Bimetallic Systems. Part 10.[1] Synthesis of Complexes of Type [(RC≡C)Pt(μ-dppm)$_2$Pt(C≡CR)] (dppm = $Ph_2PCH_2PPh_2$, R = Ph or *p*-tolyl) and their Corresponding 'A Frames' [(RC≡C)Pt(μ-dppm)$_2$(μ-H)Pt(C≡CR)]Cl or [(RC≡C)Pt(μ-dppm)$_2$(μ-X)Pt(C≡CR)] with X = CS_2 or MeOOCC≡CCOOMe

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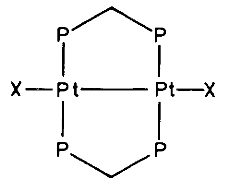
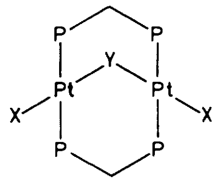
Treatment of *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] (dppm = $Ph_2PCH_2PPh_2$, R = Ph or *p*-tolyl) with *trans*-[PtH(Cl)(PPh$_3$)$_2$] gives hydride-bridged binuclear salts of type [(RC≡C)Pt(μ-dppm)$_2$ (μ-H)Pt(C≡CR)]Cl in good (86—97%) yield. These complexes are fluxional at +21 °C but when cooled to −56 °C the ^{1}H n.m.r. spectrum corresponds to a static structure with pseudo-axial and pseudo-equatorial methylene hydrogen resonances. Deprotonation of these salts with sodium isopropoxide gives the binuclear complexes, [(RC≡C)Pt(μ-dppm)$_2$Pt(C≡CR)], with platinum–platinum bonds. These react with CS_2 or with MeOOCC≡CCOOMe, 'X', to give 'A frames,' [(RC≡C)Pt(μ-dppm)$_2$(μ-X)Pt(C≡CR)], which were fully characterized. Treatment of [(PhC≡C)Pt(μ-dppm)$_2$Pt(C≡CPh)] with SO_2 probably gave the 'A frame' [(PhC≡C)Pt(μ-dppm)$_2$(μ-SO$_2$)Pt(C≡CPh)] which was not isolated but was characterized in solution by ^{31}P-{^{1}H} n.m.r. spectroscopy. N.m.r. and i.r. data are given.

Diplatinum complexes containing bridging $Ph_2PCH_2PPh_2$ (dppm) have been extensively studied. Such complexes include diplatinum(I) species of type (**1**), X = halogen, and corresponding 'A frames' of type (**2**), Y = CO, CH_2, CS_2, alkyne, *etc.*: in addition, charged (cationic) species with X = CO or Y = H or Cl are known.[2] However, hitherto, complexes of types (**1**) or (**2**) with X = C≡CR (R = alkyl or aryl) have been unknown. In this paper we describe a simple synthesis for such complexes with R = Ph or *p*-tolyl which could probably be extended to other acetylides, if required.



(**1**)



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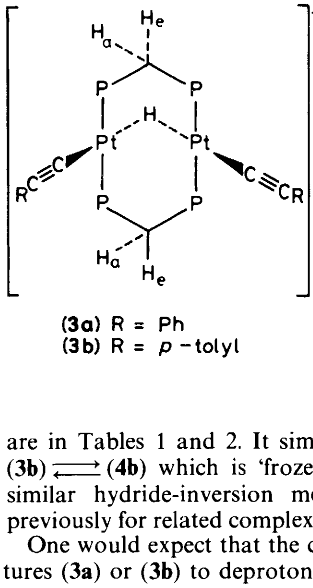
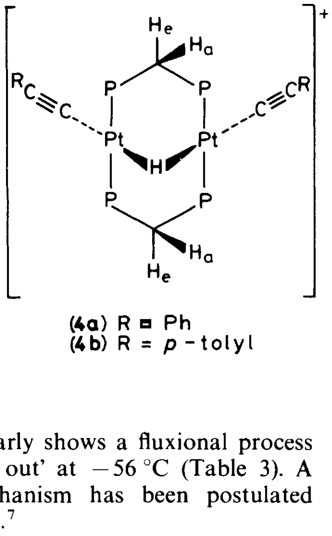


