Bimetallic Systems. Part 8.[1] Heterobimetallic Di-isonitrile or Isonitrile–Carbonyl Complexes of Rhodium or Iridium bridged to Silver or Gold by $Ph_2PCH_2PPh_2$

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Treatment of $[M_2(CNBu^t)_4(\mu\text{-dppm})_2]Cl_2$ (M = Rh or Ir, dppm = $Ph_2PCH_2PPh_2$) with dppm gave labile systems at 20 °C. $^{31}P\text{-}\{^1H\}$ N.m.r. spectroscopy at −60 °C showed complete conversion to the tris-monodentate dppm complexes $[M(CNBu^t)_2(dppm\text{-}P)_3]Cl$. Treatment of $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2][PF_6]_2$ with two moles of dppm followed by $AgNO_3$ gave the mixed rhodium–silver complexes $[(Bu^tNC)_2Rh(\mu\text{-dppm})_2Ag][PF_6][NO_3]$. Salts with other counter ions, *viz.* Cl^-, were also prepared. A rhodium–gold complex $[(Bu^tNC)_2Rh(\mu\text{-dppm})_2Au]Cl_2$ was prepared using $[AuCl(PPh_3)]$ and a $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2]Cl_2$–dppm mixture. Treatment of $[\{Ir(C_8H_{14})_2Cl\}_2]$ with four mol equivalents of dppm, six of Bu^tNC, and two of $[AuCl(PPh_3)]$ gave the fluxional molecule $[(Bu^tNC)_3Ir(\mu\text{-dppm})_2Au]Cl_2$ which showed a particularly well defined AA′XX′ $^{31}P\text{-}\{^1H\}$ n.m.r. pattern (18 of the theoretical 20 lines), and which was analysed. Treatment of $[Ir(CO)(dppm\text{-}PP')_2]Cl$ with $[AgCl(CNBu^t)]$ gave the mixed iridium–silver complex $[(OC)(Bu^tNC)Ir(\mu\text{-dppm})_2AgCl]Cl$ in good yield. The MeNC and $p\text{-}MeC_6H_4NC$ analogues were prepared similarly as were the corresponding rhodium–silver complexes, $[(OC)(RNC)Rh(\mu\text{-dppm})_2AgCl]Cl$ (R = Bu^t or *p*-tolyl).

There is much interest in binuclear complexes of $Ph_2PCH_2PPh_2$ (dppm) and the chemistry of its homonuclear complexes has been reviewed.[2] We have shown previously that complexes of the type *trans*-$[M(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (M = Pt or Pd, R = alkyl or aryl)[3] and of the type $[M(CNR)_2(dppm\text{-}P)_2]X_2$ (X = Cl, PF_6, or BPh_4)[4] can be prepared and subsequently used to synthesize a wide range of heterobimetallic complexes with metals such as Mo, W, Rh, Ir, Cu, Ag, Au, or Hg.[3–6] In this paper we describe an extension of this type of chemistry to isonitrile–dppm complexes of rhodium or iridium; isonitriles are isoelectronic with acetylides.

Figure 1. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra of $[Rh(CNBu^t)_2(dppm\text{-}P)_3]^+$ (**1a**) in CH_2Cl_2–CD_2Cl_2 at (*a*) +21 and (*b*) −60 °C

Results and Discussion

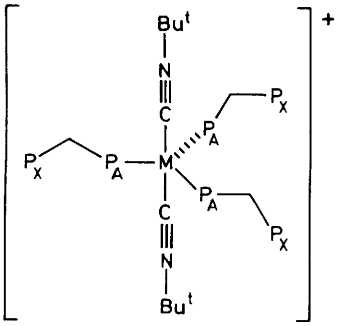
Homonuclear bis-dppm complexes of rhodium or iridium of the type $[M_2(CNR)_4(\mu\text{-dppm})_2]Cl_2$ are known[7–9] and we therefore treated them with more dppm in an attempt to form mononuclear monodentate dppm complexes. The 'face-to-face' complexes of the type $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ react with dppm to give mononuclear complexes of type *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ in high yield.[3]

Treatment of the 'face-to-face' homobinuclear rhodium–isonitrile complex $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2]Cl_2$ in dichloromethane with dppm (2.4 mol equivalents) caused a colour change from deep purple to orange-red. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this solution showed the presence of the homobinuclear rhodium starting material and, additionally, there was a broad resonance at δ −7.2 p.p.m. When the solution was cooled to −60 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum again showed the presence of the homobinuclear rhodium starting material, but the broad resonance had changed to a quartet and a doublet of quartets. When this experiment was repeated using 4.1 mol equivalents of dppm no homobinuclear rhodium starting material was detected in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at +21 °C, and the spectrum consisted solely of a broad resonance at δ −11.9 p.p.m. [Figure 1(*a*)]. When the solution was cooled to −60 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, Figure 1(*b*), consisted of a doublet of quartets and a single quartet, together with a resonance due to 'free' dppm. The low-frequency single quartet at δ = −28.8 p.p.m. has a chemical shift similar to that of dppm and is typical of an uncomplexed CH_2PPh_2 moiety. The chemical shift (16.3 p.p.m.) of the doublet of quartets resonance pattern is also typical of tertiary phosphines complexed to rhodium, $^1J(RhP)$ = 129 Hz. These experiments suggest that the product contains three moles of dppm per rhodium and we therefore formulate it as the chloride salt of $[Rh(CNBu^t)_2(dppm\text{-}P)_3]^+$ (**1a**) (see also below).

