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Transmetallation as a New Route to Heterobimetallic μ-$Ph_2PCH_2PPh_2$ Complexes

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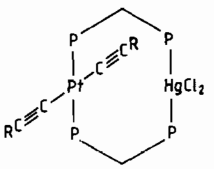
We have previously described simple, high yielding syntheses of heterobimetallic complexes of the types $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (*1*) or $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgX]$ (*2*) (R = alkyl or aryl, X = Cl or I), remarkable for their specificity [1]. We now find that d^{10}-metals, especially Hg(II) or Ag(I), can be readily displaced by other metals (transmetallation), *e.g.* by Rh(I), Ir(I), W(0), Mo(0) or Cr(0): the overall syntheses are usually very convenient and high yielding (see also following Letter).

Thus, treatment of (*1*) (R = Ph) with $[Rh_2Cl_2(CO)_4]$ in $CDCl_3$ at *ca.* 20 °C gives the previously described $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$ [2]. Reactions are essentially completed on mixing and no other phosphorus-containing products are detected (^{31}P-$\{^1H\}$ NMR evidence). Treatment of the platinum–gold complex $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$ [3] with $[Rh_2Cl_2(CO)_4]$ similarly gave $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$, but conversion was slower ($t_{1/2} \sim 5$ minutes in $CDCl_3$ at +50 °C).



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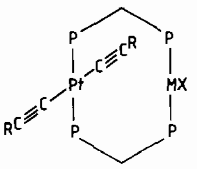

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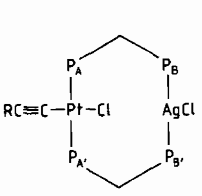

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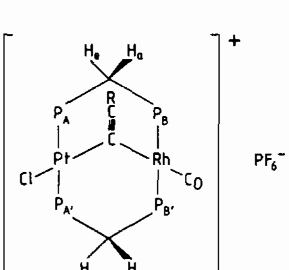

(4)

We have also investigated the possibility of using copper complexes (cuprates) in such reactions. Treatment of $[Pt(dppm)_2]2Cl$ with $LiCu(C{\equiv}CPh)_2$ (prepared *in situ* from CuI in THF at *ca.* 0 °C) gave a pale yellow solid which, from its ^{31}P-$\{^1H\}$ spectrum (at 40.25 or 161 MHz), appeared to be a single substance of type (*2*) (R = Ph, M = Cu, X = I). Although not obtained analytically pure, when treated with $[Rh_2Cl_2(CO)_4]$ in $CDCl_3$ at 20 °C this platinum–copper complex was completely converted into $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]^+$ (^{31}P-$\{^1H\}$ NMR evidence) and no other phosphorus-containing species could be detected.

Since these and previously described reactions are so specific we attempted a 'one pot' conversion of $[Pt(\eta^2\text{-dppm})_2]2Cl$ to $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]^+$ with the following steps:

$$[Pt(\eta^2\text{-dppm})_2]2Cl \rightarrow [(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$$
$$\rightarrow [(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$$

A solution of $[Pt(\eta^2\text{-dppm})_2]2Cl$ was treated with a mixture of 1.5 mol $Hg(OAc)_2$ and 3 mol of $PhC{\equiv}CH$ and after 10 minutes at 20 °C $[Rh_2Cl_2(CO)_4]$ (0.5 mol) was added. This gave the pure salt $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$ in 71% yield.

We have previously shown that $[(PhC{\equiv}C)_2Pt(\eta^1\text{-dppm})_2]$ reacts with $[Ir_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclo-octene) to give $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2IrCl]$ but this was difficult to separate from some of the diplatinum complex $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Pt(C{\equiv}CPh)_2]$ [2]. We now find that this platinum–iridium complex is better prepared by transmetallation since $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgI]$ reacts with $[Ir_2Cl_2(C_8H_{14})_4]$ in $CDCl_3$ to give it as the sole phosphorus-containing product (^{31}P-$\{^1H\}$ NMR evidence); none of the diplatinum, nor other species, could be detected.

All our previous work with binuclear μ-dppm platinum acetylides has involved two mutually *trans* acetylides per platinum. We anticipated that to do similar work with one acetylide per platinum might be difficult. However, we now find that treatment of $[Pt(\eta^2\text{-dppm})_2]2Cl$ in acetone with AgOAc (1 mol) + $HC{\equiv}CR$ (1.1 mol or excess) (R = Me, Ph or *p*-tolyl) gave good (73–83%) yields of $[(RC{\equiv}C)ClPt(\mu\text{-dppm})_2AgCl]$ (*3*), as pale yellow, crystalline complexes. Either the acetylide or the chloride ligand might bridge the two metals but we have not shown this in structure (*3*). The structures follow from microanalytical data, the absence of electrical conductivity in nitromethane, the IR spectra and particularly the ^1H-$\{^{31}P\}$ and ^{31}P-$\{^1H\}$NMR spectra. In the ^{31}P-$\{^1H\}$ NMR spectra the couplings $^1J(^{107}AgP_B)$ and $^1J(^{109}AgP_B)$ are clearly

