

Simple, High Yield Syntheses of Heterobimetallic Complexes of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) with Platinum, Mercury, and Silver

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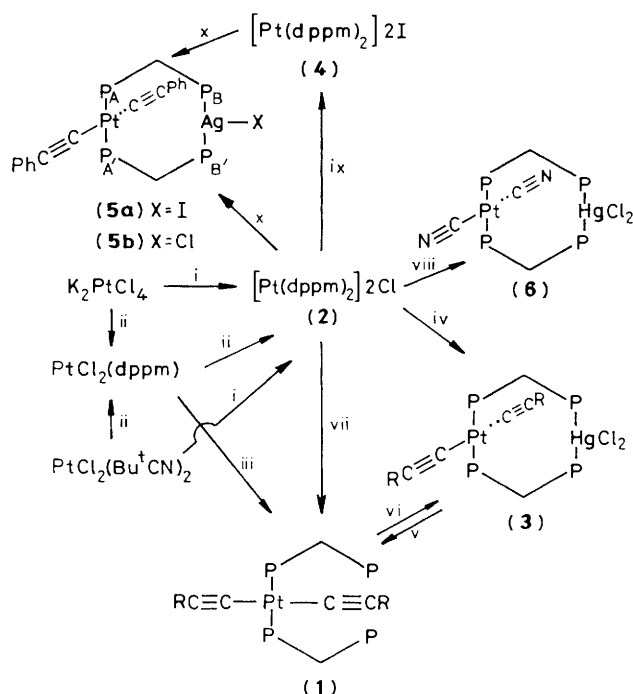
Treatment of the readily available salts $[\text{Pt}(\text{dppm})_2]2\text{X}$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with (i) $\text{Hg}(\text{C}\equiv\text{CR})_2$ or (ii) $\text{Hg}(\text{OAc}) + \text{RC}\equiv\text{CH}$ or (iii) $\text{Hg}(\text{CN})_2$ gives virtually quantitative yields of $\text{Y}_2\text{Pt}(\mu\text{-dppm})_2\text{HgX}_2$ ($\text{Y} = \text{C}\equiv\text{CR}$ or $\text{C}\equiv\text{N}$, $\text{R} = \text{Ph}$, *p*-tolyl, Me, or Pr^n , $\text{X} = \text{Cl}$) and, with $\text{AgOAc} + \text{PhC}\equiv\text{CH}$, high yields of $(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{AgX}$ ($\text{X} = \text{Cl}$ or I).

We have described how the fluxional complexes of type *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-dppm})_2]^+$ (**1**) (see Scheme 1) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) can be prepared and used in the synthesis of diplatinum and heterobimetallic complexes with rhodium, iridium, tungsten, silver, gold, cadmium, or mercury.^{2,3} We now describe some syntheses of heterobimetallic complexes and η^1 -dppm complexes which are 'one pot' syntheses, remarkable for their specificity and convenience.

The salt $[\text{Pt}(\eta^2\text{-dppm})_2]2\text{Cl}$ (**2**) is well known and very easily made in essentially quantitative yield (see Scheme 1). We now find that this salt (**2**), when treated in ethanol (or CH_2Cl_2) solution with 1 mol. equiv. (or more) of a mercury acetylide, $\text{Hg}(\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{Ph}$, *p*-tolyl, Me, or Pr^n) is rapidly converted into a heterobimetallic complex (**3**). Conversion is rapid, even at 0 °C, and in ethanol as reaction solvent the product crystallizes out in high yield, viz. 91% ($\text{R} = \text{Ph}$), 82% ($\text{R} = p\text{-tolyl}$), 89.5% ($\text{R} = \text{Me}$), and 74% ($\text{R} = \text{Pr}^n$). A ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopic study on the reaction solution in $(\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2)$ shows that the conversion is quantitative and usually no other phosphorus-containing products can be detected, e.g. the spectrum for $\text{R} = \text{Ph}$ is identical to that of the pure complex (**3**) ($\text{R} = \text{Ph}$) which we have previously prepared.² We also find that treatment of a dichloromethane solution of (**3**) ($\text{R} = \text{Ph}$) with 1 mol. equiv. of sodium sulphide in ethanol gives a precipitate of mercuric sulphide and the pure η^1 -dppm complex (**1**) ($\text{R} = \text{Ph}$)¹ is isolated in 88% yield.