(**3a**) R = Ph
(**3b**) R = *p*-tolyl



(**4a**) R = Ph
(**4b**) R = *p*-tolyl

Results and Discussion

We have previously described simple syntheses of bis(monodentate ligand) complexes of type *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$].[3,4] We now find that treatment of such complexes with *trans*-[PtH(Cl)(PPh$_3$)$_2$] gives the yellow hydro-bridged salts, (**3a**) or (**3b**), in excellent yield; preparative details for these and other complexes described below are in the Experimental section. These complexes were characterized by (*i*) elemental analyses for C, H, and Cl (Table 1), (*ii*) by the presence of an i.r. absorption band due to ν(C≡C) at 2 110 cm^{-1} (**3a**) or 2 120 cm^{-1} (**3b**) (Table 1), (*iii*) electrical conductivity, and particularly (*iv*) by ^{31}P-{^{1}H} and ^{1}H-{^{31}P} n.m.r. spectroscopy (Tables 2 and 3).

In the ^{1}H-{^{31}P} n.m.r. spectrum of complex (**3a**) there is a hydride resonance at δ = −10.3 p.p.m., ^1J(PtH) = 571 Hz and in the ^{1}H n.m.r. spectrum ^2J(*P*Pt*H*) = 9 Hz. At 21 °C, in the ^{1}H-{^{31}P} n.m.r. spectrum, the CH_2 resonance appears as a *ca.* 1:8:18:8:1 quintet at δ = 4.87 p.p.m. with ^3J(PtH) = 38 Hz. However, when the solution is cooled the CH_2 resonance separates out into pseudo-axial and pseudo-equatorial types and the fluxional process, which makes the CH_2 protons equivalent at 21 °C, is essentially 'frozen out' at −56 °C. We have observed this phenomenon in many other complexes containing a Pt(μ-dppm)$_2$M moiety and find only one of the hydrogens is coupled to platinum: this is clearly the pseudo-equatorial hydrogen (H$_e$) for the reasons discussed previously.[5,6] The fluxional process causing equivalence of H$_e$, H$_a$ is probably an inversion process (**3a**) $\rightleftharpoons$ (**4a**) with the central hydridic hydrogen passing through the ring. The *p*-tolylacetylide complex (**3b**) is exactly analogous to (**3a**): characterizing data are in Tables 1 and 2. It similarly shows a fluxional process (**3b**) $\rightleftharpoons$ (**4b**) which is 'frozen out' at −56 °C (Table 3). A similar hydride-inversion mechanism has been postulated previously for related complexes.[7]

One would expect that the cationic hydrogen-bridged structures (**3a**) or (**3b**) to deprotonate and a preliminary ^{31}P-{^{1}H} n.m.r. experiment suggested that this was so. We therefore treated *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] with *trans*-[PtH(Cl)(PPh$_3$)$_2$] to form (**3a**) *in situ* and then added an equivalent amount of sodium isopropoxide. A new product, shown to be the hoped for complex of type (**5a**), was isolated in 66% yield and the corresponding *p*-tolylacetylide complex (**5b**) was similarly prepared in 68% yield. The formulations follow from the elemental analytical data (Table 1), the occurrence of an i.r. absorption band due to ν(C≡C) (Table 1), and, particularly, from the ^{31}P-{^{1}H} and ^{1}H-{^{31}P} n.m.r. data. Thus

Table 1. Microanalytical (%), i.r., and conductivity data

Complex	Analysis[a] C	H	Cl [or S]	I.r.[b] (cm^{-1}) ν(C≡C)	Other	Λ^c/Ω^{-1} cm^2 mol^{-1}
(3a)	57.0 (56.7)	4.3 (4.0)	2.4 (2.5)	2 110		17
(3b)	57.35 (57.3)	4.15 (4.2)	2.25 (2.5)	2 120		14
(5a)	58.1 (58.2)	3.85 (4.0)		2 090		
(5b)	58.85 (58.8)	4.2 (4.2)		2 095		
(7a)·$3C_6H_6$·$0.3CS_2$[d]	59.95 (60.5)	4.2 (4.3)	[4.95 (4.9)]	2 110	980 ν(C–S)	
(7b)·$1.5C_6H_6$·$0.3CS_2$[d]	58.4 (58.6)	4.3 (4.2)	[5.35 (5.2)]	2 095	980 ν(C–S)	
(8a)·C_6H_6[d]	59.0 (59.2)	4.3 (4.2)		2 110	1 695 ν(C=O)	
(8b)	58.4 (58.05)	4.5 (4.2)		2 110	1 700 ν(C=O)	

[a] Calculated values in parentheses. [b] As KBr discs, values ±5 cm^{-1}. [c] For 10^{-3} mol dm^{-3} solutions in nitrobenzene at +20 °C. [d] The presence of this proportion of C_6H_6 was shown by the ^{1}H-{^{31}P} n.m.r. spectrum (in CD_2Cl_2 solution).

