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Synthesis of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (dppm = $Ph_2PCH_2PPh_2$) and formation of heterobimetallic complexes of platinum with silver, gold, rhodium, iridium, and tungsten *

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Abstract

Treatment of $[PtCl_2(dppm\text{-}PP')]$ (dppm = $Ph_2PCH_2PPh_2$) with $NaC{\equiv}CH$ and dppm in liquid ammonia gave $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (**1**). This complex is fluxional at 20 °C due to rapid 'end over end' motion of the dppm ligands. Treatment of **1** with various metal complexes gave heterobimetallics, usually in good yield. Thus with $[Ag_4Cl_4(PPh_3)_4]$ it gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$; with $[AuCl(PPh_3)]$, $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$; with $[Rh_2Cl_2(CO)_4]$, $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$; with $[IrCl(CO)(PPh_3)_2]$, $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2IrCl(CO)]$; and with $[W(CO)_3(NCMe)_3]$, it gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2W(CO)_3]$. IR, $^{31}P\{^1H\}$ NMR and ^1H NMR data are given.

Introduction

We have previously reported the preparation of complexes of the type $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (dppm = $Ph_2PCH_2PPh_2$; R = Me, Ph, 4-MeC_6H_4, etc.) and have shown that these complexes readily form heterobimetallic complexes with a number of metals [1]. It was of interest to see if we could prepare related complexes from ethyne itself, viz. with R = H. In this paper we report the results of these investigations.

Results and discussion

For convenience, the various syntheses and transformations are summarized in Scheme 1. Treatment of $[PtCl_2(dppm\text{-}PP']$ with $NaC{\equiv}CH$ and an excess of dppm in liquid ammonia gave $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (**1**) as pale yellow needles, in 66%

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* Dedicated to Professor Colin Eaborn on the occasion of his 65th birthday.

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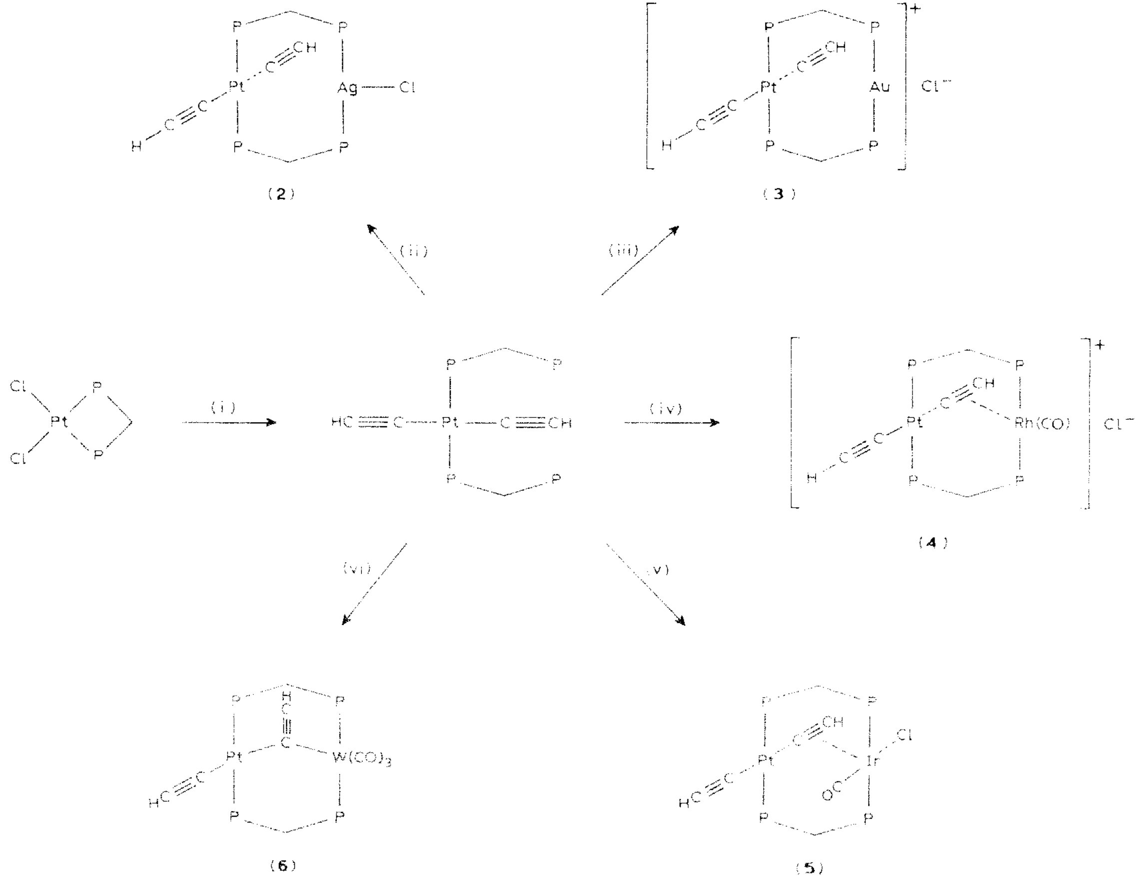

