Multinuclear Nuclear Magnetic Resonance Studies of Dirhodium and Platinum–Rhodium 'A-Frame' Complexes of Bis(diphenylphosphino)methane

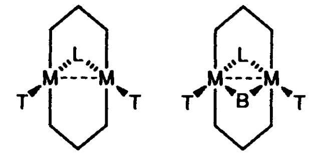
Adrienne L. Davis and Robin J. Goodfellow*
School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK

The $^{31}P-\{^1H\}$ NMR spectra of the single A-frame complexes $[Rh_2X_2(\mu-Y)(\mu-dppm)_2]^{n+}$ (dppm = $Ph_2PCH_2PPh_2$; $n = 0$, Y = CO, X = Cl, Br or I; $n = 0$, Y = SO_2, X = Cl; $n = 0$, Y = S, X = CO; $n = 1$, Y = Cl, X = CO) and the double A-frame complexes $[Rh_2X_2(\mu-Y)(\mu-CO)(\mu-dppm)_2]^+$ (Y = H or Cl, X = CO) have been successfully analysed as $[[A]_2X]_2$ spin systems allowing the $|J(RhRh)|$ and $^2J(PC)$ coupling constants to be determined. For the single A-frame complexes $|J(RhRh)|$ was found to correlate well with $^2J(PCP)$; $J(RhRh) = 0$ for both of the double A-frame complexes. In those cases where crystal-structure data are available, $^2J(PCP)$ correlates well with the Rh–Rh separation for both single and double A frames. It is concluded that $^2J(PCP)$ is a reliable indicator of the presence or absence of a metal–metal bond in these compounds. The cationic complexes $[(PhC{\equiv}C)Pt(\mu-SH)(\mu-dppm)_2Rh(CO)][BF_4]$ and $[(PhC{\equiv}C)Pt(\mu-SR)(\mu-dppm)_2Rh(CO)][PF_6]$ (R = Me or CH_2Ph) have been prepared from $[ClPt(\mu-C{\equiv}CPh)(\mu-dppm)_2Rh(CO)][PF_6]$ *via* $[(PhC{\equiv}C)Pt(\mu-S)(\mu-dppm)_2Rh(CO)]$. When static, these complexes possess no symmetry and thus two values of $^2J(PCP)$ are obtained for each molecule. These couplings are comparable in size only for $[(PhC{\equiv}C)Pt(\mu-SH)(\mu-dppm)_2Rh(CO)]^+$; in the case of both $[(PhC{\equiv}C)Pt(\mu-SR)(\mu-dppm)_2Rh(CO)]^+$ (R = Me or CH_2Ph), $^2J(PCP)$ is much larger across one dppm ligand in the molecule than across the other. This finding is attributed to steric crowding between the methylene protons of the dppm and the μ-SR ligands and is consistent with the data obtained from the $^{31}P-\{^1H\}$ NMR spectrum of $[Rh_2(CO)_2(\mu-SCH_2Ph)(\mu-dppm)_2]^+$, which has been successfully analysed as an $[ABX]_2$ spin system. Measurement and analysis of the $^{103}Rh-\{^1H\}$ NMR spectrum of $[Rh_2Br_2(\mu-CO)(\mu-dppm)_2]$ has demonstrated that $J(RhRh)$ has the same relative sign as $^2J(PRhP)$ in this system and must therefore have a positive sign. The ^{103}Rh NMR chemical shift data for the dirhodium A-frame complexes are also given.

Interest in binuclear complexes arises from the possibility that two adjacent metals may interact in a co-operative manner with other molecules and in so doing exhibit a different reactivity from mononuclear species. Consequently, the tendency of bis(diphenylphosphino)methane (dppm) to act as a bridging bidentate ligand and its ability to allow a degree of flexibility in the approach of the metal centres has generated considerable interest in complexes having an $M_2(\mu-dppm)_2$ (M = transition metal) skeleton.[1,2] Species with two mutually *trans* bridging dppm ligands are most common in rhodium(I) chemistry and have been widely studied, particularly those having the so-called A-frame structure.[3]

The 'single' A-frame structure consists of two metals linked by a bridging group L (subsequently referred to as the apex ligand) and two mutually *trans* bridging bidentate ligands; in addition, the presence of a terminal ligand T on each metal produces square-planar co-ordination in the idealized structure. The molecule may or may not possess a metal–metal bond.[4] Addition of a further bridging ligand B, *e.g.* CO, gives the 'double' A-frame structure.

In this work we have made a systematic study of the second-order NMR spectra ($^{31}P-\{^1H\}$ and $^{103}Rh-\{^1H\}$) exhibited by a series of A frames with the general formulae $[Rh_2T_2(\mu-L)(\mu-dppm)_2]^{n+}$ ($n = 0$ or 1) and $[Rh_2T_2(\mu-L)(\mu-CO)(\mu-dppm)_2]^+$ in order unambiguously to establish the magnitudes and relative signs of the coupling constants in these systems and to determine the structural significance of these data. In addition, a series of Pt–Rh A frames of the type $[(PhC{\equiv}C)Pt(\mu-SR)(\mu-dppm)_2Rh(CO)]^+$ (R = H, Me or CH_2Ph) have been synthesised enabling the specific influence of apex-ligand size on the $^{31}P-\{^1H\}$ NMR parameters to be investigated.

