Bimetallic Systems. Part 5.[1] Isonitrile–Platinum(II)– or –Palladium(II)–Bis(diphenylphosphino)methane Complexes including Heterobimetallics with Silver(I), Gold(I), or Rhodium(I)

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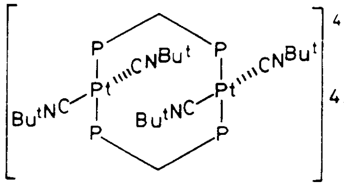
Treatment of *cis*-[$PtCl_2$(dppm-*PP'*)] with Bu^{t}NC gives [(Bu^{t}NC)$_2$Pt(μ-dppm)$_2$Pt(CNBu^t)$_2$]$^{4+}$, isolated as the PF_6^- salt (dppm = $Ph_2PCH_2PPh_2$). Treatment of [M(dppm-*PP'*)$_2$]Cl_2 (M = Pt or Pd) with two equivalents of Bu^{t}NC or MeNC gave fluxional, mononuclear isonitrile complexes of type [M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$, isolated as their PF_6^- or BPh_4^- salts. The palladium salts readily lose the CNR ligands. The unidentate-dppm complexes of type [Pt(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ react with $AgPF_6$, $HgCl_2$, or [$Rh_2Cl_2(CO)_4$] to give heterobimetallic complexes with μ-dppm ligands, but these were not isolated in a pure state. However, the salts [M(dppm-*PP'*)$_2$]Cl_2 (M = Pt or Pd) react with the compounds [AgCl(CNR)] (R = Me, Bu^t, or *p*-tolyl) to give the heterobimetallic complexes [(RNC)-ClM(μ-dppm)$_2$AgCl]$^+$ in high yield. These were isolated as Cl^-, BPh_4^-, or PF_6^- salts. The salt [Pt(CNBu^t)$_2$(dppm-*P*)$_2$]Cl_2, prepared *in situ* from [Pt(dppm-*PP'*)$_2$]Cl_2 and Bu^{t}NC, reacts with [{AgCl(PPh_3)}$_4$] or [AuCl(PPh_3)] to give [(Bu^{t}NC)ClPt(μ-dppm)$_2$MCl]Cl (M = Ag or Au). Treatment of [Pt(dppm-*PP'*)$_2$]Cl_2 with [Au(C≡CPh)(CNBu^t)] gives [(Bu^{t}NC)(PhC≡C)Pt(μ-dppm)$_2$-AuCl]Cl. Treatment of [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl with [$Rh_2Cl_2(CO)_4$] gives the complex [(Bu^{t}NC)ClPt(μ-dppm)$_2$RhCl(CO)][$RhCl_2(CO)_2$] and silver chloride in a transmetallation reaction. I.r. and ^{1}H-{^{31}P}, ^{31}P-{^{1}H}, and ^{195}Pt-{^{1}H} n.m.r. data are given and discussed.

We have described in previous papers how bimetallic complexes of type [Pt_2(C≡CR)$_4$(μ-dppm)$_2$] and fluxional monometallic complexes, [M(C≡CR)$_2$(dppm-*P*)$_2$], are readily prepared (M = Pt or Pd; R = alkyl or aryl; dppm = Ph_2-PCH_2PPh_2).[2,3] Furthermore the monometallic complexes can be used in the systematic synthesis of a wide range of heterobimetallic complexes of type [(RC≡C)$_2$M(μ-dppm)$_2$M'L_x] (M = Pt or Pd; M' = Cr, Mo, W, Rh, Ir, Cu, Ag, Au, Cd, or Hg; L = various ligands).[3–7] In this work the acetylide ligands were considered to be important in that (*i*) they are strongly bonding to platinum or palladium, and (*ii*) they have a strong preference to be mutually *trans*. It therefore seemed possible that isonitrile ligands, RNC, which are isoelectronic with acetylide ligands, RC≡C$^-$, might generate similar chemistry. Thus we hoped to be able to synthesize bimetallic tetracationic species [M_2(CNR)$_4$(μ-dppm)$_2$]$^{4+}$ and monometallic species [M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$, and the derived heterobimetallic complexes.