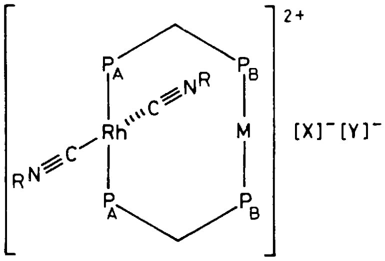
Table 1. Microanalyses, melting points, yields, and conductivities for some silver and gold containing heterobinuclear bis-dppm rhodium and iridium di-isonitrile and isonitrile–carbonyl complexes

Complex	Analysis[a] (%) C	H	N	X	M.p.[b]/°C	Yield (%)	Λ^c/ Ω^{-1} cm^2 mol^{-1}
(2a)	53.2 (53.3)	4.9 (4.6)	3.1 (3.1)	n.d.	198—199	88	128[e]
(2b)·0.5C_6H_{14}[d]	51.3 (51.2)	4.7 (4.7)	2.0 (1.4)	15.0 (15.4)	n.d.	98	199[e]
(2c)	53.9 (54.3)	4.8 (4.7)	1.9 (2.1)	Cl, 2.8 (2.7)	n.d.	69	124[e]
(2d)	56.5 (56.3)	5.1 (5.0)	2.2 (2.1)	10.8 (10.9)	n.d.	92	74[e]
(2e)	61.9 (61.7)	4.8 (4.6)	2.4 (2.2)	5.8 (5.5)	143—148	78	20
(2f)	54.9 (55.2)	5.0 (4.8)	2.0 (2.2)	5.7 (5.8)	183—186	75	19
(4)·0.5C_6H_6[d]	53.7 (53.8)	5.0 (4.9)	2.6 (2.8)	5.2 (4.7)	130—145	88	21
(6b)·CH_2Cl_2[d]	50.3 (50.2)	3.7 (3.8)	1.4 (1.1)	10.4 (11.1)	165—171	26	15
(6a)·CH_2Cl_2[d]	50.7 (51.0)	4.2 (4.2)	0.8 (0.9)	11.0 (10.9)	174—176	59	14
(6c)·0.7CH_2Cl_2[d]	53.0 (53.3)	4.1 (3.9)	1.3 (1.1)	8.4 (9.0)	185—188	85	29
(6d)·1.7CH_2Cl_2[d]	52.3 (51.9)	4.4 (4.3)	1.3 (1.1)	13.4 (14.4)	193—197	67	9
(6e)·CH_2Cl_2[d]	56.3 (56.3)	4.4 (4.2)	1.3 (1.1)	10.9 (11.1)	144—147	42	9

[a] Calculated values in parentheses. [b] With decomposition; n.d. = not determined. [c] In $PhNO_2$ at +21 °C unless stated otherwise, *ca.* 1 mmol dm^{-3}. [d] Presence of solvate verified by ^1H n.m.r. spectroscopy. [e] In acetone at +21 °C.



(1a) M = Rh
(1b) M = Ir



(2a) M = Ag, R = Bu^t, X = PF_6, Y = NO_3
(2b) M = Ag, R = Bu^t, X = Y = PF_6
(2c) M = Ag, R = Bu^t, X = PF_6, Y = Cl
(2d) M = Ag, R = Bu^t, X = Y = Cl
(2e) M = Ag, R = *p*-tolyl, X = Y = Cl
(2f) M = Au, R = Bu^t, X = Y = Cl

The variable-temperature behaviour of the complex is reminiscent of the intramolecular $MPh_2PCH_2P^*Ph_2 \rightleftharpoons MPh_2P^*CH_2PPh_2$ exchange observed previously.[3] However, the chemical shift of the broad ^{31}P-$\{^1H\}$ n.m.r. spectrum at +22 °C varies when an excess of dppm is present; this suggests that intermolecular phosphine exchange is also occurring.

The ^{31}P-$\{^1H\}$ spin system of (**1**) would be of the AA′A″XX′X″M type. The AA′A″XX′X″ system has been analysed by Bernstein and co-workers[10] for the general case and by Harris and co-workers,[11,12] for the case where $J_{XX'} = 0$. For the special case where $J_{XX'} = 0$ and $|J_{AA'}| \gg |J_{AX} - J_{AX'}|$ the spectrum consists of two deceptively simple 1:3:3:1 quartets, the two outer lines being separated by $N = |2J_{AX} + J_{AX'}|$. Clearly the low-temperature spectrum shown in Figure 1 is just such a case with further coupling to rhodium being shown by the directly bonded P nuclei. The data are $\delta(P_A) = 16.3$ p.p.m., $^1J(RhP_A) = 129$ Hz, $\delta(P_X) = -28.8$ p.p.m., $|2\,^2J_{AX} + {}^4J_{AX'}| = 46$ Hz. The same complex was formed when four mol equivalents of Bu^{t}NC were added to a solution of $[Rh_2Cl_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) in dichloromethane containing six mol equivalents of dppm. Cationic, five-co-ordinate bis-isonitrile tris-phosphine complexes of the type $[Rh(CNR)_2(PR_3)_3]^+$ (R = alkyl or aryl) have been described previously.[13] However, we have been unable to isolate the cation $[Rh(CNBu^t)_2(dppm\text{-}P)_3]^+$ (**1a**) either as its PF_6^- or BPh_4^- salts; addition of these anions to ethanolic solutions of (**1a**), prepared as above, gave only the known $[Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2]X_2$ (X = PF_6^- or BPh_4^-), even at −60 °C.