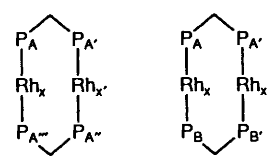


'single' A frame 'double' A frame

Experimental

Syntheses were routinely performed under an atmosphere of dry N_2 using conventional Schlenk-tube techniques. All solvents were dried, distilled and deoxygenated prior to use. The ligand dppm (Aldrich) was used without further purification. Dirhodium A-frame complexes were prepared by published methods: $[Rh_2Cl_2(\mu-CO)(\mu-dppm)_2]$[5] **1**, $[Rh_2Br_2(\mu-CO)(\mu-dppm)_2]$[5] **2**, $[Rh_2I_2(\mu-CO)(\mu-dppm)_2]$[6] **3**, $[Rh_2Cl_2(\mu-SO_2)(\mu-dppm)_2]$[7] **4**, $[Rh_2(CO)_2(\mu-H)(\mu-CO)(\mu-dppm)_2][p-MeC_6H_4SO_3]$[8] **5**, $[Rh_2(CO)_2(\mu-Cl)(\mu-CO)(\mu-dppm)_2][BPh_4]$[9] **6**, $[Rh_2(CO)_2(\mu-Cl)(\mu-dppm)_2][BPh_4]$[9] **7**, $[Rh_2(CO)_2(\mu-S)(\mu-dppm)_2]$[10] **8** and $[Rh_2(CO)_2(\mu-SCH_2Ph)(\mu-dppm)_2][BF_4]$[10] **9**; $[ClPt(\mu-C{\equiv}CPh)(\mu-dppm)_2Rh(CO)][PF_6]$[11] was also prepared by the literature method.

$[(PhC{\equiv}C)Pt(\mu-S)(\mu-dppm)_2Rh(CO)]$ **10**.—A solution of $Na_2S{\cdot}9H_2O$ (0.037 g, 0.152 mmol) in MeOH (40 cm^3) was added to a stirred solution of $[ClPt(\mu-C{\equiv}CPh)(\mu-dppm)_2Rh(CO)][PF_6]$ (0.194 g, 0.141 mmol) in acetone (60 cm^3). After stirring for 5 min the mixture was evaporated to low volume *in vacuo* producing an orange precipitate. The brown mother-liquors were discarded and the precipitate washed with two



$[[A]_2X]_2$ $[ABX]_2$

Fig. 1 The $[[A]_2X]_2$ and $[ABX]_2$ spin systems

portions (10 cm^3) of MeOH. Recrystallizations from CH_2Cl_2–MeOH and CH_2Cl_2–Et_2O afforded the product as an orange powder in 76% yield.

$[(PhC{\equiv}C)Pt(\mu\text{-}SH)(\mu\text{-dppm})_2Rh(CO)][BF_4]$ **11**.—The salt $[Et_2OH][BF_4]$ (*ca.* 0.56 mmol) was added to CH_2Cl_2 (30 cm^3). This solution was added in portions (2 cm^3) to a stirred solution of complex **10** (0.166 g, 0.135 mmol) in CH_2Cl_2 (30 cm^3) until IR measurements indicated that the reaction was complete, *i.e.* when the CO peak at 1944 cm^{-1} had been removed and replaced by a peak at 1997 cm^{-1}; see Table 2. This required addition of *ca.* 0.15 mmol of $[Et_2OH][BF_4]$. The resulting yellow solution was evaporated to low volume *in vacuo* and the product precipitated by addition of Et_2O. Recrystallization from CH_2Cl_2–Et_2O afforded the product as yellow microcrystals in 91% yield.

$[(PhC{\equiv}C)Pt(\mu\text{-}SMe)(\mu\text{-dppm})_2Rh(CO)][PF_6]$ **12**.—A solution of MeI (0.051 g, 0.357 mmol) in CH_2Cl_2 (20 cm^3) was added to a solution of complex **10** (0.073 g, 0.059 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred for 3 h during which time it changed from dark orange to yellow-orange. A solution of $[NH_4][PF_6]$ (0.050 g, 0.309 mmol) in MeOH (10 cm^3) was added and after stirring for 10 min the mixture was evaporated to dryness. The residue was extracted into CH_2Cl_2 (60 cm^3) and the resulting solution filtered and reduced to low volume. Addition of Et_2O produced the product as a yellow precipitate. Recrystallization from CH_2Cl_2–Et_2O gave yellow microcrystals in 80% yield.