Table 2. ^{31}P-{^{1}H} N.m.r. data[a]

Complex	δ(P)	^1J(PtP)	^3J(PtP)	N^b	N'^c	L^d
(3a)	+9.5	2 422	8	68		
(3b)	+9.4	2 427	5	71		
(5a)	+1.4	2 932	−71[e]	83	2 861	33
(5b)	+1.4	2 937	−72[e]	83	2 868	33
(6)	+16.4	3 237	+168	42	3 404	
(7a)	+5.8	2 852	100	37		
	+0.5	3 258	63			
(7b)	+5.6	2 856	98	34		
	+1.1	3 267	61			
(8a)	0.0	3 069	+73	24	3 142	
(8b)	−0.2	3 074	+71	22	3 145	

[a] Spectra (40.25 MHz) measured in $CDCl_3$; chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (*J*) in Hz (±3). [b] $N = |^2J(PCH_2P) + {}^4J(PCH_2PPtP)|$. [c] $N' = |^1J(PtP) + {}^3J(PtP)|$ for **(6)**, **(8a)**, and **(8b)** or $|^1J(PtP) + {}^2J(PtP)|$ for **(5a)** and **(5b)**. [d] $L = |^2J(PCH_2P) - {}^4J(PCH_2PPtP)|$. [e] ^2J(PtP) or ^3J(PtP).

for the phenylacetylide complex **(5a)** the ^{31}P-{^{1}H} n.m.r. pattern is characteristic of a diplatinum species and shows an *N'* doublet [$N' = |^1J(PtP) + {}^2J(PtP)|$] of separation 2 861 Hz. Since ^1J(PtP) = 2 932 Hz the values of ^3J(PtP) and ^1J(PtP) must be opposite in sign, *i.e.* ^3J(PtP) = −71 Hz: one-bond couplings between platinum and the phosphorus of phosphines are always large and positive.[8,9] The ^{1}H-{^{31}P} n.m.r. pattern showed the expected coupling to two platinum atoms. The *p*-tolylacetylide complex **(5b)** gave similar n.m.r. parameters to those of the phenylacetylide complex.

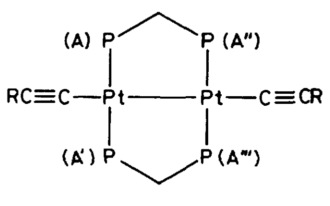
It is well established that complexes of type **(1)**, X = halogen, react with small molecules such as CO, SO_2, CS_2, and MeOOCC≡CCOOMe to give the 'A frame' adducts.[2] We find our new complexes of type **(5a)** or **(5b)** are less reactive towards these molecules but in some cases, *e.g.* with CS_2 or MeOOCC≡CCOOMe, adducts were readily isolated and characterized. When a deuteriochloroform solution of **(5a)** was treated with CO no change could be detected in the ^{31}P-{^{1}H} n.m.r. spectrum. Similar treatment with SO_2 gave an orange solution containing a new species with the following ^{31}P-{^{1}H} n.m.r. parameters: δ(P) = 16.4 p.p.m., ^1J(PtP) = 3 237, ^3J(PtP) = 168 [and the same sign as ^1J(PtP), presumably positive], and $J(P_AP_{A''}) + J(P_AP_{A'''})$ = 42 Hz. There were also a few weak resonances due to other (unidentified) products. We tentatively formulate this new species as the symmetrical SO_2 adduct **(6)**. Attempts to isolate it from solution led to decomposition, and the solid product was only isolated in a crude state. It showed i.r. bands at 1 160 and 1 030 cm^{-1} (KBr disc) which could be due to ν(SO) and a band at 2 115 cm^{-1} due to ν(C≡C). The SO_2 adduct [ClPt(μ-SO_2)(μ-dppm)$_2$PtCl] is known[10] as is the corresponding dipalladium complex.[11]