When four mol equivalents of Bu^{t}NC in dichloromethane were added to a solution of $[\{Ir(cyclo\text{-}C_8H_{14})_2Cl\}_2]$ in dichloromethane containing six mol equivalents of dppm, the ^{31}P-$\{^1H\}$ n.m.r. spectrum at −50 °C contained two deceptively simple 1:3:3:1 quartets, presumably due to the analogous species $[Ir(CNBu^t)_2(dppm\text{-}P)_3]^+$ (**1b**).

Synthesis of Heterobinuclear Complexes with Silver or Gold.—Despite being able to detect only the tris-dppm-*P* complexes of rhodium or iridium we felt it might be possible to form heterobimetallics based on a bis-dppm-*P* rhodium or iridium moiety, $(RNC)_2M(dppm)_2$, and this proved to be the case. Treatment of the homobinuclear complex $[Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2][PF_6]_2$ in acetone with two mol equivalents of dppm followed by an aqueous acetone solution of $AgNO_3$ gave the complex $[(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Ag][PF_6][NO_3]$ (**2a**). This complex was characterised by (*i*) satisfactory microanalysis, Table 1; (*ii*) i.r. spectroscopy, ν(CN) = 2 140 cm^{-1}, *i.e.* terminal isocyanide, Table 2; (*iii*) ^{31}P-$\{^1H\}$ n.m.r. spectroscopy, Table 2; (*iv*) ^1H-$\{^{31}P\}$ n.m.r. spectroscopy, Table 2; and (*v*) conductivity measurements in acetone showing the complex to be a 1:2 electrolyte (Table 1).

The ^{31}P-$\{^1H\}$ n.m.r. spectrum in $CDCl_3$ contains two deceptively simple AA′XX′ quartets and a PF_6^- resonance. One quartet showed short-range coupling to ^{103}Rh, $^1J(RhP_A)$ = 121 Hz, and the other quartet showed short-range coupling to either ^{109}Ag or ^{107}Ag, Table 2.

The ^1H-$\{^{31}P\}$ n.m.r. spectrum in CD_2Cl_2 at +21 °C contained a resonance at δ 0.70 p.p.m. assigned to the Bu^t group. The methylene resonance of the dppm occurred as a doublet

Table 2. $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ n.m.r. and i.r. data

	$^{31}P^a$						$^1H^b$				
Complex	$\delta(P_A)$	$^1J(RhP_A)$	$\delta(P_B)$	$^1J(^{109}AgP_B)$	$^1J(^{107}AgP_B)$	N^c	$\delta(CH_2)$	$\delta(Bu^t)$	$\delta(Me)$	$\nu(C\equiv N)^d/cm^{-1}$	$\nu(C\equiv O)^d/cm^{-1}$
(2a)	26.7	121	+5.5	510	437	100	3.51 3.44	0.70		2 140s 2 190w	
(2b)	27.0	117	+6.5	542	459	90	3.71^e	0.70		2 150s	
(2c)	22.7	120	-4.6^f	436	381	110	3.40	0.70		2 140s 2 190w	
(2d)	26.7	122	-5.4^f	450	386	105	3.40	0.70		2 150s 2 185w	
(2e)	30.4	127	-2.9^f	440^g		107	3.57		1.87	2 110	
(2f)	24.1	120	37.3	—	—	71	4.80	0.62		2 150s	
(4) 'or **(5)**'^{h}	5.4	—	46.4	—	—	107	5.48	0.98		2 165s	
							5.09^e	1.00^e 0.90			
(6b)	24.3	—	−11.3	430	378	93	4.26,3.43 (14)^i		2.72^i	2 170	1 965
(6a)	24.3	—	−11.3	424	364	93	4.27,3.40 (13)^i		0.59^i	2 140	1 972
(6c)	26.8	—	−8.8	439	381	93	4.26,3.47 (13)^i		2.33,2.17^i	2 180	1 980
(6d)	32.4	120	−5.2	453	391	103	4.00,3.40 (14)^i	0.48		2 130	1 980
(6e)	32.9 32.4	127 117	−5.7 −5.6	437 422	381 364	107 100	4.31,3.18 (12)^i		2.31,2.17^i	2 100	1 985

[a] In $CDCl_3$ at 40.25 MHz. Compounds **(6a)**—**(6e)** were measured at −50 °C, the remainder were measured at +20 °C except for **(2c)** (− 70 °C). Chemical shifts (δ) in p.p.m. (±0.1 p.p.m.) to high frequency of 85% H_3PO_4; coupling constants (*J*) in Hz (±3 Hz). [b] In $CDCl_3$ at 100 MHz and at 20 °C unless stated otherwise. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) to high frequency of $SiMe_4$. [c] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [d] KBr discs, error ±2 cm^{-1}. [e] At −50 °C. [f] $^3J(RhP_B) = 5 \pm 2$ Hz. [g] Individual couplings to ^{107}Ag and ^{109}Ag not resolved. [h] See Discussion section for other data. [i] At −50 °C. Two resonances due to pseudo-axial and pseudo-equatorial hydrogens, $H_{ax.}$ and $H_{eq.}$. For each compound the resonance of lower δ was broader than the other, due to coupling to silver, and was assigned to $H_{eq.}$. The numbers in parentheses are $^2J(H_{eq.}H_{ax.})$.

at δ 3.47. We tentatively suggest that the splitting is caused by silver, $^3J(AgCH) = 7$ Hz, since we have previously found similar couplings in silver–dppm complexes, *e.g.*, in $[Cl(MeNC)Pd(\mu\text{-dppm})_2AgCl]$.