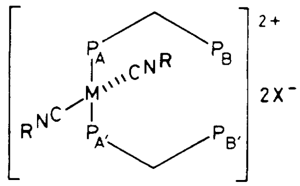
Results and Discussion

Organic isonitriles, RNC, are good ligands for platinum(II) and palladium(II); they can form stable *cis* or *trans* complexes when the other ligands are tertiary phosphines, and will readily displace a chloride ligand to form salts.[8,9] When we treated a methanolic suspension of *cis*-[$PtCl_2$(dppm-*PP'*)] with Bu^{t}NC a colourless solution formed, the ^{31}P-{^{1}H} n.m.r. spectrum of which showed it to contain the diplatinum cationic complex [(Bu^{t}NC)$_2$Pt(μ-dppm)$_2$Pt(CNBu^t)$_2$]$^{4+}$, as the sole phosphorus-containing product. Evaporation of the solution gave a chloride salt which we formulate as (1a) but which was not obtained analytically pure. However, addition of a methanolic solution of NH_4PF_6 to a methanolic solution of (1a) gave the corresponding hexafluorophosphate salt (1b) as a white microcrystalline solid. This showed the same ^{31}P-{^{1}H} n.m.r. resonance pattern as the chloride salt (1a) (see Table 1) (in addition to the septet due to PF_6^-). This salt was somewhat unstable and difficult to purify and although it gave satisfactory elemental analytical data for H and N (Table 2) the percentage carbon content was slightly high and that of fluorine slightly low. The i.r. absorption spectrum of (1a) or (1b) showed a band at 2 240 cm^{-1} typical of co-ordinated isonitrile [8] and the ^{195}Pt-{^{1}H} n.m.r. spectrum a triplet of triplets with δ(Pt) = −159 p.p.m. Unfortunately, the salt was insoluble in chlorinated solvents or acetone and, although it was soluble in CD_3OD or $(CD_3)_2SO$, both these solvents showed impurity peaks close to the regions where CH_2 and Bu^t absorb in the ^{1}H-{^{31}P} n.m.r. spectrum. Thus, although the resonances for CH_2 and Bu^t were readily identified (Table 3), accurate integrations were not obtained. However, the formulations (1a) and (1b) are very probably correct; the isoelectronic dirhodium complex ions [Rh_2(CNR)$_4$(μ-dppm)$_2$]$^{2+}$ have been well characterized.[10–13]

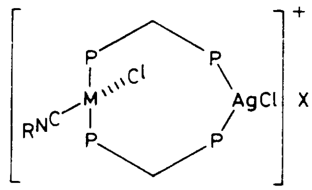
Since organic isonitriles, RNC, are isoelectronic with acetylides, RC≡C$^-$, we anticipated that they should give similar bis(dppm-*P*) complexes with platinum or palladium of type [M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ (M = Pt or Pd). Whilst this work was in progress the paper by Balch and co-workers [14] describing the crystal structure of [Pd(CNBu^t)$_2$(dppm-*P*)$_2$]-[BPh_4]$_2$ was published. We found that when ethanolic solutions of the bis(dppm)-platinum or -palladium salts [M(dppm-*PP'*)$_2$]Cl_2 were treated with 2 mol equivalents of an organic isonitrile (Bu^{t}NC or MeNC), mononuclear bis(dppm) di-isonitrile complexes of type [M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ (M = Pd or Pt; R = Me or Bu^t) were formed and could be isolated as their PF_6^- or BPh_4^- salts, by addition of NH_4PF_6 or $NaBPh_4$, respectively. Preparative details are in the Experimental section and microanalytical, n.m.r., i.r., and electrical conductivity data are in the Tables. The palladium salts, even in the solid state, are prone to lose the isonitrile ligands and revert back to [Pd(dppm-*PP'*)$_2$]X_2 (X = BPh_4^- or PF_6^-) as evidenced from ^{31}P-{^{1}H} n.m.r. spectroscopy. The platinum complexes were more stable, showing less tendency to lose isonitrile ligands. The complexes [M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ showed fluxionality, corresponding to intramolecular 'end over end' exchange of the dppm ligands, as we have previously reported for the diacetylide complexes *trans*-[M(C≡CR)$_2$-(dppm-*P*)$_2$]. The ^{31}P-{^{1}H} n.m.r. spectrum of [Pt(CNMe)$_2$-(dppm-*P*)$_2$]Cl_2, prepared *in situ* in EtOH at −21 °C, consists of a broad singlet at δ = −13.7 p.p.m., $w_{\frac{1}{2}}$ = 56 Hz, with



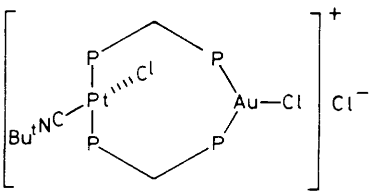
(1a) X = Cl
(1b) X = PF_6



	M	R	X
(2a)	Pt	Me	BPh_4
(2b)	Pt	Me	PF_6
(2c)	Pt	Me	Cl
(2d)	Pt	Bu^t	BPh_4
(2e)	Pt	Bu^t	PF_6
(2f)	Pt	Bu^t	Cl
(2g)	Pd	Me	BPh_4
(2h)	Pd	Me	PF_6
(2i)	Pd	Bu^t	BPh_4
(2j)	Pd	Bu^t	PF_6



	M	R	X
(3a)	Pt	Me	Cl
(3b)	Pt	Bu^t	Cl
(3c)	Pt	*p*-tolyl	Cl
(3d)	Pt	Bu^t	BPh_4
(3e)	Pd	Me	Cl
(3f)	Pd	Bu^t	Cl
(3g)	Pd	*p*-tolyl	Cl



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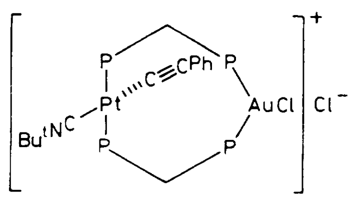

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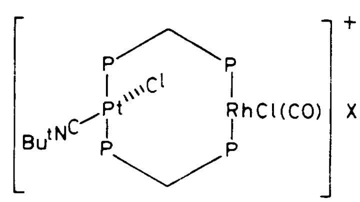

(6a) X = $RhCl_2(CO)_2$
(6b) X = BPh_4

platinum satellites, J(PtP) = 1 265 Hz (see Figure 1), which we interpret in terms of rapid ' end over end ' intramolecular exchange. On cooling these resonances broaden then separate until at −90 °C the ^{31}P-{^{1}H} n.m.r. spectrum (Figure 1) corresponds to the static structure (2c) with an AA′BB′ (or AA′XX′) pattern of deceptively simple triplets plus platinum satellites.