Scheme 1. $\overset{\frown}{P\ \ P}$ = $Ph_2PCH_2PPh_2$ = dppm: (i) NaC≡CH/dppm in liquid ammonia, (ii) $[Ag_4Cl_4(PPh_3)_4]$, (iii) $[Au(PPh_3)Cl]$, (iv) $[Rh_2Cl_2(CO)_4]$, (v) $[IrCl(CO)(PPh_3)_2]$, (vi) $[W(CO)_3(NCMe)_3]$.

Table 1

Analytical (%) and IR (cm^{-1}) data for complexes **1**–**6**

Complex	Infrared [a]			Analyses (Found (calcd.) (%)) [b]		
	ν(C≡C)	ν(C–H)	ν(CO)	C	H	Cl
1	1975	3295		63.8	4.5	
				(63.9)	(4.5)	
2·C_6H_6	1978	3275		58.3	4.2	2.9
				(58.3)	(4.2)	(2.9)
3	1978	3275		51.9	3.8	3.1
				(52.0)	(3.7)	(2.8)
4	1980	3242	1985	55.9	4.0	2.8
				(55.9)	(3.9)	(3.0)
	1913	3277				
5	1960	3280	2041	52.3	3.6	2.8
				(52.0)	(3.6)	(2.8)
6·0.5C_6H_6	1983	3219	1947	54.3	3.9	
				(54.5)	(3.7)	
		3275	1848			
			1821			

[a] Recorded as Nujol mulls. [b] The presence of solvent of crystallization was confirmed by ^{1}H NMR spectroscopy.

yield (see Experimental for details, and Tables 1 and 2 for analytical and spectroscopic data). Complex **1** showed an IR absorbtion at 1975 cm^{-1} (Nujol mull) due to ν(C≡C). The $^{31}P\{^1H\}$ NMR spectrum showed it to be fluxional; at 20 °C, there were two broad resonances ($w_{1/2}$ ~ 80 Hz) at 8.9 and −25.9 ppm. However, at −50 °C, the $^{31}P\{^1H\}$ NMR pattern corresponded to the static structure **1** and the value of ^1J(PtP) (2539 Hz) was consistent with a *trans*-arrangement of phosphines [2]; the chemical shift of the uncoordinated phosphorus atom (−27.7 ppm) is very close to that of free dppm. This fluxionality is due to 'end over end' exchange viz. $PtPPh_2CH_2\overset{*}{P}Ph_2 \leftrightharpoons Pt\overset{*}{P}Ph_2CH_2PPh_2$; we have observed a similar fluxionality with other complexes of the type $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ [3]. We have also prepared **1** (but in low (4%) yield) by treating $[PtCl_2(dppm\text{-}P)_2]$ with LiC≡CH, formed from $LiBu^n$ and ethyne in tetrahydrofuran; the main platinum-containing product was $[Pt(Ph_2PCHPPh_2)_2]$, obtained in 40% yield [4].

We have previously shown that complexes of the type $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (R = alkyl or aryl) could be used for the systematic synthesis of a variety of heterobimetallic complexes containing a $Pt(\mu\text{-dppm})_2M$ moiety, where M is a variety of other metals [1]. It was of interest to see if one could make similar complexes from $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$, since the ethynyl hydrogen in **1** might be displaced, and other reactions could occur.

