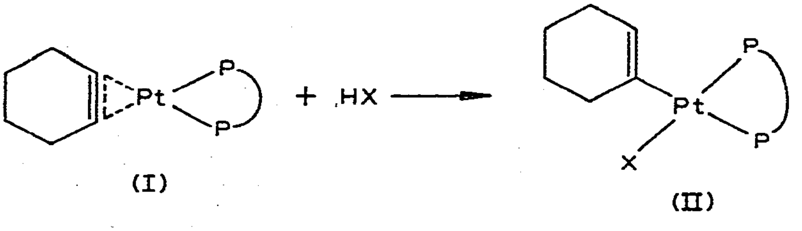
SUMMARY

The (hydroxo) methyl complex Pt(OH)(CH_3)(Diphos) [Diphos = $Ph_2PCH_2CH_2PPh_2$] reacts with compounds containing acidic C–H bonds (HX) to give unsymmetrical *cis*-dialkyls of general formula Pt(CH_3)X(Diphos) [X = CH_2COCH_3, $CH(COCH_3)_2$, CH_2CN or CH_2NO_2]; both the methyl and the cyclohexenyl complexes Pt(OH)R(Diphos) (R = CH_3 or C_6H_9) insert carbon monoxide to give hydroxycarbonyl complexes PtR(CO_2H)(Diphos) which are remarkably stable to decomposition by β-elimination.

An outstanding feature of the chemistry of the platinum(0)–cyclohexyne complex (I) is the ease with which it is protonated, not only by strong acids such as HCl and CF_3CO_2H[1], but by weak protonic acids such as water, methanol, acetone, acetophenone and nitromethane to give stable platinum(II)-cyclohexenyls (II)[2]*. We now find that a similar series of compounds containing methyl in place of cyclohexenyl can be



X = OH, OCH_3, CH_2COCH_3,
$CH_2COC_6H_5$, or CH_2NO_2

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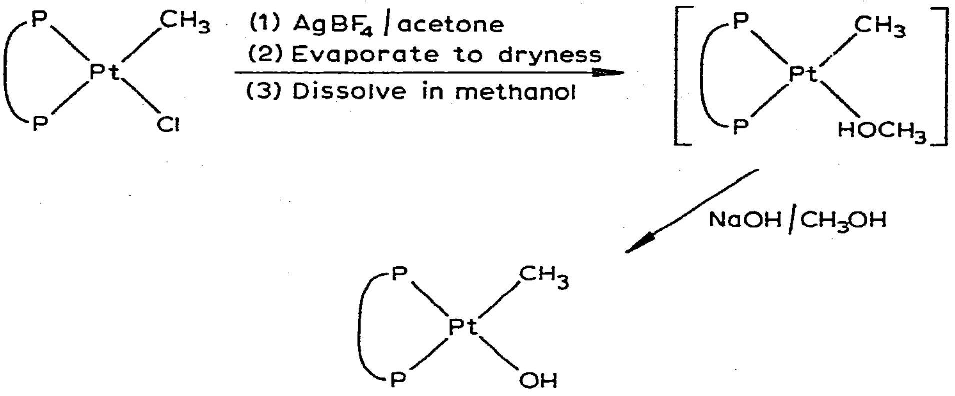
[*] Abbreviations: $\widehat{PP}$, Diphos = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; C_6H_9 = cyclohexenyl; Salen = *N,N'*-ethylenebis(salicylideneiminato)

made starting from the (hydroxo) methyl complex, Pt(OH)(CH_3)(Diphos) (III), prepared as outlined in Scheme 1. (III) is a colourless, air-stable solid which is very soluble in

Scheme 1



dichloromethane and methanol. It reacts with chloroform at room temperature, and less rapidly with dichloromethane, to give PtCl(CH_3)(Diphos) and with a variety of weakly acidic hydrocarbon compounds, *e.g.* acetone, acetylacetone, acetonitrile or nitromethane, according to the equation:

$$\mathrm{Pt(OH)(CH_3)(Diphos) + HX \xrightarrow{25^\circ} PtX(CH_3)(Diphos) + H_2O}$$
$$\mathrm{X = CH_2COCH_3,\ CH(COCH_3)_2,\ CH_2CN,\ CH_2NO_2}$$