The occurrence of deceptively simple triplets is indicative of a large value of ^2J(*P*–Pt–*P*), *i.e. trans*-phosphines, as is the value of ^1J(PtP$_A$) = 1 997 Hz. We found that a similar behaviour with temperature was exhibited by the ^{31}P-{^{1}H} n.m.r. spectra of the corresponding BPh_4^- and PF_6^- salts (2a) and (2b) and indicates that the chloride ion is not playing a significant role in the fluxionality. Whereas these di-isonitrile complexes [Pt(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ required a very low temperature (−90 °C) before the rapid ' end over end ' exchange ceased, the corresponding exchanges in the isoelectronic diacetylides [Pt(C≡CR)$_2$(dppm-*P*)$_2$] were frozen out at −30 °C.[2,3] It is possible that the dipositive charge on the di-isonitrile complexes causes the metal centre to interact more strongly with the remote phosphorus nuclei, hence lowering $\Delta G^‡$. As mentioned above, Balch and co-workers [14] prepared [Pd(CNBu^t)$_2$(dppm-*P*)$_2$]$^{2+}$ but reported the ^{31}P-{^{1}H} n.m.r. spectrum to consist of a broad singlet, at *ca.* −23 p.p.m., even at −80 °C. However, we observe the expected AA′XX′ pattern at −90 °C in CD_2Cl_2 and a singlet resonance at δ = −13.3 p.p.m. at +21 °C (see Table 1 and footnotes). We suggest that the spectra they observed were of the dication [Pd(dppm-*PP*′)$_2$]$^{2+}$ which shows δ(P) = *ca.* −23 p.p.m. and, as reported above, the di-isonitrile complexes [Pd(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$ readily lose isonitrile to give [Pd(dppm-*PP*′)$_2$]$^{2+}$.

Heterobimetallic Complexes.—We have reported that complexes of type *trans*-[MX$_2$(dppm-*P*)$_2$] (M = Pt or Pd; X = C≡CR or CN) can readily form heterobimetallic complexes with other metals such as Mo, W, Rh, Ir, Cu, Ag, Au, Cd, or Hg.[1,5–7,15–17] We similarly hoped to make heterobimetallic complexes using the di-isonitrile complex dications *trans*-[M(CNR)$_2$(dppm-*P*)$_2$]$^{2+}$. ^{31}P-{^{1}H} N.m.r. studies showed that addition of $AgPF_6$, [{AgCl(PPh$_3$)}$_4$], $HgCl_2$, or [Rh$_2$Cl$_2$(CO)$_4$] to these unidentate bis(dppm) di-isonitrile complexes [M(CNR)$_2$(dppm-*P*)$_2$][X]$_2$ (X = PF_6^- or BPh_4^-, M = Pt or Pd, R = Me or Bu^t) gave heterobimetallic complexes of the expected types, *viz.* [(RNC)$_2$M(μ-dppm)$_2$M′L$_x$]$^{n+}$ (M = Pt or Pd; M′ = Ag, Hg, or Rh; L = Cl, CO, *etc.*), but these were always contaminated with other species, *e.g.* [MCl$_2$(dppm-*PP*′)], and none was characterized. We then tried to make heterobimetallic complexes by a different route. We have shown previously that salts of type [M(dppm-*PP*′)$_2$]Cl$_2$ (M = Pt or Pd) react with acetylides of d^{10} metals, *e.g.* Hg(C≡CR)$_2$, CuC≡CPh, AuC≡CPh, or AgO$_2$CMe–HC≡CR to give heterobimetallic complexes.[1,4,5] We reasoned therefore that the readily prepared silver–isonitrile complexes, [AgCl(CNR)],[18] might react similarly with [M(dppm-*PP*′)$_2$]Cl$_2$. Hence, we treated dichloromethane solutions of these salts with the equivalent amounts of [AgCl(CNR)] (R = Me, Bu^t, or *p*-tolyl) and found smooth conversion into the required heterobimetallic complexes [(RNC)ClM(μ-dppm)$_2$AgCl]$^+$ (3a)—(3g). Details are in the Experimental section and elemental analytical, i.r., and n.m.r. data are in the Tables.

The electrical conductivity in nitrobenzene solution showed the compounds to be 1 : 1 electrolytes (Table 2). At ambient temperatures the ^{31}P-{^{1}H} n.m.r. spectrum of [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl (3b) showed sharp resonances due to P$_A$ but slightly broadened resonances due to P$_B$ although the fine structure due to coupling with ^{107}Ag and ^{109}Ag was still resolved. The slight broadening is probably due to some silver–phosphine exchange. However, at lower temperatures, the ^{31}P-{^{1}H} n.m.r. pattern is sharper; this is reproduced in Figure 2. The observed ratio ^1J(^{109}AgP$_B$)/^1J(^{107}AgP$_B$) = 473/408 = 1.16, close to the ratio of the gyromagnetic ratios (1.15). Long range coupling of platinum-195 to P$_B$ was also

Table 1. $^{31}P-\{^1H\}$ [a] and $^{195}Pt-\{^1H\}$ [b] n.m.r. and i.r. data [c]