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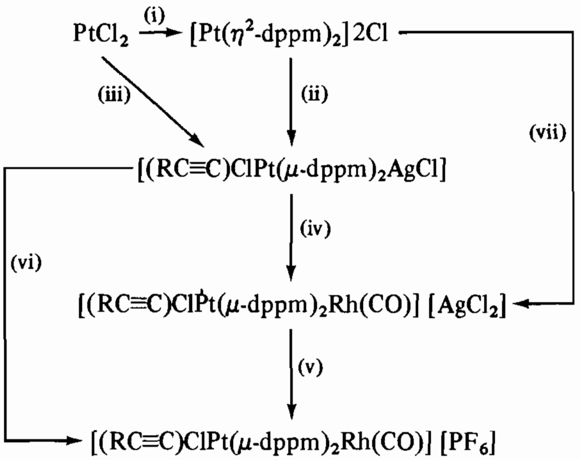

Scheme 1. Some reactions of platinum, platinum–silver and platinum–rhodium complexes, including transmetallation.

(i) $PtCl_2$ + dppm (2 mol) in boiling acetone (5 h). Yield *ca.* 100%.

(ii) AgOAc (1 mol) + RC≡CH (≥1.1 mol) in acetone (20 °C, 2 h). Yields 72–80%.

(iii) Dppm (2 mol) in boiling acetone (5 h) then AgOAc (1 mol) + PhC≡CH (1.1 mol) added. Stirred 3 h at 20 °C. Yield 83%.

(iv) $[Rh_2Cl_2(CO)_4]$ (0.5 mol) stir. 30 min in acetone at 20 °C. Yields 60–86%.

(v) Excess of NH_4PF_6 in acetone.

(vi) $[Rh_2Cl_2(CO)_4]$ (0.5 mol) for 30 min in acetone at 20 °C then add NH_4PF_6 (10 mol) in acetone. Yields 74–84%.

(vii) As for (ii), followed by (iv), in one pot. Yields 31–40%.

resolved at 20 °C {contrast with the corresponding diacetylides $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ which show broad resonances due to P_B at 20 °C but sharp ones at −40 °C} [1, 3]. For R = Ph the data are ($CDCl_3$): δP_A = 15.5 ppm, $^1J(PtP_A)$ = 2586 Hz, δP_B = −11.1 ppm, $^1J(^{107}AgP_B)$ = 394 Hz, $^1J(^{109}AgP_B)$ = 457 Hz, $^3J(PtP_B)$ = 200 Hz, $^2J(P_AP_B) + {}^4J(P_AP_{B'})$ = 90 Hz. We also find that these platinum–silver compounds of type (*3*) readily undergo transmetallation when treated with the equivalent amount of $[Rh_2Cl_2(CO)_4]$. The products $[(RC{\equiv}C)ClPt(\mu\text{-dppm})_2Rh(CO)]$ $[AgCl_2]$ are salts of the anion $AgCl_2^-$, but are readily converted to the corresponding PF_6^- salts, when treated with an excess of NH_4PF_6 in acetone: see Scheme 1 for details. The NMR data for the platinum–rhodium complex (*4*) (R = Me) in CD_2Cl_2 are: $^{31}P\text{-}\{^1H\}$, δP_A = 0.7 ppm, $^1J(PtP_A)$ = 2383 Hz, δ_{PB} = 19.9 ppm, $^1J(RhP_B)$ = 115 Hz, $^2J(P_AP_B) + {}^4J(P_AP_{B'})$ = 34 Hz. $^1H\text{-}\{^{31}P\}$: $\delta(CH_3)$ = 0.69 ppm, $^4J(PtH)$ = 16 Hz, $^4J(RhH)$ = 1.8 Hz; the CH_2 hydrogens are non-equivalent, δH_e = 3.52 ppm, $^3J(PtH_e)$ = 89 Hz, $^3J(RhH_e)$ = 1.5 Hz, δH_a = 4.29 ppm. H_a showed no detectable coupling to platinum (see ref. 2). The $^1H\text{-}\{^{31}P\}$ NMR results indicate strongly that the C≡CR group in (*4*) is bridging both metals.

Preliminary $^{31}P\text{-}\{^1H\}$ NMR studies show that these platinum–silver mono-acetylide complexes of type (*3*) when treated with $[Ir_2Cl_2(C_8H_{14})_4]$ undergo transmetallation to give deep green platinum–iridium species, probably of type $[(RC{\equiv}C)ClPt(\mu\text{-dppm})_2\text{-}IrCl]$; the diacetylides are also green [2].

For convenience the platinum–silver and platinum–rhodium mono-acetylide chemistry is summarised in the reaction Scheme including some convenient 'one pot' syntheses. We anticipate that these mono-acetylide complexes will generate some interesting chemistry since in complexes of type $[PtR'(C{\equiv}CR)(PR''_3)_2]$ the acetylide ligand is readily converted into carbenes *etc.* [4, 5].

Acknowledgements

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