Treatment of a benzene solution of complex **(5a)** with CS_2

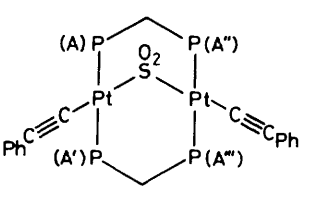
Table 3. ^{1}H- and ^{1}H-{^{31}P}[a] n.m.r. data

Complex	CH$_2$ δ(H$_e$)	^3J(*Pt*PC*H*$_e$)	δ(H$_a$)	^2J(H$_e$H$_a$)	Other resonances
(3a)[b]	5.34	71	4.13	13	δ(Pt*H*Pt) −10.3 ^1J(PtH) = 571, ^2J(PH) = 9
(3b)[c]	5.32	72	4.12	14	δ(Pt*H*Pt) = −10.3 ^1J(PtH) = 569, ^2J(PH) = 9 δ(Me) = 2.16
(5a)	δ(CH$_2$)	4.96	^3J(PtH) =	57	
(5b)	δ(CH$_2$)	4.96	^3J(PtH) =	57	δ(Me) = 2.09
(7a)	3.65	77	4.16	13	
(7b)	3.65	75	4.17	13	δ(Me) = 2.23 and 2.14
(8a)	3.54	62	4.16	13	δ(COOMe) = 2.54
(8b)	3.53	63	4.16	13	δ(COOMe) = 2.54 δ(C_6H_4*Me*) = 2.68

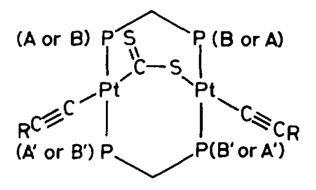
[a] Spectra (100 MHz) measured in $CDCl_3$ at +21 °C unless otherwise stated. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (*J*) in Hz (±0.1). [b] Spectra at −56 °C; at +21 °C the CH$_2$ resonance formed a *ca.* 1:8:18:8:1 quintet at δ 4.87 p.p.m. with ^1J(PtH) = 38 Hz. [c] Spectra at −56 °C; at +21 °C the CH$_2$ resonance formed a *ca.* 1:8:18:8:1 quintet at δ 4.87 p.p.m. with ^1J(PtH) = 37 Hz.



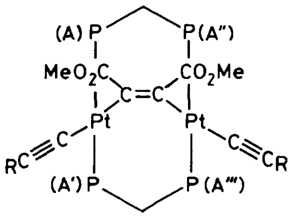
(5a) R = Ph
(5b) R = *p*-tolyl



(6)



(7a) R = Ph
(7b) R = *p*-tolyl



(8a) R = Ph
(8b) R = *p*-tolyl

readily gave the CS_2 adduct. The formulation follows from the microanalytical (Table 1) and i.r. data (Table 1), and particularly from the $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ n.m.r. data (Tables 2 and 3). The $^1H-\{^{31}P\}$ n.m.r. data show that the molecule is not fluxional at *ca.* 20 °C, *i.e.* individual resonances for the pseudo-equatorial methylene proton (H_e) coupled to platinum-195, $^3J(PtH_e)$ = 77 Hz, and the pseudo-axial proton (H_a), which is not coupled to platinum-195, can be seen. The $^{31}P-\{^1H\}$ n.m.r. data (Table 2) are of the AA'BB' type, in agreement with the CS_2 being bonded as shown in structure **(7a)**. The di(*p*-tolylacetylide) complex **(7b)** was similarly characterized and showed similar n.m.r. parameters to the phenylacetylide complex. A CS_2 adduct $[ClPt(\mu-CS_2)(\mu-dppm)_2PtCl]$ is known[12] and the bonding of the CS_2 is as depicted in **(7a)**. We have also made $[ClPt(\mu-CS_2)(\mu-dppm)_2PdCl]$.[13]

Treatment of the platinum–platinum bonded complex **(5a)** with MeOOCC≡CCOOMe gave an adduct, formulated as **(8a)**. The analogous chloro-complex (**1a**; X = Cl) reacts with electronegative acetylenes such as MeOOCC≡CCOOMe to give adducts of an analogous type[14] and dipalladium analogues are also known.[15] The formulation as **(8a)** follows from the elemental analytical and i.r. data (Table 1). The $^{31}P-\{^1H\}$ n.m.r. spectrum (Table 2) is characteristic of a symmetrical diplatinum species containing a $Pt(\mu-dppm)_2Pt$ moiety. The $^1H-\{^{31}P\}$ n.m.r. spectrum showed individual methylene hydrogen resonances for the pseudo-equatorial and pseudo-axial hydrogens, with $^3J(PtH_e)$ = 62 Hz and $^3J(PtH_a)$ being too small to observe. The di(*p*-tolylacetylide) complex **(8b)** was also prepared and characterized, see Experimental section and Tables 1—3.