Complex	δ(P)	$^1J(PtP)$	δ(Pt) [b]	$^3J(PtP)$	ν(C≡N) [c]/cm^{-1}
(1a) [d]	−1.5	2 246	−159	−56	2 240

Unidentate complexes of type (2) [e]

Complex	δ(P_A)	$^1J(PtP_A)$	δ(P_B)	$^3J(PtP_B)$	$^2J(P_AP_B)$ + $^4J(P_AP_{B'})$	ν(C≡N) [c]/cm^{-1}
(2a) [f]	+4.9	1 936	−28.7	90	120	2 265
(2b)	+7.8	1 950	−28.2	n.r.	105	2 280
(2c) [f]	+7.5	1 997	−27.0	34	123	—
(2d)	+6.1	1 970	−29.5	85	125	2 215
(2e)	+6.2	1 980	−29.7	n.r.	122	2 230
(2f) [g,h]	+6.4	2 077	−29.8	142	105	—
(2g) [i]	+18.9	—	−24.5	—	120	2 255
(2h) [j]	+19.5	—	−24.9	—	117	2 260
(2i) [k]	+15.3	—	−26.6	—	119	2 225
(2j) [l]	+15.5	—	−27.0	—	127	2 230

Heterobimetallic complexes of types (3)—(5) [m]

Complex	δ(P_A)	$^1J(PtP_A)$	δ(P_B)	$^1J(^{109}AgP_B)$	$^1J(^{107}AgP_B)$	$^3J(PtP_B)$	$^2J(P_AP_B)$ + $^4J(P_AP_{B'})$	ν(C≡N)/cm^{-1}
(3a)	+18.2	2 153	−7.2	469	405	67	83	2 265
(3b)	+17.3	2 156	−7.9	473	408	64	81	2 230
(3c)	+18.7	2 140	−7.5	471	408	60	81	2 220
(3d)	+17.2	2 156	−7.9	474	410	n.r.	81	2 230
(3e)	+24.1	—	−4.9	459	411	—	86	2 260
(3f)	+23.6	—	−5.3	478	429	—	86	2 238
(3g)	+24.7	—	−4.8	475	410	—	88	2 210
(4)	+13.8	2 192	+22.8	—	—	48	54	2 240
(5)	+8.2	2 336	+26.2	—	—	103	51	2 220 [ν(C≡C) 2 120]

Platinum–rhodium complexes of type (6) [n]

Complex	δ(P_A)	$^1J(PtP_A)$	δ(P_B)	$^1J(RhP_B)$	$^2J(P_AP_B)$ + $^4J(P_AP_{B'})$	ν(C≡N)/cm^{-1}	ν(C≡O)/cm^{-1}
(6a)	+4.9	2 293	+14.7	127	44	2 230	2 070, 1 994
(6b)	+5.1	2 290	+12.2	122	42	2 225	1 995, 1 980 (sh)

[a] Chemical shifts (δ) (in p.p.m.; ±0.1 p.p.m.) relative to 85% H_3PO_4 (positive shift to high frequency); coupling constants (*J*) in Hz (±3 Hz). The phosphorus atoms P_A are co-ordinated to either Pt or Pd; atoms P_B are either unco-ordinated as in compounds of type (2) or co-ordinated to another metal, as in compounds of types (3)—(6). n.r. = Not resolved. [b] A negative shift (in p.p.m.) is to low frequency of $\Xi(^{195}Pt)$ = 21.4 MHz. [c] As Nujol mulls. [d] In CD_3OD. [e] In CD_3COCD_3 at −90 °C, unless stated otherwise. [f] In CD_2Cl_2 at −90 °C. [g] Not isolated, measured in EtOH at −90 °C with external CD_3COCD_3 lock. [h] The $^{31}P-\{^1H\}$ n.m.r. spectrum in EtOH at +21 °C showed a single broad central peak at δ = −15.2 p.p.m., $w_{\frac{1}{2}}$ = 56 Hz, with satellites, $^1J(PtP)$ = 1 225 Hz. [i] The $^{31}P-\{^1H\}$ n.m.r. spectrum at +21 °C showed a broad singlet at δ = −14.2 p.p.m., $w_{\frac{1}{2}}$ = 34 Hz. [j] The $^{31}P-\{^1H\}$ n.m.r. spectrum at +21 °C showed a broad singlet at δ = −13.6 p.p.m., $w_{\frac{1}{2}}$ = 57 Hz. [k] The $^{31}P-\{^1H\}$ n.m.r. spectrum at +21 °C showed a broad singlet at δ = −13.3 p.p.m., $w_{\frac{1}{2}}$ = 40 Hz. [l] The $^{31}P-\{^1H\}$ n.m.r. spectrum at +21 °C showed a broad singlet at δ = −10.6 p.p.m., $w_{\frac{1}{2}}$ = 44 Hz. [m] In $CDCl_3$ at −50 °C. [n] In $CDCl_3$.

observed, $^3J(PtP_B)$ = 64 Hz. The $^1H-\{^{31}P\}$ n.m.r. spectrum of the corresponding methyl isocyanide complex [(MeNC)-ClPt(μ-dppm)$_2$AgCl]Cl (3a) shows a well defined 1 : 4 : 1 triplet due to coupling to ^{195}Pt, $^4J(PtCNCH_3)$ = 21 Hz, indicating that the methyl isocyanide has indeed been transferred from silver to platinum. At *ca.* +20 °C the CH_2 resonance is broad but at −50 °C it consists of a broad AB pattern. Unfortunately the coupling constants to platinum could not be measured, the satellite peaks being very broad. The corresponding tetraphenylborate salt [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]-BPh_4 (3d) was readily prepared by adding $NaBPh_4$ to an ethanol solution of the corresponding chloride salt; it was fully characterized (see Tables).