The corresponding bis-hexafluorophosphate salt $[(Bu^tNC)_2Rh(\mu\text{-dppm})_2Ag][PF_6]_2$ **(2b)** was prepared in an analogous way from $AgPF_6$, characterising data are given in Tables 1 and 2. The $^{31}P-\{^1H\}$ n.m.r. data of **(2b)** and **(2a)** although very similar, are nevertheless sufficiently different to suggest that in solution there may be interaction of the counter ions with the binuclear cation. The main differences arise in the parameters associated with the silver atom. The silver–phosphine complex $[Ag(NO_3)(PPh_3)_2]$ has been shown to be non-ionic in solution, the oxygen atoms of the nitrate ligand possibly acting in a bidentate manner to form a tetrahedral arrangement around the silver atom.[14] A similar, but weaker, interaction is possibly occurring in the salt **(2a)**, its electrical conductivity is less than that of **(2b)**. The values of $^1J(^{109}AgP_B)$ and $^1J(^{107}AgP_B)$ are slightly smaller than those of other two-co-ordinate silver halide bis-phosphine complexes.[15]

Treatment of the homobinuclear rhodium complex $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2][PF_6]_2$ in dichloromethane with two mol equivalents of dppm followed by $[\{AgCl(PPh_3)\}_4]$ gave a heterobinuclear bis-dppm complex tentatively assigned as $[(Bu^tNC)_2Rh(\mu\text{-dppm})_2Ag][PF_6]Cl$ **(2c)**. Characterising data are given in Tables 1 and 2. The $^{31}P-\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at −40 °C was particularly well resolved, Figure 2, showing long-range $^3J(RhP_B)$ coupling to the silver-bonded phosphorus nuclei P_B. It is interesting that the chloride ion does not appear to be bound to the silver atom, resulting in a 1:2 salt, although the conductivity (124) is less than that of **(2b)** (199) it is too high for a 1:1 salt (70 Ω^{-1} cm^2 mol^{-1}). However the values of $^1J(^{109}AgP_B)$ and $^1J(^{107}AgP_B)$ are similar to those of three-co-ordinate silver halide bis-phosphine complexes [$^1J(^{107}AgP)$ *ca.* 380 Hz] rather than two-co-ordinate silver bis-phosphine complexes [$^1J(^{107}AgP)$ *ca.* 490 Hz]. This behaviour is discussed below.

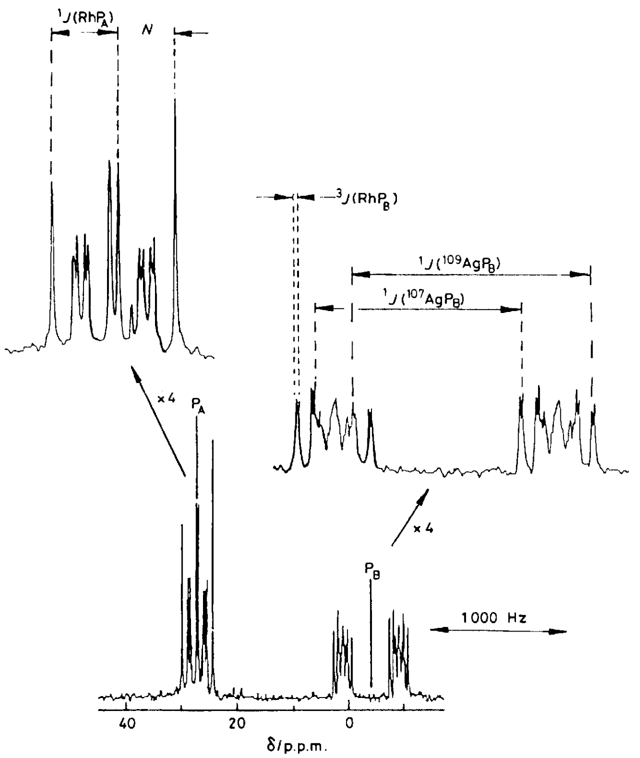
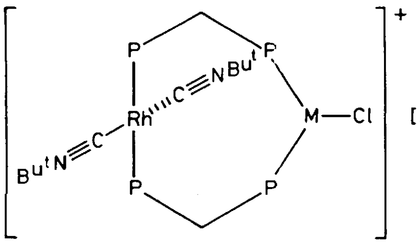


Figure 2. $^{31}P\{^1H\}$ N.m.r. spectrum of $[(Bu^tNC)_2Rh(\mu\text{-dppm})_2Ag][PF_6]Cl$ **(2c)** at −40 °C