$[(PhC{\equiv}C)Pt(\mu\text{-}SCH_2Ph)(\mu\text{-dppm})_2Rh(CO)][PF_6]$ **13**.—A solution of $PhCH_2Br$ (0.067 g, 0.394 mmol) in CH_2Cl_2 (12 cm^3) was added to a solution of complex **10** (0.096 g, 0.078 mmol) in CH_2Cl_2 (20 cm^3). The mixture was stirred for 2 h during which time it changed from orange to yellow. A solution of $[NH_4][PF_6]$ (0.026 g, 0.162 mmol) in MeOH (20 cm^3) was added, and after stirring for 10 min the solvent was removed *in vacuo*. The residue was extracted into CH_2Cl_2 (50 cm^3), filtered and evaporated to dryness. Fractional recrystallization from CH_2Cl_2–hexane followed by recrystallization from CH_2Cl_2–Et_2O afforded the product as a yellow powder in 65% yield.

All NMR spectra were measured in CD_2Cl_2 or CH_2Cl_2–CD_2Cl_2 solvent on a JEOL GX 400 spectrometer at the following frequencies: 399.8 (^1H), 161.8 (^{31}P), 85.6 (^{195}Pt) and 12.6 MHz (^{103}Rh). Chemical shifts are quoted to high frequency of these references: internal $SiMe_4$ (^1H), 85% H_3PO_4 (^{31}P), $\Xi(^{195}Pt) = 21.4$ MHz and $\Xi(^{103}Rh) = 3.16$ MHz. The IR spectra were measured on a Nicolet MX-1 spectrometer as CH_2Cl_2 solutions between NaCl windows.

Simulation of the $^{31}P\text{-}\{^1H\}$ *NMR Spectra.*—The $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **1**–**8** were all successfully analysed by assuming the molecules possess an $[[A]_2X]_2$ spin system. The notation used for this system is given in Fig. 1. From theoretical treatments[12–14] it is known that half the intensity of the A resonance resides in a pair of lines separated by $|J(AX) + J(AX')|$ centred on $\delta(A)$, one quarter of the intensity consists of four 'AB' subspectra also centred on $\delta(A)$ with 'apparent' coupling constants given by $|J(AA') \pm J(AA'') \pm J(XX')|$ and an 'apparent' chemical shift separation of $|J(AX) - J(AX')|$ and the remaining intensity consists of 'complex' lines the positions of which are not explicitly predictable.

Preliminary identification of the 'AB' subspectra followed by calculation of the 'complex' line positions using NUMARIT,[15] in order to confirm the assignment, allowed a set of couplings and shifts to be obtained; the accuracy of these parameters was then optimized using NUMARIT in the iterative mode to get the best fit between observed and calculated line positions. This process cannot give a complete solution. The relative sign of J(RhRh) cannot be obtained from the $^{31}P\text{-}\{^1H\}$ NMR spectrum. In addition, ^1J(RhP) and ^nJ(RhP) cannot be immediately assigned by this method since the J(AX) and J(AX') coupling constants cannot be distinguished, and although their signs are correlated with each other they cannot be correlated with any other coupling. However, it is well known that one-bond Rh–P couplings are at least tens of hertz in magnitude and negative in sign[16] and so the distinction is easily made. A further problem is that the J(AA') and J(AA'') coupling constants cannot be distinguished and therefore ^2J(PCP) and ^nJ(PP) cannot be immediately assigned. This assignment has instead been made by noting that the analogous ^nJ(PP) coupling constant in the head-to-tail 2-(diphenylphosphino)pyridine (dppy) A-frame complexes $[Rh_2T_2(\mu\text{-}L)_2(\mu\text{-dppy})_2]^{n+}$ (n = 0, T = Cl, L = SO_2 or CO; n = 1, T = CO, L = Cl) falls into the range 6–16 Hz;[17,18] consequently, we assign ^nJ(PP) in the dppm systems as the smaller of the two couplings (*i.e.* in the range −12.9 to +21.9 rather than +39.0 to +86.8 Hz). The signs of ^nJ(PP) and ^2J(PCP) are correlated with each other and with ^2J(PRhP). This latter type of coupling is known to be large (several hundred hertz) when the phosphine ligands are mutually *trans*, and to have a positive sign.[19,20]

In all cases the only solution which could feasibly apply to each of these molecules is the one given in this paper since all reasonable alternatives were tested and discarded.

The low-temperature (−60 °C) $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **9** was successfully analysed as the AB region of an $[ABX]_2$ system (see Fig. 1). Calculations with NUMARIT using trial values of J(AB) and J(AB') allowed the strongest transitions to be assigned and gave accurate values for $\delta(A)$, $\delta(B)$, J(AB) and J(AB'). Further calculations varying $|J(AA') \pm J(BB')|$ identified sufficient transitions for a successful iterative fitting to the data. Once again the sign of J(XX') was not determinable nor could the signs of J(AX), J(AX') or J(BX), J(BX') relative to any other coupling be established. However, as described above, the latter information is readily available. All other parameters are unequivocally established relative to J(AB) which must be large (several hundred hertz) and positive in sign.