We report above that treatment of [Pt(dppm-*PP'*)$_2$]Cl_2 with Bu^{t}NC gives [Pt(CNBu^t)$_2$(dppm-*P*)$_2$]Cl_2. We also find that when this cation is prepared *in situ* in dichloromethane and [{M'Cl(PPh$_3$)}$_n$] added (M' = Ag, *n* = 4; M' = Au, *n* = 1), addition of diethyl ether then precipitates the mixed platinum–silver or –gold complexes [(Bu^{t}NC)ClPt(μ-dppm)$_2$M'Cl]-Cl [M' = Ag (3b) or Au (4)] respectively; *i.e.* loss of one Bu^{t}NC ligand from platinum occurs. Treatment of a deuteriochloroform solution of [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl with another mol of Bu^{t}NC causes partial conversion into another species, probably the bis(t-butyl isocyanide) complex [(Bu^t-NC)$_2$Pt(μ-dppm)$_2$AgCl]Cl_2. This was not isolated but was characterized in solution by its $^{31}P-\{^1H\}$ n.m.r. spectral parameters: δ(P_A) = +10.3 p.p.m., $^1J(PtP_A)$ = 2 124 Hz, δ(P_B) = −6.0 p.p.m., $^1J(^{109}AgP_B)$ = 471 Hz, $^1J(^{107}AgP_B)$ = 403 Hz, and $^2J(P_AP_B)$ + $^4J(P_AP_{B'})$ = 23 Hz.

Since acetylide groups can be transferred from Cu, Ag, Au, or Hg to platinum (or palladium) and isonitriles from silver or gold to platinum or palladium it was of interest to see if both groups could be transferred from one of these d^{10} metals to platinum. We therefore treated [Pt(dppm-*PP'*)$_2$]Cl_2 with [Au(C≡CPh)(CNBu^t)] prepared *in situ* from AuC≡CPh[19] and Bu^{t}NC in dichloromethane. A $^{31}P-\{^1H\}$ n.m.r. study of the reaction mixture suggested that the conversion into the desired complex [(Bu^{t}NC)(PhC≡C)Pt(μ-dppm)$_2$AuCl]Cl (5) had probably occurred. This complex was isolated (see Experimental section) and gave satisfactory elemental analysis (Table 2); it behaved as a 1 : 1 electrolyte in nitrobenzene solution, and in its i.r. spectrum showed ν(C≡C) at 2 120 cm^{-1} and ν(CN) at 2 220 cm^{-1}. The $^{31}P-\{^1H\}$ n.m.r. spectrum was broadened at *ca.* 20 °C but at −50 °C showed a deceptively

Table 2. Microanalytical, melting point, and electrical conductivity data

Complex	Analyses (%) [a,b] C	H	N	Other	M.p. (°C) [c]	Λ [d]/ Ω^{-1} cm^2 mol^{-1}
(1b) [e]	42.2 (40.6) [e]	3.8 (3.9)	3.15 (2.7)	F, 21.25 (22.0)	>320	
(2a)	72.8 (72.7)	5.7 (5.4)	1.6 (1.7)		n.d.	102
(2b)	48.2 (48.6)	3.7 (3.8)	2.1 (2.1)	F, 17.4 (17.1)	310—312	136
(2d)	72.9 (72.7)	5.8 (5.8)	1.6 (1.6)		n.d.	125
(2e)	50.5 (50.2)	4.6 (4.5)	1.9 (1.8)	F, 15.6 (16.5)	296—298	160
(2g)	76.0 (76.0)	5.7 (5.6)	1.6 (1.7)		n.d.	152
(2h)	51.8 (52.0)	3.9 (4.0)	2.2 (2.3)	F, 18.5 (18.3)	215—216	140
(2i) [f]	77.1 (76.5)	6.1 (6.1)	1.6 (1.2)		n.d.	160
(2j) [g]	53.0 (54.1)	4.6 (4.7)	2.0 (2.1)		n.d.	208
(3a)·0.5CH_2Cl_2	50.1 (50.0)	4.0 (3.8)	0.9 (1.1)	Cl, 11.0 (11.2)	164—166	25 [h]
(3b)·CH_2Cl_2	49.9 (50.0)	4.0 (4.1)	1.0 (1.0)	Cl, 12.9 (13.2)	190—193	23 [h]
(3c)·CH_2Cl_2	51.5 (51.3)	3.9 (3.9)	1.1 (1.0)	Cl, 12.4 (12.8)	178—181	22 [h]
(3d)	61.6 (61.4)	4.7 (4.8)	1.1 (0.9)	Cl, 4.3 (4.6)	168—172	14 [h]
(3e)·0.4CH_2Cl_2	53.9 (54.0)	4.0 (4.1)	1.0 (1.2)	Cl, 11.8 (11.6)	178—185	13 [h]
(3f)·0.5CH_2Cl_2	54.6 (54.9)	4.3 (4.5)	1.1 (1.2)	Cl, 11.8 (11.7)	180—183	15 [h]
(3g)·0.8CH_2Cl_2	55.0 (55.4)	4.3 (4.2)	1.6 (1.1)	Cl, 12.8 (12.8)	>230	10 [h]
(4)·0.85CH_2Cl_2	47.2 (46.9)	3.9 (3.7)	1.0 (0.8)	Cl, 11.7 (11.2)	187—190	23 [h]
(5)	53.4 (53.4)	4.3 (4.2)	1.0 (1.0)	Cl, 5.0 (5.0)	225—230	15 [h]
(6a)	46.8 (47.1)	3.6 (3.6)	0.9 (1.0)	Cl, 9.9 (9.6)	>350	18 [h]
(6b)·0.2CH_2Cl_2	60.4 (60.7)	4.6 (4.7)	1.1 (0.9)	Cl, 5.75 (5.4)	162—165	28 [h]