Treatment of the homobinuclear rhodium complex $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2]Cl_2$ in dichloromethane with two mol equivalents of dppm followed by addition of $[\{AgCl(PPh_3)\}_4]$ gave a heterobinuclear bis-dppm complex, the conductivity of which in acetone, Table 1, suggested a 1:1 rather than a 1:2 electrolyte. In view of the results above where the chloride ion did not appear to be bonded to the silver atom this conductivity behaviour is possibly a result of ion-pair formation. The heterobinuclear platinum–silver diacetylide complexes $[(\mathrm{RC{\equiv}C})_2\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{AgX}]$ (R = Me, Ph, *p*-tolyl, *etc.*; X = Cl or I) were shown to be non-electrolytes.[5] However, addition of large anions, such as $\mathrm{BPh_4}^-$, caused formation of the salts $[(\mathrm{RC{\equiv}C})_2(\mu\text{-dppm})_2\mathrm{Ag}][\mathrm{BPh_4}]$, indicating that the silver–halide bond is easily ionised. Hence, for the rhodium–silver complexes it is difficult to determine whether a dispositive cation exists in close association with a chloride anion, *i.e.* an ion pair, or if a monopositive cation exists with easily ionisable chloride ligands as in (**3a**) or (**3b**). The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. parameters, *i.e.* $^1J(\mathrm{AgP})$, of both the $[\mathrm{PF_6}]\mathrm{Cl}$ and $\mathrm{Cl_2}$ salts suggest three-co-ordinate silver, as in (**3a**) or (**3b**), yet the conductivity of the $[\mathrm{PF_6}]\mathrm{Cl}$ salt suggests that the silver is two-co-ordinate, as in (**2c**). These differences may be due to the different solvents used to record the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra and to measure the conductivities in. When a non-co-ordinating large counter ion such as $\mathrm{PF_6}^-$ is present, acetone is a sufficiently good solvent to prevent ion-pair formation of the cation and chloride ion, hence a 1:2 salt. When both counter ions are small and capable of co-ordinating, acetone is not a sufficiently good solvent to prevent substantial ion-pair formation, hence a 1:1 salt. In $\mathrm{CDCl_3}$, ion-pair formation is not prevented, and the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. parameters suggest three-co-ordinate silver.



(**3a**) M = Ag, X = $\mathrm{PF_6}$
(**3b**) M = Ag, X = Cl
(**3c**) M = Au, X = Cl

The complex (**2d**) or (**3b**) was also prepared in a 'one-pot' reaction by successive addition of stoicheiometric amounts of dppm, $\mathrm{Bu^tNC}$, and $[\{\mathrm{AgCl(PPh_3)}\}_4]$ to a solution of $[\mathrm{Rh_2Cl_2(cod)_2}]$ in dichloromethane. A similar treatment with *p*-tolyl isocyanide gave the deep blue compound $[(p\text{-}\mathrm{MeC_6H_4NC})_2\mathrm{Rh}(\mu\text{-dppm})_2\mathrm{Ag}]\mathrm{Cl_2}$ (**2e**). Characterising data are given in Tables 1 and 2. This complex lost isonitrile in the solid state and especially in solution.

Treatment of the homobinuclear rhodium complex $[\mathrm{Rh_2(CNBu^t)_4}(\mu\text{-dppm})_2]\mathrm{Cl_2}$ in dichloromethane with two mol equivalents of dppm followed by addition of two mol equivalents of $[\mathrm{AuCl(PPh_3)}]$ gave the rhodium–gold complex (**2f**). The conductivity of this complex in nitrobenzene suggested a 1:1 electrolyte, Table 1, yet as gold(I) tends to be two- rather than three-co-ordinate, ion-pair formation is again possible, although the structure may be as depicted in (**3c**) with a gold–chloride bond. The complex was characterised by (*i*) satisfactory microanalysis, Table 1; (*ii*) i.r. spectroscopy, Table 2; (*iii*) $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectroscopy, Table 2; and (*iv*) $^1\mathrm{H}\text{-}\{^{31}\mathrm{P}\}$ n.m.r. spectroscopy, Table 2.

The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum in $\mathrm{CDCl_3}$ at −50 °C gave the expected deceptively simple AA′XX′ spectrum with coupling of $\mathrm{P_A}$ to $^{103}\mathrm{Rh}$. The $^1\mathrm{H}\text{-}\{^{31}\mathrm{P}\}$ n.m.r. spectrum in $\mathrm{CDCl_3}$ at *ca.* +21 °C contained a broad resonance for the methylene protons of the dppm ligands; cooling the solution to −50 °C failed to render these protons inequivalent. The $\mathrm{Bu^t}$ resonance occurred as a single resonance indicating equivalence of both isonitriles. This behaviour suggests that there is little, if any, interaction between the isonitrile ligands and the gold metal centre; therefore all the dppm methylene protons are equivalent, even down to −50 °C.

Treatment of the iridium binuclear species [{Ir(cyclo-

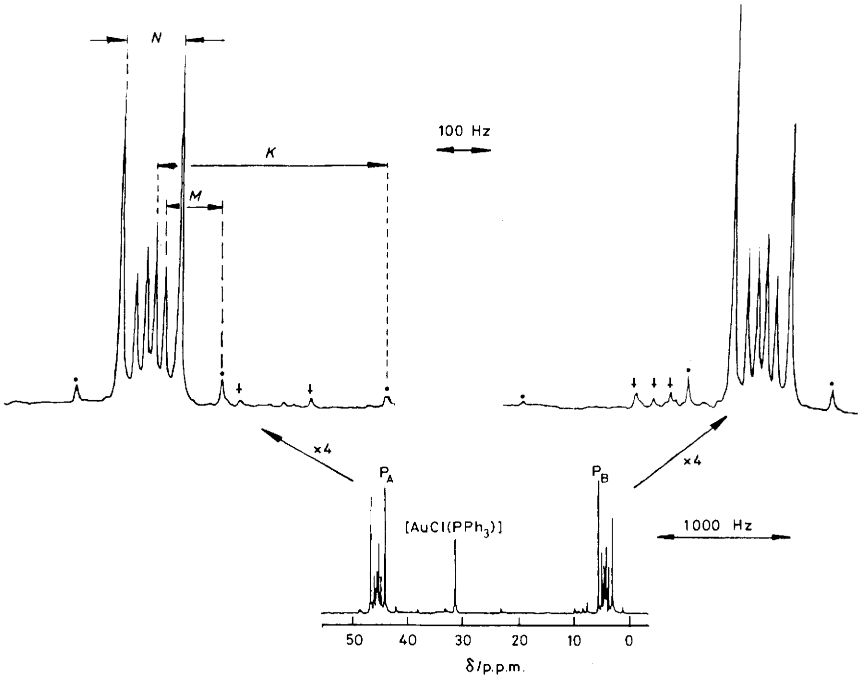
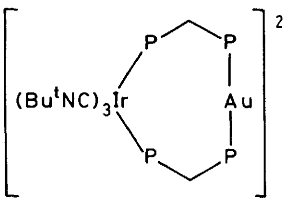