Results and Discussion

$^{31}P\text{-}\{^1H\}$ *NMR Data.*—The data obtained from the analyses of the $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **1**–**9** are given in Table 1. Observed and simulated spectra of **1** and **9** are shown in Figs. 2 and 3. A structural feature of interest in this group of complexes is the Rh–Rh distance [d(RhRh)] since this is an indicator of this extent to which the metals interact, *i.e.* the presence or absence of a metal–metal bond. X-Ray crystallography has demonstrated that **1**,[21] **2**,[22] **4**,[7] **5**[8] and **6**[23] possess a metal–metal bond whilst **7**[24] and **8**[10] do not. Data are not presently available for **3** and **9**. If we consider the single A frames only, it can be seen that a correlation exists between J(RhRh) and d(RhRh): **1**, **2** and **4** [$2.726 \leqslant d(RhRh) \leqslant 2.784$ Å] have J(RhRh) > 9.0 Hz whilst **7** and **8** [d(RhRh) = 3.152 and 3.154 Å respectively] have J(RhRh) < 2.8 Hz. However, the double A frames (*i.e.* **5** and **6**) do not fit this pattern since they have J(RhRh) = 0 in spite of the fact that they possess a metal–metal bond. A relationship also exists for the single A frames between ^nJ(RhP) and d(RhRh): **1**, **2** and **4** have ^nJ(RhP) > +2.6 Hz whilst **7** and **8** have ^nJ(RhP) < +0.4 Hz, These correlations are analogous to those previously described by Seddon and co-workers[25] for complexes containing the $Pt_2(\mu\text{-dppm})_2$ skeleton.

Here we further note that there is a correlation between

Table 1 $^{31}P-\{^1H\}$ NMR data for complexes **1**–**9**[a]

Complex	δ(P)	J(RhRh)[b]	^1J(RhP)	^nJ(RhP)[c]	^2J(PCP)[d]	^nJ(PP)[d]	^2J(PRhP)
1	19.8	10.6 ± 0.1	−120.5 ± 0.2	+3.4	+86.8	+21.8	+426 ± 15
2	18.8	10.5 ± 0.1	−118.9 ± 0.2	+3.5	+85.1	+21.9	+415 ± 30
3	16.2	9.6 ± 0.2	−117.8 ± 0.2	+3.0	+82.8	+21.3	+408 ± 15
4	22.6	9.1 ± 0.2	−118.7 ± 0.2	+2.7	+75.9	+21.6	+409 ± 30
5[e]	28.5	0.0 ± 0.3	−109.2 ± 0.3	+0.8	+78.6	+41.1	+272 ± 85
6[f]	29.2	0.0 ± 0.2	−93.2 ± 0.2	−0.8	+68.5	+21.5	+315 ± 50
7[g]	18.9	2.0 ± 0.1	−113.8 ± 0.2	+0.3	+39.5	+3.2	+446 ± 60
8	16.8	2.7 ± 0.2	−130.9 ± 0.2	+0.2	+39.0	−12.9	+451 ± 80
9[f]	22.9 (A)	0.4 ± 1.0	−123.7 ± 0.2 (AX)	−1.2 (AX′)	+64.1 (AA′)	+6.9 ± 0.3	+323.2 ± 0.3
	14.8 (B)	(XX′)	−114.7 ± 0.2 (BX)	+0.4 (BX′)	+37.9 (BB′)	(AB′)	(AB)

[a] Spectra measured in CH_2Cl_2–CD_2Cl_2 solvent at 161.8 MHz and ambient temperature unless otherwise stated. Coupling constants in Hz. [b] Sign determined only for complex **2** (positive). [c] Error in this parameter same as for ^1J(RhP). [d] Unless otherwise stated, error in this parameter same as for J(RhRh). [e] −30 °C. [f] −60 °C. [g] −10 °C.

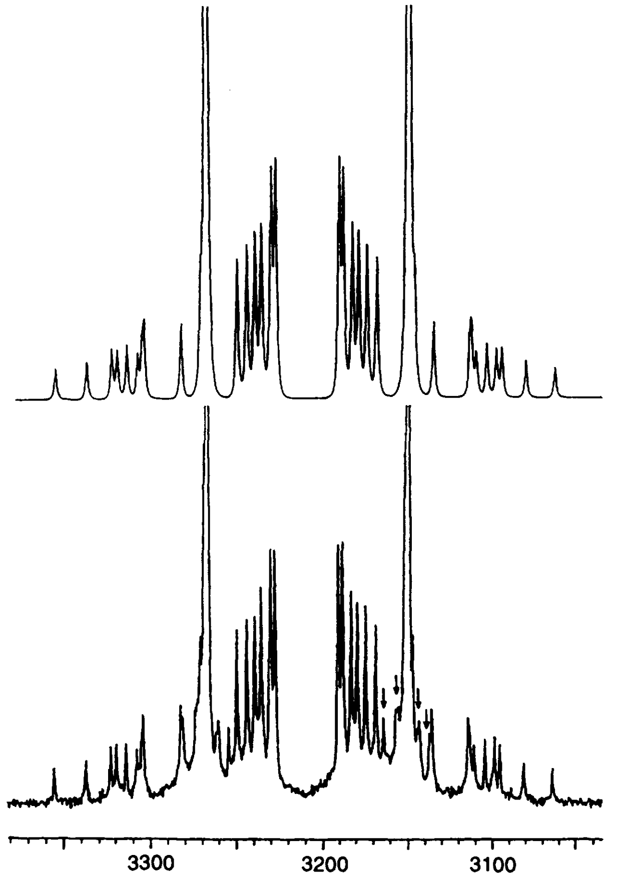


Fig. 2 Simulated (above) and observed (below) $^{31}P-\{^1H\}$ NMR spectrum of complex **1**; arrowed peaks are ^{13}C satellites

