

Systematic Syntheses of Heterobimetallic Complexes of Platinum with Rhodium(I), Iridium(I), Iridium(III), or Tungsten(0) bridged by $\text{Ph}_2\text{PCH}_2\text{PPh}_2$

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Complexes of type $\text{trans}-[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ (R = Me, Ph, or *p*-tolyl), are used to effect systematic, high-yield syntheses of heterobimetallic complexes with Rh^{I} , Ir^{I} , Ir^{III} (bridging hydride), and W^0 .

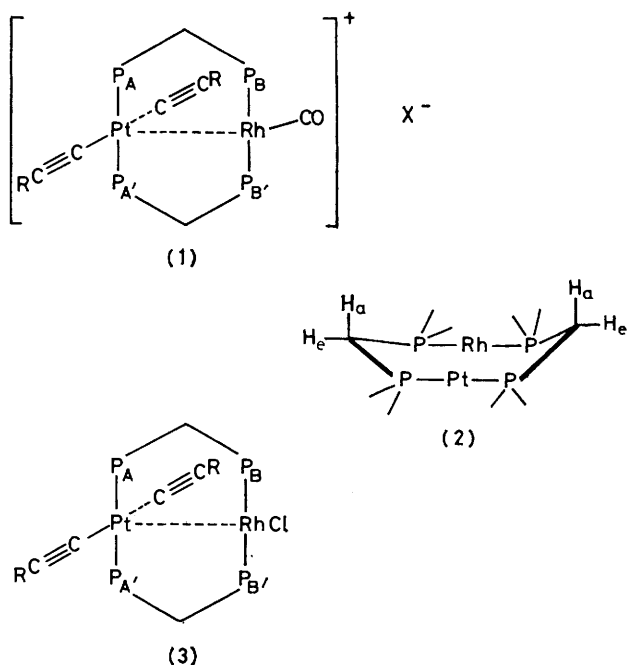
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ is an excellent ligand for stabilizing homobimetallic compounds with metal-metal bonds,¹ 'A-frames',² and 8-membered rings.^{3,4} Hitherto very few such complexes with two different metals ('heterobimetallic' complexes) have been made and methods which give homobimetallic complexes will not normally be adaptable for the synthesis of heterobimetallic complexes.

We have described high-yield syntheses of η^1 -dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) complexes, $\text{trans}-[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-dppm})_2]$, with R = Me, Ph, or *p*-tolyl.⁵ We now show that these η^1 -dppm complexes can be used in high-yield syntheses of hetero-

bimetallic complexes with d^8 - or d^6 -metals, *viz.* Rh^{I} , Ir^{I} , Ir^{III} , and W^0 .

Treatment of $\text{trans}-[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-dppm})_2]$ (R = Me, Ph, or *p*-tolyl) with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ in benzene at *ca.* 50 °C for 15 min gave the orange salts $[\text{Pt}(\text{C}\equiv\text{CR})_2(\mu\text{-dppm})_2\text{Rh}(\text{CO})]^{+}\text{Cl}^{-}$ in >90% yield. We formulate these complexes as (1) (X = Cl) on the basis of (i) microanalytical data; (ii) the conductivity in acetone of the Cl or PF_6 salts (1) (X = Cl or PF_6), corresponding to 1:1 electrolytes; (iii) the second-order ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum, shown in Figure 1; (iv) the ^1H and ^1H - $\{^{31}\text{P}\}$ n.m.r. spectra which show fluxionality at 20 °C, *i.e.* a broad CH_2

resonance, but at -21°C the CH_2 resonance shows inequivalent hydrogens, one showing large coupling to ^{195}Pt , $^3J(\text{PtH})$ 76 Hz, and the other not showing detectable coupling; (v) the $^{195}\text{Pt}\{-^1\text{H}\}$ n.m.r. pattern ($\text{R} = p\text{-tolyl}$) which shows a well defined 1:2:1 triplet of doublets corresponding to $^1J(\text{PtP})$ 2405 Hz, $J(\text{PtRh})$ 65 Hz, and $^3J(\text{PtP})$ ca. 0 Hz; (vi) the i.r. spectrum [*e.g.* for $\text{R} = p\text{-tolyl}$], $\nu(\text{C}=\text{O})$ 1978 cm^{-1} and $\nu(\text{C}\equiv\text{C})$ 2118 and 2060 cm^{-1} (KBr disc). We suggest the presence of a donor-acceptor rhodium-platinum bond in these complexes



(1) by analogy with $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$,⁶ also $d^8\text{-}d^8$; the observation of $^{103}\text{Rh}\text{-}^{195}\text{Pt}$ coupling agrees with this formulation. We also suggest that the single hydrogen of the CH_2 that is coupled to platinum in a $\text{Pt}\text{-PPh}_2\text{-C-H}$ moiety is pseudo-equatorial as depicted in (2). The $\text{Pt}\text{-PPh}_2\text{-C-H}_e$ dihedral (torsion) angle of 180° might be expected to give a much larger vicinal coupling, $^3J(\text{PtH}_e)$, than the corresponding coupling to the axial hydrogen, by analogy with the well known Karplus relationship for H-C-C-H couplings.⁷ The phenomenon should be useful in assigning stereochemistry (conformation) of binuclear platinum complexes of $\text{Ph}_2\text{PCHRPPH}_2$ *etc.* ($\text{R} = \text{substituent}$).