Figure 3. $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ N.m.r. spectrum of $[(\mathrm{Bu^tNC})_3\mathrm{Ir}(\mu\text{-dppm})_2\mathrm{Au}]\mathrm{Cl_2}$ (**4**) at 21 °C; ↓ = impurities, ● = outer lines of AA′XX′ ab sub-spectra



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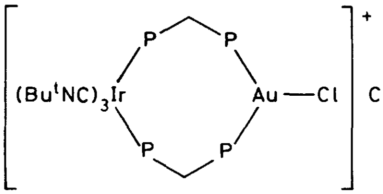


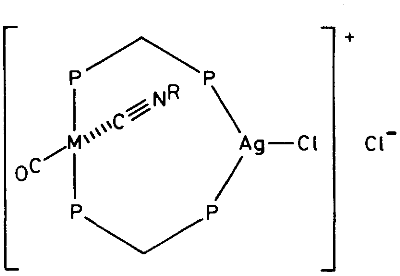
(5)

$C_8H_{14})_2Cl\}_2]$ in dichloromethane with four mol equivalents of dppm and six mol equivalents of Bu^{t}NC, followed by $[AuCl(PPh_3)]$, gave the heterobinuclear iridium–gold bis-dppm tris-isonitrile complex $[(Bu^tNC)_3Ir(\mu\text{-dppm})_2Au]Cl_2$ (**4**) in 88% yield. This formulation was based on (*i*) satisfactory microanalysis, Table 1; (*ii*) i.r. spectroscopy, Table 2; (*iii*) $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy, Table 2; (*iv*) $^1H\text{-}\{^{31}P\}$ n.m.r. spectroscopy, Table 2 and see below; and (*v*) conductivity measurements in $PhNO_2$ which suggested a 1:1 electrolyte, possibly due to ion-pair formation as mentioned above, although a three-co-ordinate gold species $[(Bu^tNC)_3Ir(\mu\text{-dppm})_2AuCl]Cl$ (**5**) cannot be dismissed.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at +21 °C showed a particularly well resolved AA′XX′ spectrum. At −50 °C the signal-to-noise ratio was sufficiently good to allow 18 of the expected 20 lines to be observed (Figure 3). The spectrum allows all the couplings between the phosphorus nuclei to be calculated, although we cannot say whether P_A or P_X is bonded to iridium. Analysis gave $^2J(P_AP_{A'}) = 260$, $^2J(P_XP_{X'}) = 151$, $^2J(P_AP_X) = 114$, and $^4J(P_AP_{X'}) = -7$ Hz.

The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum at +21 °C in $CDCl_3$ contained a broad resonance for the methylene protons of the dppm ligands at an unusually higher chemical shift of δ 5.48 p.p.m., $\omega_{\frac{1}{2}} = 4$ Hz. The Bu^t resonance at +21 °C occurred as a singlet indicating equivalence of all the isonitriles, this singlet integrated for 27 protons with respect to the 4 methylene protons. When the solution was cooled to −50 °C the Bu^t resonance separated into two components of relative intensities 1:2 at δ 1.00 and δ 0.90 p.p.m., respectively. The methylene proton resonances remained as a singlet at δ 5.09 p.p.m. This would correspond to structures such as (**4**) or (**5**) where, presumably, 'ring flipping' occurs to make all the methylene protons equivalent. At +21 °C the isonitriles must be exchanging rapidly by some, as yet, undetermined process. Attempts to make an iridium–silver complex in the same way failed.

Monocarbonyl–Monoisonitrile Complexes.—We have previously shown that isonitrile derivatives of silver chloride, $[AgCl(CNR)]$, gave heterobimetallic complexes of platinum or palladium of the type $[(RNC)ClM(\mu\text{-dppm})_2AgCl]$, when treated with the bis-chelate salts $[M(dppm\text{-}PP')_2]Cl_2$.[4] We have therefore treated the readily prepared five-co-ordinate salt, $[Ir(CO)(dppm\text{-}PP')_2]Cl$ in dichloromethane with $[AgCl(CNBu^t)]$ and obtained the desired mixed carbonyl–isonitrile iridium–silver complex $[(OC)(Bu^tNC)Ir(\mu\text{-dppm})_2AgCl]Cl$



(**6a**) M = Ir, R = Bu^t
(**6b**) M = Ir, R = Me
(**6c**) M = Ir, R = *p*-tolyl
(**6d**) M = Rh, R = Bu^t
(**6e**) M = Rh, R = *p*-tolyl