We also found that when MeOOCC≡CCOOMe was heated with $[Pt_2(C\equiv CPh)_2(\mu-dppm)_2]$ as catalyst in boiling benzene solution the trimer hexamethoxycarbonylbenzene was produced and identified by its mass spectrum, m/e = 426, for the parent molecular ion.

Experimental

The general procedures and apparatus used were the same as in other recent publications from this laboratory.[1]

Preparations.—$[Pt_2(C\equiv CPh)_2(\mu-H)(\mu-dppm)_2]Cl$ **(3a)**. The complexes *trans*-$[Pt(C\equiv CPh)_2(dppm-P)_2]$ (300 mg, 0.26 mmol) and $[PtH(Cl)(PPh_3)_2]$ (205 mg, 0.27 mmol) were dissolved in CH_2Cl_2 (10 cm^3) and the solution stirred for 5 min. The solution was evaporated to dryness under reduced pressure and the residue triturated with Et_2O. This gave the required product as a yellow powder. Yield 350 mg (97%). Complex **(3b)** was made similarly in 86% yield.

$[Pt_2(C\equiv CPh)_2(\mu-dppm)_2]$ **(5a)**. The complex *trans*-$[PtH(Cl)(PPh_3)_2]$ (205 mg, 0.27 mmol) was added to a solution of *trans*-$[Pt(C\equiv CPh)_2(dppm-P)_2]$ (300 mg, 0.26 mmol) in dry tetrahydrofuran (10 cm^3). A solution of sodium isopropoxide in propan-2-ol (1.24 cm^3, 0.21 mol dm^{-3}, 0.26 mmol) was added. The solution was then evaporated to dryness under reduced pressure and the residue was triturated with Et_2O. The solid was washed with water and dried *in vacuo* over P_2O_5. This gave the required product as yellow microcrystals. Yield 233 mg (66%). Complex **(5b)** was made similarly in 68% yield.

$[Pt_2(C\equiv CPh)_2(\mu-CS_2)(\mu-dppm)_2]\cdot 3C_6H_6\cdot 0.3CS_2$ **(7a)**. Carbon disulphide (36 μl, 0.45 mg, 0.59 mmol) was added to a solution of $[Pt_2(C\equiv CPh)_2(\mu-dppm)_2]$ (80 mg, 0.059 mmol) in benzene (5 cm^3). After 90 min the solution was evaporated to *ca.* 1 cm^3 under reduced pressure and MeOH (5 cm^3) was added: the evaporation and dilution with MeOH was repeated. This gave the required product as orange microcrystals. Yield 65 mg (75%). Complex **(7b)** was made similarly in 68% yield.

$[Pt_2(C\equiv CPh)_2(\mu-MeOOCC\equiv CCOOMe)(\mu-dppm)_2]\cdot C_6H_6$ **(8a)**. Dimethyl acetylenedicarboxylate (35 μl, 30 mg, 0.214 mmol) was added to a solution of complex **(5a)** (80 mg, 0.059 mmol) in benzene (5 cm^3). After 0.5 h, MeOH (20 cm^3) was added and the solution was evaporated to *ca.* 2 cm^3 under reduced pressure. This gave the required product as yellow microcrystals. Yield 58 mg (62%). The *p*-tolylacetylide analogue **(8b)** was made similarly, as a yellow solid, in 62% yield.

Action of Sulphur Dioxide on $[Pt_2(C\equiv CPh)_2(\mu-dppm)_2]$.—Sulphur dioxide was bubbled through a solution of complex **(5a)** (20 mg) in $CDCl_3$ (0.5 cm^3) for *ca.* 5 min during which time the solution turned orange. The $^{31}P-\{^1H\}$ n.m.r. spectrum showed that the main phosphorus-containing species present was a symmetrical diplatinum complex to which we assign structure **(6)**. Attempts to isolate this product led to decomposition.

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