Treatment of **1** with $[Ag_4Cl_4(PPh_3)_4]$ gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ (**2**) in 84% yield (characterizing data are in the Tables). Similar treatment of **1** with $[Au(PPh_3)Cl]$ gave the platinum-gold complex $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2Au]Cl$ (**3**). In contrast, treatment of **1** with $HgCl_2$ gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ initially ($^{31}P\{^1H\}$ NMR evidence), but this decomposed rapidly in solution to give a large number of products (again based on $^{31}P\{^1H\}$ NMR evidence), none of which was characterized: possibly mercuration of the acidic ethynyl hydrogens occurred. We have previously reported that complexes of the type $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ reacted

Table 2

$^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR data

Complex	^{31}P [a,b]					^1H [b,c]			
	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^1J(MP_B)$	N	PCH_2P		$C{=}CH$	
						$\delta(H)$	$^3J(PtH)$	$\delta(H)$	$^3J(PtH)$
1	7.5	2539 [d]	−27.7 [d]			3.77	27.0	1.80	45.2
2	12.0	2593	−12.1	455, 393	93	3.98	36.4	2.00	43.8
3	9.0	2590	31.5		51	4.68	36.4	1.92	43.8
4	−0.3	2415	21.1	112	34	4.19	37.6		
						3.74 [e]	75.6	2.33 [d]	48.6
						4.54 [e]	< 0.5	1.77 [e]	
5	−0.6	3054	−30.1		95	3.52		1.95	
6	14.0	2548	17.8		43	3.80 [f]		0.87 [f]	

[a] Chemical shifts (δ) in ppm ($\pm$0.1 ppm) relative to 85% phosphoric acid (positive to high frequency); coupling constants (J) in Hz ($\pm$2 Hz). P_A is bonded to platinum and P_B is either uncoordinated or bound to the second metal. $N = |^2J(P_AP_X) + {}^4J(P_AP_{X'})|$. [b] In $CDCl_3$ at 21 °C, unless stated otherwise. [c] Chemical shifts (δ) in ppm ($\pm$0.01 ppm) to high frequency of tetramethylsilane; coupling constants (J) in Hz ($\pm$ 0.1 Hz). [d] Data obtained at −50 °C. [e] Data obtained at 0 °C. [f] Broad resonances at 21 °C and still broad at −50 °C.

with $HgCl_2$ to give heterobimetallics of the types $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$, (R = alkyl or aryl) and that these were quite stable [3].

Treatment of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(CO)_4]$ in benzene gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]Cl$ (**4**) as pale yellow microcrystals. This same complex **4** was also made by treating $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ with $[Rh_2Cl_2(CO)_4]$, i.e. by transmetallation. The $^{31}P\{^1H\}$ NMR spectrum of **4** gave the expected AA′XX′M pattern with satellites due to further splitting by platinum-195; an electrical conductance measurement in nitrobenzene showed it to be a 1/1 electrolyte, and the infrared spectrum had two bands in the $\nu(C{\equiv}C)$ and two bands in the $\nu(C\text{-}H)$ (ethynyl) region (Table 1). The analogous complex $[(MeC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)][PF_6]$ has been shown by X-ray crystallography to have one acetylide ligand σ-bonded to the platinum and weakly interacting with the rhodium in a side-on or π-bonded fashion; the other acetylide is terminally bound to the platinum [5]. It thus seems likely that a similar interaction of one of the ethynyl groups with the rhodium is occurring in **4**, although we could not detect any rhodium coupling to the ethynyl hydrogen in the $^1H\{^{31}P\}$ NMR spectrum.

The analogous platinum-iridium complex **5** was prepared by treating *trans*-$[IrCl(CO)(PPh_3)_2]$ with $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ in boiling benzene. The microanalytical and spectroscopic data are consistent with the formulation **5**, completely analogous to our previously described complexes of type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2Ir(CO)Cl]$ (R = alkyl or aryl) [1].