These reactions probably do not proceed via ionic intermediates of the type [Pt(CH_3)(HX)(Diphos)]OH, because although the hydroxo-ligand is readily replaced by anionic ligands such as Cl^- or NCO^-, it resists substitution by neutral ligands such as pyridine. Moreover, the cation $[Pt(CH_3)(NCCH_3)(Diphos)]^+$ undergoes hydroxide ion attack at the coordinated nitrile to give the *N*-bonded amido-complex Pt(CH_3)($NHCOCH_3$)(Diphos) [*] (also formed from (III) and acetamide), whereas (III) with acetonitrile gives exclusively the C-bonded product Pt(CH_3)(CH_2CN)(Diphos).

The nitromethyl complexes PtR(CH_2NO_2)(Diphos) (R = CH_3 or C_6H_9) are unaffected on heating in toluene, but in refluxing nitromethane they lose water to give the fulminato-complexes PtR(CNO)(Diphos)[**].

The hydroxo-complexes (II) and (III) react with carbon monoxide at 25°/1 atm in dichloromethane to give the first known hydroxycarbonyl complexes of platinum(II), PtR(CO_2H)(Diphos) [R = CH_3 (IV) or C_6H_9 (V)][***]. An analogous methoxycarbonyl

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[*] *cf.* Attack of methanol on coordinated perfluoroarylnitriles to give Pt–NH=C(OCH_3)–ArF[3].

[**] *cf.* Reaction of Pt(PPh_3)$_4$ with nitromethane to give *trans*-Pt$(CNO)_2(PPh_3)_2$[4].

[***] A related iridium (III) hydroxycarbonyl complex, $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$ is known[5].

complex can be made by insertion of CO into the Pt—OCH_3 bond of $Pt(OCH_3)(C_6H_9)$-(Diphos)[6]. It is worth noting for comparison that the reaction of either *trans*-$PtCl(CO_2CH_3)(PEt_3)_2$ or *trans*-$[PtCl(CO)(PEt_3)_2]^+$ with water gives *trans*-$PtHCl(PEt_3)_2$[7], which is presumably formed in both cases by spontaneous decarboxylation of an intermediate hydroxycarbonyl $PtCl(CO_2H)(PEt_3)_2$. In contrast, both (IV) and (V) are stable in the solid state and in their solutions in dichloromethane or chloroform. This reluctance to undergo β-elimination appears to be characteristic of σ-bonded organo-substituents X in the series PtXR(Diphos) (R = CH_3 or C_6H_9) *cf.* the stability of $Pt(OCH_3)(C_6H_9)$(Diphos)[2].

Remarkably, on heating the (hydroxo) cyclohexenyl complex (II) in methanol, a CO group is abstracted to give (V). Under the same conditions, the (hydroxo) methyl complex (II) gives an orange precipitate which, from analytical and molecular weight data, appears to be a tetranuclear cluster complex $[Pt(Diphos)]_4$; the hydroxycarbonyl complex (IV) is not an intermediate in this process, since on prolonged heating in methanol it gives the methoxycarbonyl complex $Pt(CH_3)(CO_2CH_3)$(Diphos) as a major product.

The chemistry of platinum(II) hydroxo-complexes bears a striking similarity to that of hydroxo-derivatives of vitamin B12 analogues *e.g.* $Co(OH)(H_2O)$(Salen), which readily form stable Co—C σ-bonded complexes on treatment with acetone, acetonitrile or nitromethane[8], and react with carbon monoxide to give unstable Co—CO_2H compounds[9]. This is therefore another instance of the qualitative similarity in properties of cobalt(III) in vitamin B12 analogues and platinum(II) in tertiary phosphine complexes[10].

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