(**6a**) as a dichloromethane solvate; preparative details are given in the Experimental section, elemental analytical and conductivity data are in Table 1. The i.r. spectrum showed an absorption due to ν(CN) at 2 140 cm^{-1} and ν(CO) at 1 972 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at −50 °C consisted of an AA′XX′ spin system with the X region showing coupling to ^{109}Ag or ^{107}Ag (Table 2). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum in $CDCl_3$ at +21 °C contained a broad methylene resonance of the dppm ligands and a single resonance at δ 0.68 p.p.m. for the Bu^t group, at −50 °C the methylene region had resolved into an AB pattern. The pseudo-axial proton at δ 4.27 p.p.m., while being broad, showed proton–proton coupling, $^2J(H_{eq.}H_{ax.}) = 13$ Hz, while the pseudo-equatorial proton was a very broad signal, at δ 3.40 p.p.m.; the broadening was possibly due to coupling to silver. The Bu^t resonance had separated into two broad resonances suggesting the presence of isomers. The $^{31}P\text{-}\{^1H\}$ n.m.r. parameters of these isomers must be very similar as only one set of resonances was observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum.

The complexes $[(OC)(MeNC)Ir(\mu\text{-dppm})_2AgCl]Cl$ (**6b**) and $[(OC)(p\text{-}MeC_6H_4NC)Ir(\mu\text{-dppm})_2AgCl]Cl$ (**6c**) were prepared in a similar way. The rhodium analogues (**6d**) and (**6e**) were prepared by adding four mol equivalents of dppm to a dichloromethane solution of $[\{Rh(CO)_2Cl\}_2]$ under an atmosphere of CO and adding $[AgCl(CNR)]$ (R = Bu^t or *p*-tolyl). The MeNC–Rh derivative could not be prepared, decomposition to a homobinuclear rhodium complex occurring. Characterising data for the rhodium–silver complexes are given in Tables 1 and 2. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at −50 °C of the *p*-tolyl isonitrile derivative contained two species in roughly equal amounts; the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum at −50 °C contained two broad resonances for the methyl group of the *p*-tolyl isonitrile ligands, indicating the presence of two species although the PCH_2P pattern consisted of one broad AB pattern (data in Table 2). It is possible that the two species indicated by the low-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. and the $^1H\text{-}\{^{31}P\}$ n.m.r. (Me of *p*-tolyl) patterns are as depicted in (**6e**) but at −50 °C the fluxionality of the eight-membered ring has been frozen out; in one species the methylene hydrogens will be on the same side as the $p\text{-}MeC_6H_4NC$ ligand and, in the other species, on the same side as the CO ligand.

It is possible that heterobimetallic derivatives of rhodium or iridium with metals other than silver or gold of similar types to those described above could be made, but we have not yet studied this.

Experimental

The general methods were the same as those described in previous papers from this laboratory.[16]

Preparation of $[\mathrm{Rh(CNBu^t)_2(dppm}\text{-}P)_3]\mathrm{Cl}$ (**1a**) *in situ.*—*Method A.* A solution of dppm (0.038 g, 0.091 mmol) in dichloromethane (0.15 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2]Cl_2}$ (0.030 g, 0.022 mmol) in dichloromethane (0.25 $\mathrm{cm^3}$).

Method B. A solution of $\mathrm{Bu^tNC}$ (0.035 g, 0.421 mmol) in dichloromethane (*ca.* 0.15 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{Rh_2Cl_2(cod)_2}]$ (0.050 g, 0.101 mmol) and dppm (0.240 g, 0.624 mmol) in dichloromethane (1.5 $\mathrm{cm^3}$).

$[\mathrm{Ir(CNBu^t)_2(dppm}\text{-}P)_3]\mathrm{Cl}$ was prepared *in situ* from $[\{\mathrm{Ir(C_8H_{14})_2Cl}\}_2]$ in the same way as Method B.

Preparation of $[\mathrm{(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Ag][PF_6][NO_3]}$ (**2a**).—dppm (0.160 g, 0.416 mmol) was added to a solution of $[\mathrm{Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2][PF_6]_2}$ (0.300 g, 0.198 mmol) in acetone (10 $\mathrm{cm^3}$). When all the solids had dissolved the orange solution was cooled to *ca.* −70 °C and a solution of $\mathrm{AgNO_3}$ (0.071 g, 0.418 mmol) in acetone (5 $\mathrm{cm^3}$) and water (0.1 $\mathrm{cm^3}$) was added. The mixture was stirred for 5 min at *ca.* −70 °C and then allowed to warm to *ca.* +21 °C. The resultant solution was filtered to remove a small amount of pink solid and the filtrate taken to dryness under reduced pressure. The solid residue was triturated with diethyl ether, filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$. The crude product was recrystallised from acetone–n-hexane to give the required product as red-brown microcrystals. Yield 0.470 g (88%).

Preparation of $[\mathrm{(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Ag][PF_6]_2}$ (**2b**).—dppm (0.100 g, 0.260 mmol) was added to a solution of $[\mathrm{Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2][PF_6]_2}$ (0.300 g, 0.125 mmol) in dichloromethane (6 $\mathrm{cm^3}$), followed by a solution of $\mathrm{AgPF_6}$ (0.065 g, 0.257 mmol) in acetone (4 $\mathrm{cm^3}$). The solution was stirred for 5 min, diethyl ether (20 $\mathrm{cm^3}$) was added, and the resultant solution filtered from a small amount of dark solid. The filtrate was taken to dryness under reduced pressure, the orange residual solid was triturated with diethyl ether, filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$. The product was recrystallised from acetone–n-hexane. Yield 0.363 g (98%).