^2J(PCP) and d(RhRh) which appears to apply to both single and double A frames. In addition, ^2J(PCP) correlates well with J(RhRh) in single A-frame complexes (Fig. 4). These are more interesting than the correlations described above since no significant component of ^2J(PCP) is expected to be transmitted *via* the metals. A more likely explanation for this behaviour is that the presence or absence of a metal–metal bond influences the P–C–P bond angle across the dppm ligands and hence affects the ^2J(PCP) coupling constant. Data published by other workers for diplatinum A-frame complexes lend some support to this theory, with good correlations existing between ^2J(PCP) and d(PtPt) or mean P–C–P bond angle (Fig. 5). The correlation between ^2J(PCP) and P–C–P bond angle in the dirhodium complexes is less satisfactory.

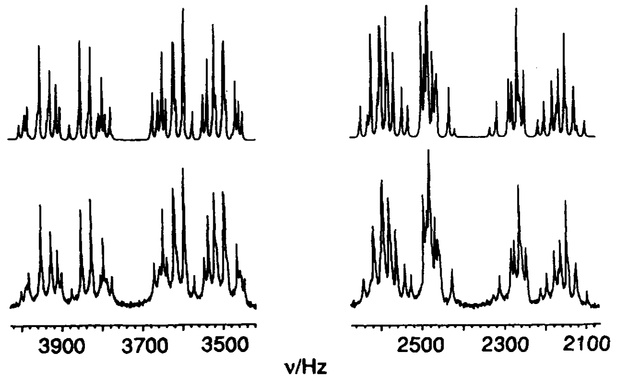


Fig. 3 Simulated (above) and observed (below) $^{31}P-\{^1H\}$ NMR spectrum of complex **9**

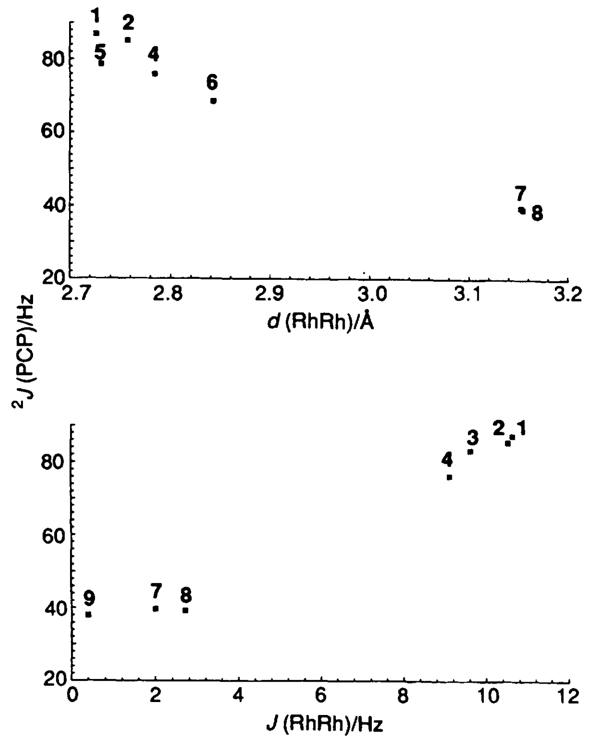


Fig. 4 Correlation of ^2J(PCP) with d(RhRh) for single and double A frames (above) and with J(RhRh) for single A frames only [below; J(BB′) is plotted for complex **9**, see text]

However, the metal–metal separation is not the only factor which influences the magnitude of ^2J(PCP) as the data for complex **9** indicate. The ambient-temperature $^{31}P-\{^1H\}$ NMR