When heated in boiling toluene for 3 h the salt (1) ($\text{X} = \text{Cl}$, $\text{R} = p\text{-tolyl}$) lost CO and was converted into a single, deep red, complex which we formulate as (3) ($\text{R} = p\text{-tolyl}$). Complex (3) was stable in boiling toluene for 10 h [$^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. evidence]. When treated with carbon monoxide in toluene at 20°C (3) ($\text{R} = p\text{-tolyl}$) rapidly gave the orange salt (1) ($\text{X} = \text{Cl}$) in essentially quantitative yield. Treatment of $[\text{Rh}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4](\text{C}_8\text{H}_{14} = \text{cyclo-octene})$ with $[\text{Pt}(\text{C}\equiv\text{C}\text{-}p\text{-tolyl})_2(\eta^1\text{-dppm})_2]$ also gave (3).

Treatment of *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ with $[\text{Pt}(\text{C}\equiv\text{C}\text{-}p\text{-tolyl})_2(\eta^1\text{-dppm})_2]$ in refluxing benzene gave, after 5 min, a deep purple solution which paled to red after 1 h. From the solution the yellow neutral complex, $[\text{Pt}(\text{C}\equiv\text{C}\text{-}p\text{-tolyl})_2(\mu\text{-dppm})_2\text{IrCl}(\text{CO})]$ (4) was isolated in $>80\%$ yield. The formulation follows from microanalytical, i.r., and n.m.r. data as for the rhodium complexes (above). We have not identified the purple intermediate. Treatment of $[\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4]$ with $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\eta^1\text{-dppm})_2]$ (1:1 proportion) in C_6H_6 at 20°C gave the dark green neutral complex $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{-IrCl}]$ (5) (fully characterized). This reacted rapidly with H_2 (1 atm) to give a yellow dihydride $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{IrHCl}]$ (6). This structure is based on elemental analysis (C, H, Cl), the i.r. and $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra, and particu-

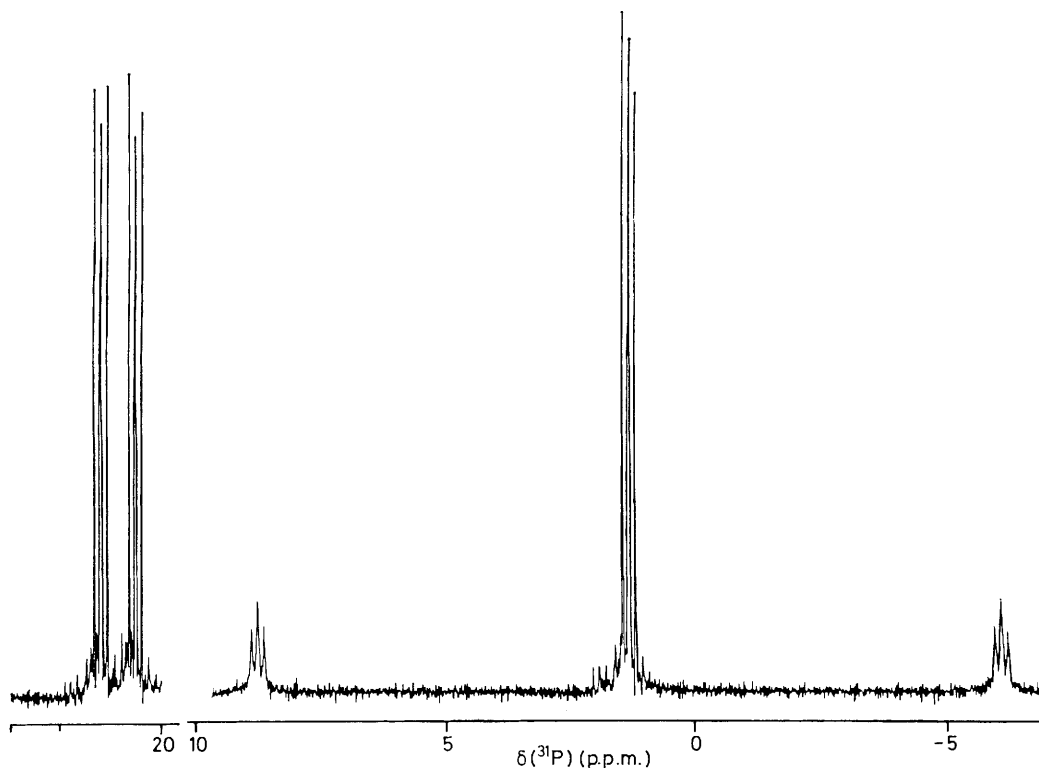
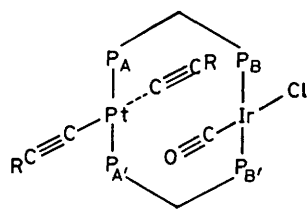
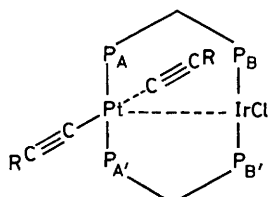