This route is particularly useful for the synthesis of the methylacetylide complex (**1**) ($\text{R} = \text{Me}$), in a yield of 73% from (**3**) ($\text{R} = \text{Me}$), since methods involving $\text{LiC}\equiv\text{CMe}$ give poorer yields¹ (see Scheme 1). Since mercury acetylides, $\text{Hg}(\text{C}\equiv\text{CR})_2$ are readily made and will tolerate a variety of functional groups, R , these novel, high yield, syntheses of complexes of types (**3**) and (**1**) should be very useful. Moreover, we have subsequently found that the mercury acetylide complex can be formed *in situ*. Thus when an ethanol solution of the salt (**2**) was added to the solution formed by treating mercuric acetate with phenylacetylene in ethanol, the required complex (**3**) ($\text{R} = \text{Ph}$) crystallized out in 88% yield [the solid reactants were in equivalent, molar amounts and the phenylacetylene was in slight (5%) excess]. Moreover, addition of 2.1 mol. equiv. of phenylacetylene to a suspension of mercuric acetate in CDCl_3 , followed by addition of the equivalent amount of the salt (**2**) gives a clear solution. A ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of this solution showed that conversion of (**2**) into (**3**) ($\text{R} = \text{Ph}$) was quantitative and rapid at 20 °C, i.e. complete in a few minutes. No other phosphorus-containing species could be detected. A similar result was obtained with methylacetylene.

We have done similar work with silver. The salt (**2**) is easily converted into the corresponding and less soluble diiodide (**4**) by treatment with a large (ca. 20-fold) excess of sodium iodide in ethanol. On heating this salt under reflux



Scheme 1. Some interconversion reactions of η^1 -, η^2 -, and μ -dppm complexes of platinum and syntheses of heterobimetallic complexes with mercury and silver. i, 2 mol dppm in ethanol; ii, 1 mol dppm in ethanol; iii, 1 mol dppm, 2 mol $\text{RC}\equiv\text{CLi}$ in tetrahydrofuran (THF)-benzene; yields 35–50% for $\text{R} = \text{Ph}$, *p*-tolyl, or Me (ref. 1); iv, 1 mol $\text{Hg}(\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{Ph}$, *p*-tolyl, Me, or Pr^n) in ethanol, or 1 mol $\text{Hg}(\text{OAc})_2 + \text{PhC}\equiv\text{CH}$ in ethanol; v, 1 mol Na_2S in ethanol added to solution of complex in CH_2Cl_2 ; vi, 1 mol HgCl_2 in THF (ref. 2); vii, 2 mol $\text{PhC}\equiv\text{CLi}$ in THF-benzene; the yield is 38%, the other products contain deprotonated dppm ligands; viii, $\text{Hg}(\text{CN})_2$ in ethanol; ix, an excess of NaI in ethanol; x, 2.15 mol $\text{AgOAc} + 2.4$ mol $\text{PhC}\equiv\text{CH}$ in CH_2Cl_2 .

with 2.15 mol. equiv. of silver acetate and 2.4 mol. equiv. of phenylacetylene in dichloromethane for 1 h and filtering off the silver iodide, the previously prepared platinum-silver complex (5a)² was readily isolated from the solution in yields

of ca. 70%. This complex was characterized previously by its crystal structure² but we did not record its low temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. We now find that at -50°C the coupling of ^{31}P to ^{107}Ag and ^{109}Ag can be identified whereas we were unable to do this for the salt $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ag}]\text{PF}_6$.² For (5a) at -50°C in CDCl_3 $\delta(\text{P}_A)$ 13.3 p.p.m., $^1J(\text{PtP}_A)$ 2534 Hz, $\delta(\text{P}_B) - 11.7$ p.p.m., $^1J(^{107}\text{AgP}_B)$ 364 Hz, $^1J(^{109}\text{AgP}_B)$ 422 Hz, $^3J(\text{PtP}_B)$ 166 Hz, and $^2J_{AB} + ^4J_{AB'}$, 93 Hz. We find that similar treatment of the chloride salt (2) with silver acetate and phenylacetylene in boiling dichloromethane gives the platinum-silver chloride complex (5b), which also gives a well defined $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum at -50°C .

We have also treated the salt (2) with 1 mol. equiv. of mercuric cyanide in warm ethanol solution. The previously described⁴ μ -dppm complex *trans*- $[\text{Pt}(\text{CN})_2(\mu\text{-dppm})_2\text{HgCl}_2]$ (6) crystallized out in 86% yield and was shown to be identical with an authentic sample by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy.

Preliminary ($^{31}\text{P}\{-^1\text{H}\}$ n.m.r.) studies⁵ show that the Pt-Ag and Pt-Hg acetylide complexes described in this communication, when treated with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$, $[\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4]$, or $[\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ give the heterobimetallic Pt acetylide-Rh, -Ir, or -W complexes, of the types we have previously described,³ in good yield, *i.e.* Ag or Hg are readily displaced by Rh, Ir, or W (transmetallation).

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