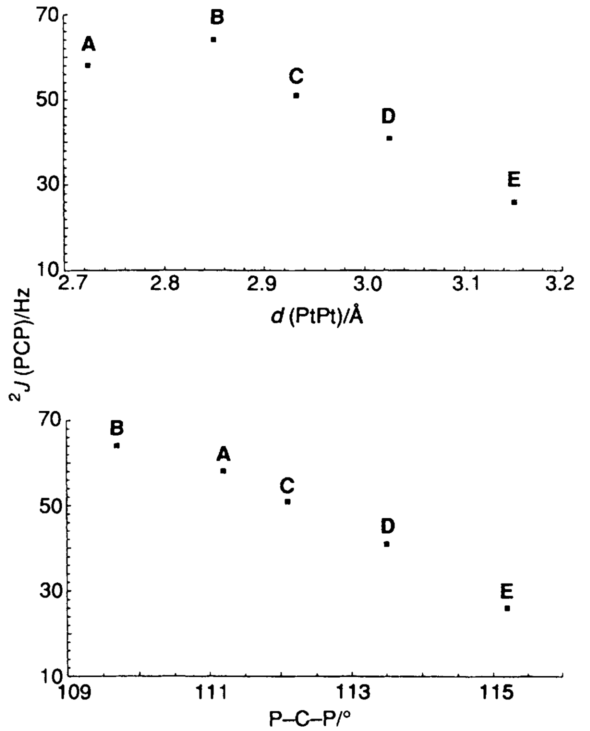


Fig. 5 Correlation of ^2J(PCP) with d(PtPt) (above) and with mean P–C–P bond angle (below) for diplatinum A frames: $[Pt_2Cl_2(\mu\text{-}HgCl_2)(\mu\text{-}dppm)_2]$[26] **A**, $[Pt_2(C{\equiv}CBu^t)_2(\mu\text{-}AuI)(\mu\text{-}dppm)_2]$[27] **B**, $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$[28] **C**, $[Pt_2Me_2(\mu\text{-}C{\equiv}CMe)(\mu\text{-}dppm)_2]^+$[29] **D** and $[Pt_2Cl_2(\mu\text{-}HgCl_2)(\mu\text{-}dppm)_2]$[30,31] **E**

Table 2 Microanalytical and infrared data for complexes **10**–**13**

	Analysis (%)[a]			IR (cm^{-1})[b]	
Complex	C	H	S	ν(CO)	ν(C≡C)
10	57.0 (57.7)	3.9 (4.0)	2.8 (2.6)	1944	2106
11	53.6 (53.9)	4.0 (3.8)	2.5 (2.4)	1997	2130
12	51.9 (51.9)	3.7 (3.8)	2.4 (2.3)	1995	2130
13	n.d.	n.d.	n.d.	1995	2128

[a] Calculated values in parentheses; n.d. = not determined. [b] In CH_2Cl_2. Bands due to ν(CO) are all high intensity, bands due to ν(C≡C) are all medium intensity.

Table 3 $^{31}P\text{-}\{^1H\}$ NMR data for complexes **11**–**13**[a]

	11[b]	**12**[c]	**13**[d]
$\delta(P_A)$	−0.3	−0.5	−0.5
$\delta(P_B)$	6.4	8.0	7.7
$\delta(P_C)$	14.3	12.3	11.8
$\delta(P_D)$	19.9	22.3	21.9
$^1J(PtP_A)$	2420	2451	2446
$^1J(PtP_B)$	2452	2583	2562
$^1J(RhP_C)$	115.4	115.6	115.2
$^1J(RhP_D)$	119.2	126.3	125.6
$^2J(P_AP_B)$	+433.7	+451.7	+451.1
$^2J(P_CP_D)$	+312.3	+308.5	+307.2
$^2J(P_AP_C)$	+33.9	+29.0	+29.8
$^2J(P_BP_D)$	+35.6	+49.8	+50.0
$^4J(P_AP_D)$	+3.0	+4.6	+4.4 [e]
$^4J(P_BP_C)$	+4.8	+4.5	+6.1
$^4J(P_AP_D)$	−6.0	−7.9	−7.2 [e]
$^4J(P_BP_C)$	−8.1	−7.9	−8.9

[a] Spectra measured in CH_2Cl_2–CD_2Cl_2 solvent at 161.8 MHz. Coupling constants in Hz. Signs of coupling constants have been assigned by analogy to **1**–**9** or other complexes as described in text. [b] −50 °C. [c] −35 °C. [d] −40 °C. [e] Alternative sets of solutions obtained by iterative fit using NUMARIT.

Table 4 Proton and $^{195}Pt\text{-}\{^1H\}$ NMR data for complexes **11**–**13**[a]

^1H	**11**[b]	**12**[c]	**13**[d]
δ(Ph)	6.34–7.87	6.36–8.19	6.29–8.24
$\delta(H^1)$[e]	4.42	4.75	4.64
$\delta(H^2)$[e]	4.22	4.14	4.29
$\delta(H^3)$[e]	3.94	3.86	3.88
$\delta(H^4)$[e]	3.84	3.4	3.35
$^2J(H^1H^4)$	14.2	13.4	12.5
$^2J(H^2H^3)$	14.9	14.9	14.9
^{195}Pt	[f]	[d]	[c]
δ(Pt)	−266	−165	−154
J(PtRh)	n.r.	n.r.	24[c]

[a] Spectra were measured in CH_2Cl_2–CD_2Cl_2 solvent at 85.6 MHz (^{195}Pt), or CD_2Cl_2 at 399.8 MHz (^1H). Coupling constants in Hz; n.r. = not resolved. [b] −60 °C; δ(SH) −0.23 (br m). [c] −40 °C; $\delta(SCH_3)$ 1.98, $^3J(PtH)$ = 25 Hz, br s with platinum satellites. [d] −35 °C; $\delta(SCH_2)$ 3.45 (br s). [e] Broad multiplet. [f] −50 °C.