Treatment of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ with $[W(CO)_3(NCMe)_3]$ gave $[(HC{\equiv}C)_2Pt(\mu\text{-dppm})_2W(CO)_3]$ (**6**) as brown microprisms, in low yield; further details are in the Experimental and characterizing data are in the Tables. Of note are the two ethynyl IR bands at 3219 and 3275 cm^{-1}, which we assign to bridging and terminal $C{\equiv}CH$ groups, respectively. Only one $\nu(C{\equiv}C)$ band, at 1983 cm^{-1}, was visible; we assign this to the terminal $C{\equiv}C$ and presume that the bridging $\nu(C{\equiv}C)$ band is buried beneath the intense carbonyl bands. An X-ray crystal structure of the related complex $[(4\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-dppm})_2W(CO)_3]$ showed that the bridging $RC{\equiv}C$ group was η^1-bonded to both metals in an approximately symmetrical fashion [6]; presumably the same happens in complex **6**, which we described here.

Experimental

The general methods used were as described in recent papers from this laboratory [7].

$[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (1). $[PtCl_2(dppm\text{-}PP')]$ (3.60 g, 5.53 mmol) was added to a solution of $NaC{\equiv}CH$, prepared by bubbling ethyne into a solution of $NaNH_2$, made from sodium (1.35 g, 0.059 mol), in liquid ammonia (100 cm^3) at −78 °C. After 5 min, a solution of dppm (3.0 g, 7.8 mmol) in toluene (45 cm^3) was added. The resultant mixture was then stirred at −78 °C for 1 h, and then at −33 °C for 2 h. Ammonium bromide (1.5 g, 15.3 mmol) was then added, with vigorous stirring, to neutralize the excess of $NaC{\equiv}CH$. The ammonia was then allowed to boil off, and the resultant residue was extracted with benzene (3 × 100 cm^3) to give a yellow solution. The required product was isolated from the benzene layer by evaporation and was purified by recrystallization from benzene/light petroleum (b.p. 60–80 °C). It formed pale yellow needles. Yield 3.7 g, 66%.

$[(HC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ (2). A solution of $[Ag_4Cl_4(PPh_3)_4]$ (**2**) (0.030 g, 0.018 mmol) in dichloromethane (4 cm^3) was added to a solution of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (0.100 g, 0.099 mmol) in benzene (5 cm^3), and the mixture was then stirred for 1 h. The resultant solution was then evaporated to 2 cm^3, to give the required product as a white microcrystalline solid, which was collected, washed with diethyl ether and dried. Yield 0.096 g, 84%.

$[(HC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Au]Cl$ (3). A solution of $[AuCl(PPh_3)]$ (0.024 g, 0.049 mmol) in dichloromethane (2 cm^3) was added to a solution of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (0.050 g, 0.049 mmol) in dichloromethane (1 cm^3). The solvent was then evaporated under reduced pressure, and the residue triturated with diethyl ether to give the required product as pale yellow microcrystals. Yield 0.055 g, 89%.

$[(HC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Rh(CO)]Cl$ (4). $[Rh_2Cl_2(CO)_4]$ (0.021 g, 0.053 mmol) was added to a carbon monoxide saturated solution of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (0.100 g, 0.099 mmol) in benzene (5 cm^3). Carbon monoxide was evolved, and the required product separated as pale yellow microcrystals. Yield 0.066 g, 57%.

$[(HC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ir(CO)Cl]$ (5). A mixture of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (0.200 g, 0.19 mmol) and *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.150 g, 0.19 mmol) in benzene (10 cm^3) was heated under reflux for 45 min. The resultant solution was then evaporated to dryness under reduced pressure and the residue triturated with diethyl ether. This gave the required product as yellow microcrystals. Yield 0.15 g, 59%.

$[(HC{\equiv}C)_2Pt(\mu\text{-}dppm)_2W(CO)_3]$ (6). A mixture of $[Pt(C{\equiv}CH)_2(dppm\text{-}P)_2]$ (0.200 g, 0.19 mmol) and $[W(CO)_3(NCMe)_3]$ (0.061 g, 0.19 mmol) in benzene (5 cm^3) was heated under reflux for 1.5 h. When the resultant reaction mixture was cooled, it gave the required product as light brown microprisms. Yield 0.064 g, 27%.

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