[a] Calculated values are in parentheses. [b] The presence of dichloromethane of crystallization in some of the complexes was verified by ^{1}H n.m.r. spectroscopy. [c] Corrected. All complexes decompose on melting. n.d. = Not determined. [d] In acetone at +21 °C unless stated otherwise. [e] See Discussion. [f] Also prepared by Balch and co-workers [14] (see text). [g] Prone to lose Bu^{t}NC, hence poor microanalysis and conductivity data. [h] In nitrobenzene.

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

Complex	Temperature (°C)	δ(CH_2)	^3J(PtH)	Other
(1b)	21	5.30	33	δ(Bu^t) 0.64
(2a)	−80 [b]	4.44	70	δ(Me) 2.46
(2b)	−80 [b]	4.19	80	δ(Me) 3.00
(2d)	−80 [b]	4.48	60	δ(Bu^t) 0.93
(2e)	−80 [b]	4.73	70	δ(Bu^t) 0.93
(2g)	−80 [b]	4.43		δ(Me) 2.65
(2h)	−80 [b]	4.42		δ(Me) 3.06
(2i)	−80 [b]	4.44		δ(Bu^t) 0.84
(2j)	−80 [b]	4.66		δ(Bu^t) 0.90
			^2J(HH)	
(3a)	−50	{4.16, 3.75}	14	δ(Me) 2.93, $^4J(PtCH_3)$ 21
(3b)	−50	{4.20, 3.72}	13	δ(Bu^t) 0.78
(3c)	−50	{4.21, 3.73}	14	δ(Me) 2.29
(3d)	−50	{4.16, 3.51}	14	δ(Bu^t) 0.73, $^3J(AgPCH_2)$ *ca.* 6 Hz [c]
(3e)	−50	{4.22, 3.50}	13	δ(Me) 3.09
(3f)	−50	{4.25, 3.18}	13	δ(Bu^t) 0.87
(3g)	−50	{4.20, 4.50}	14	δ(Me) 2.31, $^3J(AgPCH_2P)$ 6 Hz [c]
(4)	−50	{4.29, 3.92}	12	δ(Bu^t) 0.71

[a] Spectra measured in $CDCl_3$, unless otherwise stated, at the temperatures shown; chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to δ($SiMe_4$) = 0.00 p.p.m.; coupling constants (*J*) in Hz (±1 Hz). [b] In CD_3COCD_3. [c] Individual couplings to ^{109}Ag and ^{107}Ag not resolved.

simple AA′XX′ pattern with satellites due to platinum-195 coupling, *viz.* δ(P_A) = 8.2 p.p.m., ^1J(PtP_A) = 2 336 Hz, δ(P_B) = 26.2 p.p.m., ^3J(PtP_B) = 103 Hz, and $^2J(P_AP_B)$ + $^4J(P_AP_{B'})$ = 51 Hz. There was also a singlet resonance in the ^{31}P-{^{1}H} n.m.r. spectrum at δ 33.0 p.p.m. which was probably due to a gold–dppm complex but which we did not identify. In the ^{1}H-{^{31}P} n.m.r. pattern at −50 °C, in the chemical shift region where PCH_2P protons absorb (δ 4.4—4.5 p.p.m.), there were overlapping broad resonances which we could not analyse. The t-butyl resonance occurred at δ 0.73 p.p.m.

Transmetallations.—We have shown in previous papers [5,6] that d^{10} metal ions (Cu^I, Ag^I, Au^I, or Hg^{II}) are readily displaced by Rh^I or Ir^I (d^8) (transmetallation) to form their