spectrum of this species is broadened by a fluxional process which we presume to be the well known phenomenon of pyramidal inversion at sulfur:[32] this has been shown to occur in the diplatinum A frame $[Pt_2H_2(\mu\text{-}SH)(\mu\text{-}dppm)_2]$.[33] At −60 °C a well resolved spectrum of **9** is obtained which was successfully analysed as the AB region of an $[ABX]_2$ system to give the data in Table 1. When the fluxionality is frozen out **9** possesses inequivalent dppm ligands and the ^2J(PCP) coupling constant across each of these ligands [J(AA′) and J(BB′)] is measurable. Of interest is the large difference in size of these parameters (64.1 and 37.9 Hz). Further to investigate this phenomenon a series of platinum–rhodium analogues have been prepared.

Treatment of $[ClPt(\mu\text{-}C{\equiv}CPh)(\mu\text{-}dppm)_2Rh(CO)][PF_6]$ with $Na_2S{\cdot}9H_2O$ generates the A-frame species $[(PhC{\equiv}C)Pt(\mu\text{-}S)(\mu\text{-}dppm)_2Rh(CO)]$ **10**. Microanalytical data and IR assignments are given in Table 2. The NMR evidence ($^{31}P\text{-}\{^1H\}$, $^{195}Pt\text{-}\{^1H\}$ and ^1H) is consistent with this formulation, with spectra being qualitatively very similar in appearance to those of the starting material.[11] The $^{31}P\text{-}\{^1H\}$ NMR spectrum contains resonances identified as the AB region (plus platinum satellites) of an $[AB]_2X$ spin system [$\delta(P_A)$ = 13.9, $\delta(P_B)$ = 4.0, $^1J(RhP_A)$ = 133.6 and $^1J(PtP_B)$ = 2694.0 Hz]; the $^{195}Pt\text{-}\{^1H\}$ resonance is a triplet with an additional small Pt–Rh coupling [δ(Pt) = −206, J(PtRh) = 42 Hz] and the ^1H NMR spectrum contains two resonances assigned to PCHH′P protons [δ(phenyl) = 6.55–7.95, δ(H) = 5.41, δ(H′) = 3.12, ^3J(RhH′) = 3.2, ^3J(PtH′) = 62 and ^2J(HH′) = 12.5 Hz]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum is of no further interest since it is reproducible using a large number of feasible phosphorus–phosphorus coupling constants.

Compound **10** reacts with 1 equivalent of $[Et_2OH][BF_4]$ to give the species $[(PhC{\equiv}C)Pt(\mu\text{-}SH)(\mu\text{-}dppm)_2Rh(CO)][BF_4]$ **11**. Reaction of **10** with an excess of MeI or $PhCH_2Br$ followed by NH_4PF_6 generates $[(PhC{\equiv}C)Pt(\mu\text{-}SR)(\mu\text{-}dppm)_2Rh(CO)][PF_6]$ (R = Me **12** or CH_2Ph **13**, as appropriate). The cationic A-frame complexes **11**–**13** display moderate stability to air both in the solid state and in solution. Microanalytical data and IR assignments are given in Table 2. Further evidence for these formulations is provided by the $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra which are qualitatively very similar for the three compounds. As in the case of **9** broadening due to pyramidal inversion at sulfur is observed at ambient temperature, but low-temperature spectra are well resolved and show that the static molecules possess no symmetry. The $^{31}P\text{-}\{^1H\}$ NMR spectra are approximately first order, with each phosphorus in the $Pt(\mu\text{-}dppm)_2Rh$ skeleton being chemically inequivalent; furthermore,

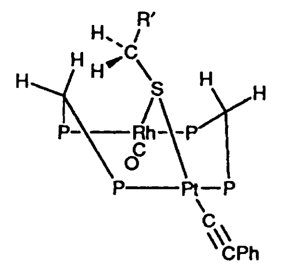


Fig. 6 Steric crowding of methylene protons in complexes **12** and **13** (R' = H or Ph); for clarity phenyl groups are omitted

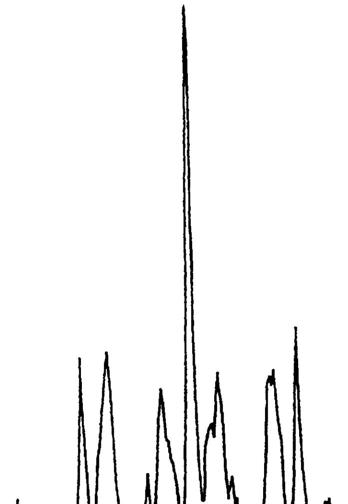


Fig. 7 The ^{103}Rh-{^{1}H} NMR spectrum of complex **2**

Table 5 ^{103}Rh-{^{1}H} NMR data for complexes **1**–**9**[a]

Complex	δ(Rh)
1	229
2	157
3	0
4	949
5[b]	−482
6[c]	−109
7	−466
8	−603
9[d]	−622

[a] Spectra were measured in CH_2Cl_2–CD_2Cl_2 solvent at 12.6 MHz and ambient temperature otherwise stated. [b] −30 °C. [c] −35 °C. [d] −60 °C.