The complex $[\mathrm{(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Ag][PF_6]Cl}$ (**2c**) was prepared in a similar way as an orange solid in 69% yield using $[\{\mathrm{AgCl(PPh_3)}\}_4]$ in dichloromethane as a soluble source of silver chloride.

Preparation of $[\mathrm{(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Ag]Cl_2}$ (**2d**).—*Method A.* $[\{\mathrm{AgCl(PPh_3)}\}_4]$ (0.300 g, 0.187 mmol) was added to a solution of $[\mathrm{Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2]Cl_2}$ (0.500 g, 0.360 mmol) and dppm (0.290 g, 0.750 mmol) in dichloromethane (5 $\mathrm{cm^3}$). Diethyl ether (20 $\mathrm{cm^3}$) was then carefully added to the resulting clear orange solution. The resultant orange precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$, to give the required product. Yield 0.799 g (82%) isolated as a dichloromethane solvate.

The complex $[\mathrm{(Bu^tNC)_2Rh(\mu\text{-}dppm)_2Au]Cl_2}$ (**2f**) was prepared in a similar way as an orange solid in 75% yield.

Method B. A solution of $\mathrm{Bu^tNC}$ (0.150 g, 1.80 mmol) in dichloromethane (*ca.* 2 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{Rh_2Cl_2(cod)_2}]$ (0.200 g, 0.406 mmol) and dppm (0.680 g, 1.77 mmol) in dichloromethane (5 $\mathrm{cm^3}$), followed by $[\{\mathrm{AgCl(PPh_3)}\}_4]$ (0.365 g, 0.225 mmol). When all solids had dissolved to form a clear orange solution, diethyl ether (30 $\mathrm{cm^3}$) was carefully added. The resultant orange precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$ giving the required product. Yield 0.974 g (92%), isolated as the dichloromethane solvate.

The complex $[\mathrm{(Bu^tNC)_3Ir(\mu\text{-}dppm)_2Au]Cl_2}$ (**4**) ['or (**5**)'] was made in a similar way using $[\{\mathrm{Ir(cyclo\text{-}C_8H_{14})_2Cl}\}_2]$ with six equivalents of $\mathrm{Bu^tNC}$. The crude product was recrystallised from dichloromethane–benzene to give the hemibenzene solvated complex.

Preparation of $[\mathrm{(OC)(Bu^tNC)Ir(\mu\text{-}dppm)_2AgCl]Cl}$ (**6a**).—$[\mathrm{AgCl(CNBu^t)}]$ (0.045 g, 0.199 mmol) was added to a solution of $[\mathrm{Ir(CO)(dppm}\text{-}PP')_2]\mathrm{Cl}$ (0.200 g, 0.195 mmol) in dichloromethane (5 $\mathrm{cm^3}$). Diethyl ether (10 $\mathrm{cm^3}$) was added to the resultant clear orange solution and the mixture stored at *ca.* +5 °C for 48 h. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$ giving the required product. Yield 0.163 g (59%) isolated as the dichloromethane solvate.

The complexes $[\mathrm{(OC)(MeNC)Ir(\mu\text{-}dppm)_2AgCl]Cl}$ (**6b**) and $[\mathrm{(OC)}(p\text{-}\mathrm{MeC_6H_4NC)Ir(\mu\text{-}dppm)_2AgCl]Cl}$ (**6c**) were isolated as orange solids in the same way.

Preparation of $[\mathrm{(OC)}(p\text{-}\mathrm{MeC_6H_4NC)Rh(\mu\text{-}dppm)_2AgCl]Cl}$ (**6e**).—$[\mathrm{AgCl(CNC_6H_4Me}\text{-}p)]$ (0.045 g, 0.173 mmol) was added to a solution of $[\{\mathrm{Rh(CO)_2Cl}\}_2]$ (0.040 g, 0.081 mmol) and dppm (0.130 g, 0.338 mmol) in dichloromethane (2 $\mathrm{cm^3}$) under an atmosphere of CO. Diethyl ether (20 $\mathrm{cm^3}$) was then slowly added to precipitate the purple product which was filtered off, washed with diethyl ether, and dried *in vacuo* over $\mathrm{P_2O_5}$. Yield 0.088 g (42%), isolated as the dichloromethane solvate.

The complex $[\mathrm{(OC)(Bu^tNC)Rh(\mu\text{-}dppm)_2AgCl]Cl}$ (**6d**) was prepared in a similar way as an orange-red solid in 67% yield.

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References

1 Part 7, F. Hassan, D. P. Markham, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 279.

2 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, 99.

3 C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2487.

4 C. R. Langrick, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1233.

5 G. R. Cooper, A. T. Hutton, C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 855.

6 A. Blagg, A. T. Hutton, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1815.

7 A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 8049.

8 C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1982, **21**, 2119.

9 J. T. Mague and S. H. DeVries, *Inorg. Chem.*, 1980, **19**, 3743.

10 R. G. Jones, R. C. Hirst, and H. J. Bernstein, *Can. J. Chem.*, 1965, **43**, 683.

11 E. G. Finer and R. K. Harris, *J. Chem. Soc. A*, 1969, 1972.

12 R. K. Harris, J. P. Woplin, and R. Schmutzler, *Ber. Bunsenges. Phys. Chem.*, 1971, **75**, 134.

13 J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1973, 2046.

14 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.

15 P. S. Pregosin and R. W. Kunz, '^{31}P and ^{13}C N.M.R. of Transition Metal Phosphine Complexes,' Springer–Verlag, Berlin, Hamburg, New York, 1979.

16 H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 1960.

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