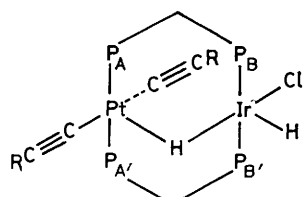
Figure 1. $^{31}\text{P}\text{-}\{^1\text{H}\}$ N.m.r. spectrum (161 MHz) of $[\text{Pt}(\text{C}\equiv\text{C}\text{-}p\text{-tolyl})_2(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{Cl}$ in CDCl_3 at 20°C . $\delta(\text{P}_A)$ (platinum) 1.2 p.p.m., $^1J(\text{PtP}_A)$ 2357 Hz, $\delta(\text{P}_B)$ (rhodium) 20.2 p.p.m., $^1J(\text{RhP}_B)$ 112 Hz, $J(\text{P}_A\text{P}_B) + J(\text{P}_A\text{P}_B')$ 43 Hz.



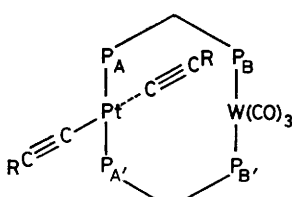
(4)



(5)



(6)



(7)

larly the ^1H and $^1\text{H}\{-^{31}\text{P}\}$ n.m.r. spectra. The $^1\text{H}\{-^{31}\text{P}\}$ n.m.r. spectrum in the hydride region showed a resonance at $\delta -12.5$ p.p.m. as a broad doublet, $^2J(\text{HH})$ ca. 2 Hz with satellites due to platinum-195, $^1J(\text{PtH})$ 615 Hz. We assign this to the bridging hydrogen shown in (6). Similar values for $^1J(\text{PtH})$ are also found for a bridging hydrogen in $[\text{Pt}_2\text{H}_3(\mu\text{-dppm})_2]^{\text{+8}}$ or $[\text{Et}_3\text{P}(\text{Ph})\text{Pt}(\mu\text{-H})_2\text{IrH}(\text{PEt}_3)_2]^{\text{+9}}$. The resonance of the second hydride in (6) occurs at $\delta -19.85$ p.p.m. $^2J(\text{HH})$ ca. 2 Hz, $^3J(\text{PtH})$ 25 Hz.

Treatment of *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-dppm})_2]$ with *fac*- $[\text{W}(\text{CO})_3(\text{NCMe})_3]$ in refluxing benzene for 2 h gave a single, dark red, binuclear platinum-tungsten complex in each case: we tentatively formulate these as (7) ($\text{R} = \text{Me}, \text{Ph},$ or *p*-tolyl). Yields were ca. 40%. This formulation is based on elemental analysis, i.r., and $^{31}\text{P}\{-^1\text{H}\}$, $^1\text{H}\{-^{31}\text{P}\}$, and $^{195}\text{Pt}\{^1\text{H}\}$ n.m.r. spectroscopy.

We believe that it will be possible to carry out much chemistry with the above-mentioned complexes without breaking down the heterobimetallic system. Thus preliminary $^{31}\text{P}\{-^1\text{H}\}$, ^1H , and $^1\text{H}\{-^{31}\text{P}\}$ n.m.r. studies show that $[(\text{PhC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{IrCl}(\text{CO})]$ reacts rapidly with NaBPh_4 , NaBF_4 , or NH_4PF_6 to give a single cationic species, presumably the iridium analogue of (1), which in turn reacts with H_2 (to give a dihydride), CO , allene, buta-1,3-diene, $\text{PhC}\equiv\text{CH}$, etc. to give a single heterobimetallic product (different in each case). Rhodium-platinum complexes of type (1) react immediately with NaBH_4 or LiBEt_3H to give an intensely red product.¹⁰

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