^2J(PPtP) and ^2J(PRhP) are both large (> 300 Hz) and thus the Pt(μ-dppm)$_2$Rh skeleton must have a *trans-trans* structure.[20] The ^{1}H NMR spectra each possess resonances assignable to the μ-SR (R = H, Me or CH_2Ph) protons and also four dppm methylene proton resonances, confirming the lack of symmetry. The ^{31}P-{^{1}H}, ^{195}Pt-{^{1}H} and ^{1}H NMR data are given in Tables 3 and 4.

The ^{31}P-{^{1}H} NMR data in Table 3 demonstrate that there is very little variation in any given metal–phosphorus or phosphorus–phosphorus coupling within this group of compounds, with the exception of the ^2J(PCP) type couplings, in particular $^2J(P_BP_D)$. Both **12** and **13** have ^2J(PCP) considerably larger across one of their dppm ligands than across the other [$^2J(P_BP_D)$ *ca.* 50 and $^2J(P_AP_C)$ *ca.* 30 Hz]; clearly, in this respect they behave similarly to the dirhodium complex **9**. By contrast, **11** has near-identical values for its two ^2J(PCP) couplings [$^2J(P_BP_D)$ and $^2J(P_AP_C)$ *ca.* 34 Hz]. We believe that the reason for this difference is the variation in size of the SR apex ligand when R = CH_2Ph, Me or H (see below).

It is obvious from the inequivalence of the dppm ligands in the low-temperature NMR spectra of complexes **11**–**13** that the R group of each complex must lie to one side of the PtRhS plane when the pyramidal inversion at sulfur is frozen out. Furthermore, it is usual in A-frame complexes of dppm for the methylene groups of the dppm ligands to fold towards the apex ligand in order to relieve steric interactions between the phenyl rings and the terminal ligands (see refs. 7, 8, 10, 21–24, 28 and 31). Models indicate that when this conformation is adopted by **12** or **13** severe crowding occurs between the protons of the apex ligand and the methylene protons on one of the dppm ligands (Fig. 6). Consequently, some distortion of the dppm ligand from its ideal geometry may be expected. By contrast, **11** should be able to adopt the usual A-frame geometry without steric overcrowding of this kind. Attempts to grow suitable crystals of **12** or **13** in order to examine their structure by X-ray crystallography have so far proved unsuccessful. However, the observations above are consistent with the ^{31}P-{^{1}H} NMR data since of the four complexes **9** and **11**–**13**, only **11** has comparable values for the ^2J(PCP) coupling constant in both halves of the molecule. Since the $^2J(P_AP_C)$ coupling constant of **12** and **13** is closer in size to the ^2J(PCP) values of **11**, we assign this as the coupling across the 'unhindered' dppm ligand as opposed to the larger alternative, $^2J(P_BP_D)$. This is consistent with the data for complex **9** where the smaller of its two ^2J(PCP) type couplings, *J*(BB'), is the one that best fits the ^2J(PCP) *vs.* *J*(RhRh) relationship for dirhodium single A-frame complexes (Fig. 4).

^{103}Rh-{^{1}H} *NMR Data.*—As described above, analysis of the ^{31}P-{^{1}H} NMR spectrum of a Rh$_2$(μ-dppm)$_2$ A frame cannot determine the relative sign of *J*(RhRh). However, under ideal conditions it can be determined from the ^{103}Rh-{^{1}H} NMR spectrum. The sensitivity problems associated with ^{103}Rh NMR spectra permitted a sufficiently good spectrum to be obtained for only one compound, [Rh$_2$Br$_2$(μ-CO)(μ-dppm)$_2$] **2** (Fig. 7). Comparison of the measured NMR spectrum to spectra simulated using the best-fit parameters obtained from the ^{31}P-{^{1}H} spectrum and with *J*(RhRh) set either positive or negative unequivocally demonstrates that here *J*(RhRh) has the same sign as ^2J(PRhP), *i.e.* positive. To the knowledge of the authors this is the first time the (relative) sign of *J*(RhRh) has been determined. The ^{103}Rh chemical shift data for complexes **1**–**9** are given in Table 5. Although the more positive ^{103}Rh chemical shifts correspond to the complexes with Rh–Rh bonds, δ(^{103}Rh) cannot be directly related to the degree of metal–metal bonding in this series of complexes.

Conclusion

The ^2J(PCP) coupling constant is generally a reliable indicator of the metal–metal distance in complexes of the type [Rh$_2$T$_2$(μ-L)(μ-dppm)$_2$]$^+$ (*n* = 0 or 1) and [Rh$_2$T$_2$(μ-L)(μ-CO)(μ-dppm)$_2$]$^+$. However, steric factors such as the size of the apex ligand L can influence the magnitude of ^2J(PCP) and make its interpretation more hazardous.

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