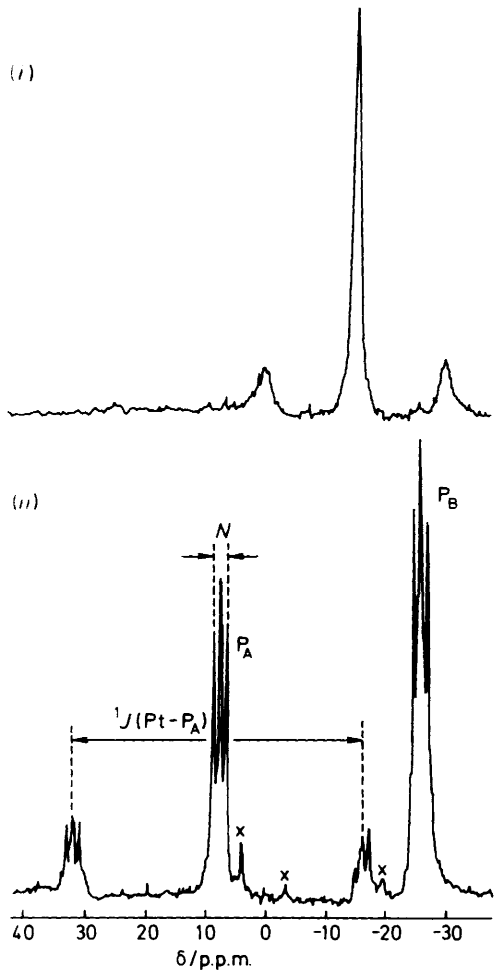

Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectrum of *trans*-[Pt(CNMe)$_2$(dppm-*P*)$_2$]Cl$_2$ (2c) in EtOH: (*i*) at +21 °C, (*ii*) at −90 °C. × = Impurity

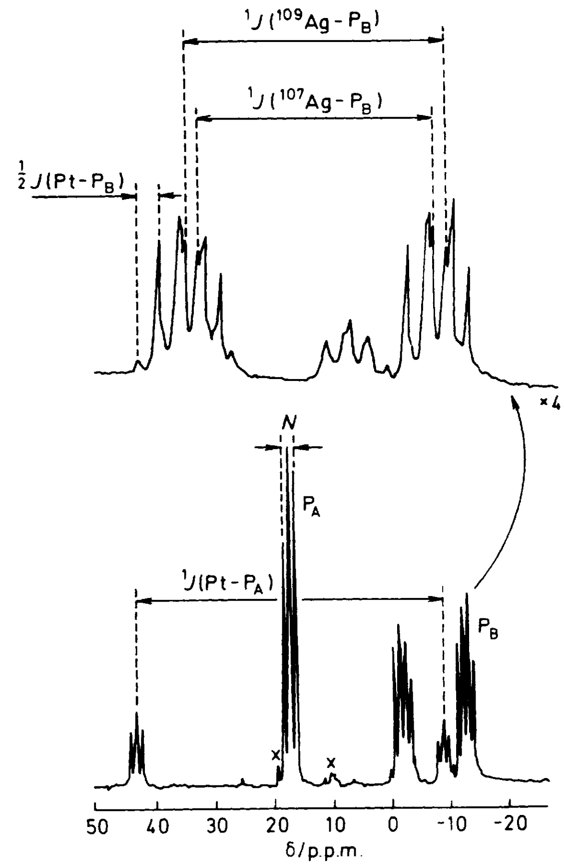

Figure 2. $^{31}P-\{^1H\}$ N.m.r. spectrum of [(Bu^{t}NC)ClPt(μ-dppm)$_2$-AgCl]Cl (3b) in CDCl$_3$ at −50 °C. × = Impurity

heterobimetallic complexes with platinum or palladium acetylides. It was clearly of interest to see if one could effect similar displacements of Ag from the heterobimetallic isonitrile complexes already discussed in the present paper. Treatment of [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl in dichloromethane with [Rh$_2$Cl$_2$(CO)$_4$] caused rapid precipitation of silver chloride. From the mother-liquors the salt [(Bu^{t}NC)-ClPt(μ-dppm)$_2$RhCl(CO)][RhCl$_2$(CO)$_2$] (6a) was isolated and characterized, see Experimental section and Tables. We also made the corresponding BPh$_4^-$ salt (6b) by treating [(Bu^{t}NC)-ClPt(μ-dppm)$_2$AgCl][BPh$_4$] (3d) in dichloromethane with the equivalent amount of [Rh$_2$Cl$_2$(CO)$_4$]. This tetraphenylborate salt (6b) has $^{31}P-\{^1H\}$ n.m.r. parameters which are very similar to those of the corresponding [RhCl$_2$(CO)$_2$]$^-$ salt (6a) (Table 1). Preliminary work also suggested that the silver of the mixed palladium–silver complex [(*p*-MeC$_6$H$_4$NC)ClPd(μ-dppm)$_2$AgCl]Cl (3g) when treated with [Rh$_2$Cl$_2$(CO)$_4$] could be replaced by Rh(CO) to give [(*p*-MeC$_6$H$_4$NC)ClPd(μ-dppm)$_2$-RhCl(CO)]Cl; this product was not isolated but characterized by $^{31}P-\{^1H\}$ n.m.r. spectroscopy in CDCl$_3$ solution, *viz.* $\delta(P_A) = +11.9$ p.p.m., $\delta(P_B) = +20.8$ p.p.m., $^1J(RhP_B) = 81$ Hz, and $^2J(P_AP_B) + {}^4J(P_AP_{B'}) = 80$ Hz. $^{31}P-\{^1H\}$ N.m.r. studies on the effect of treating complexes (3a), (3c), (3e), and (3f) with [Rh$_2$Cl$_2$(CO)$_4$] also showed that displacement of silver by rhodium occurred but we did not isolate the products.

It is probable that displacement of silver by other metals from complexes of type (3) could be effected.

Experimental

The general techniques and apparatus used were the same as in other recent papers from this laboratory.[20]

Preparations.—Salts of the cation [Pt$_2$(CNBu^t)$_4$(μ-dppm)$_2$]$^{4+}$ (1a). A suspension of [PtCl$_2$(dppm-*PP'*)] (0.30 g, 0.46 mmol) in methanol (10 cm^3) was treated with Bu^{t}NC (0.10 g, 1.2 mmol) and the mixture stirred for 15 min at *ca.* 20 °C. The resultant clear solution was evaporated under reduced pressure and the residue triturated with diethyl ether. This gave the chloride salt (1a) as a white solid. Yield 0.30 g (80%).

A solution of this chloride salt (0.10 g, 0.062 mmol) in methanol (10 cm^3) was added to a solution of NH$_4$PF$_6$ (0.10 g, 0.61 mmol) in methanol (10 cm^3). The resultant white precipitate was filtered off, washed with methanol, and dried *in vacuo* to give (1b). Yield 0.11 g (87%).

[Pt(CNBu^t)$_2$(dppm-*P*)$_2$][PF$_6$]$_2$ (2e) *and other salts of type* (2). A solution of Bu^{t}NC (0.35 g, 4.15 mmol) in methanol (2 cm^3) was added to a solution of [Pt(dppm-*PP'*)$_2$]Cl$_2$ (2.00 g, 1.93 mmol) in methanol (40 cm^3). A solution of NH$_4$PF$_6$ (0.66 g, 4.05 mmol) in aqueous methanol [water (6 cm^3), MeOH (10 cm^3)] was then added. The white precipitate was stirred for 1.5 h, filtered off, washed with water and diethyl ether, and dried *in vacuo* to give the required product (2.51 g, 95%).

Complexes (2b) (73%), (2h) (96%), and (2j) (86%) were made in a similar manner. The tetraphenylborate salts were made by addition of NaBPh$_4$ in aqueous methanol (instead of

NH_4PF_6). Yields: (2a) (81%), (2d) (90%), (2g) (96%), and (2i) (94%).

[(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl (3b) *and analogous complexes of type* (3). The compound [AgCl(CNBu^t)] (0.045 g, 0.199 mmol) was added to a stirred solution of [Pt(dppm-*PP'*)$_2$]Cl$_2$ (0.200 g, 0.193 mmol) in dichloromethane (5 cm^3). When a clear solution had formed, diethyl ether (10 cm^3) was added. The resultant mixture was cooled to *ca.* 5 °C and over a period of 2 d the required product separated as white microcrystals of the dichloromethane solvate. Yield 0.211 g (81%).

The following were prepared in a similar manner in the yields shown: (3a) (77%), (3c) (61%), (3d) (72%), (3e) (80%), (3f) (85%), and (3g) (56%).

Complex (3b) *by the alternative method.* A solution of Bu^{t}NC (0.042 g, 0.505 mmol) in dichloromethane (1.2 cm^3) was added to a solution of [Pt(dppm-*PP'*)$_2$]Cl$_2$ (0.500 g, 0.483 mmol) in dichloromethane (10 cm^3); [{AgCl(PPh$_3$)}$_4$] (0.200 g, 0.123 mmol) was then added. The mixture was then stirred for 5 min, and diethyl ether (20 cm^3) added to the resultant solution. This precipitated out the required product which was isolated as above, and identified by its $^{31}P-\{^1H\}$ n.m.r. and i.r. spectra. Yield 0.438 g (72%). When 2 instead of 1 mol equivalents of Bu^{t}NC were added to [Pt(dppm-*PP'*)$_2$]Cl$_2$ the yield of complex (3b) was 95%.

[(Bu^{t}NC)ClPt(μ-dppm)$_2$AuCl]Cl (4). This was made from [Pt(dppm-*PP'*)$_2$]Cl$_2$, Bu^{t}NC, and [AuCl(PPh$_3$)] in a similar manner, and obtained as a pale yellow solid in 81% yield.

[(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl][BPh$_4$]. A solution of the corresponding chloride salt (0.50 g, 0.371 mmol) in ethanol (5 cm^3) was treated with a solution of $NaBPh_4$ (0.150 g, 0.438 mmol) in ethanol (5 cm^3). This gave the required compound as a white precipitate. Yield 0.414 g (71%).

[(Bu^{t}NC)(PhC≡C)Pt(μ-dppm)$_2$AuCl]Cl (5). A solution of [Pt(dppm-*PP'*)$_2$]Cl$_2$ (0.042 g, 0.041 mmol) in dichloromethane (0.4 cm^3) was added to a suspension prepared by treating AuC≡CPh (0.012 g, 0.040 mmol) with Bu^{t}NC (0.0035 g, 0.042 mmol) in dichloromethane (0.067 cm^3). Benzene was then added to cloud point and the mixture cooled to 5 °C. The required complex crystallized out as a pale yellow solid. A further quantity was obtained by reducing the volume of the mother-liquor under reduced pressure and adding benzene. Yield 0.014 g (98%).

[(Bu^{t}NC)ClPt(μ-dppm)$_2$RhCl(CO)][RhCl$_2$(CO)$_2$] (6a). The compound [Rh$_2$Cl$_2$(CO)$_4$] (0.060 g, 0.154 mmol) was added to a solution of [(Bu^{t}NC)ClPt(μ-dppm)$_2$AgCl]Cl (0.20 g, 0.149 mmol) in methanol (10 cm^3). The mixture was then stirred for 1 h at *ca.* 20 °C, when silver chloride precipitated. This was filtered off, n-hexane (15 cm^3) added to the filtrate, and the solution reduced in volume (to *ca.* 2 cm^3) under reduced pressure. This gave the required product as yellow microcrystals (0.140 g, 64%).

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