Magnetic Double-resonance Measurements of Rhodium, Phosphorus, Fluorine, and Proton Nuclear Magnetic Resonance Parameters in some Rhodium(I) and Rhodium(III) Compounds

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A number of related compounds containing rhodium–carbon bonds have been examined by ^{1}H and ^{19}F single-resonance and ^{1}H-{^{19}F}, ^{1}H-{^{31}P}, ^{1}H-{^{103}Rh}, ^{19}F-{^{31}P}, and ^{19}F-{^{103}Rh} double-resonance n.m.r. spectroscopy. Chemical shifts and signs and magnitudes of coupling constants involving these nuclei are presented and discussed.

THE development of theories to account for the n.m.r. parameters of the heavier nuclei is important in connection with the use of these parameters to gain an understanding of electronic and molecular structure. Unfortunately, at present relatively few experimental measurements have been reported, particularly for the transition elements. Only in the case of ^{195}Pt (spin quantum number, $I = \frac{1}{2}$; natural abundance, 34%) is

TABLE 1

Analytical (%; calculated values in parentheses) and infrared (cm^{-1}) data for new organorhodium compounds

Compound [a,b]	C	H	I	ν(CO) [c]	ν(RhCl) [c]
$[\mathrm{RhI_2Me(CO)L_2}]$ (4)	32.65,[d] 31.5 [e] (32.0)	3.15,[d] 3.15 [e] (3.7)	37.2 (37.55)	2 068, 2 040	
$[\mathrm{RhCl(I)Me(CO)L_2}]$ (7)	37.45,[d] 35.8 [e] (37.0)	4.3,[d] 4.1 [e] (4.3)	22.1 (21.7)	2 060, 2 040	298
$[\mathrm{RhBr(I)Me(CO)L_2}]$ (8)	33.6,[d] 35.1 [e] (34.4)	3.95,[d] 3.9 [e] (4.0)	19.65 (20.2)	2 062, 2 039	
$[\mathrm{RhI_2(CF_3)(CO)L_2}]$ (12)	29.8,[d] 28.4 [e] (29.6)	3.45,[d] 3.25 [e] (3.05)	35.5 (34.75)	2 095, 2 085	
$[\mathrm{RhBr(I)(CF_3)(CO)L_2}]$ (13)	32.15,[d] 30.85 [e] (31.65)	3.8,[d] 3.05 [e] (3.25)	18.0 (18.6)	2 090, 2 080 (sh)	
$[\mathrm{RhCl(I)(CF_3)(CO)L_2}]$ (14)	36.4,[d] 33.15 [e] (33.85)	3.1,[d] 3.4 [e] (3.45)		2 085br	283

[a] Numbering and stereochemistry as in Table 2. [b] L = Dimethylphenylphosphine. [c] Nujol mull. [d] Compounds recrystallised from benzene–light petroleum (b.p. 40—60 °C). [e] Compounds recrystallised from dichloromethane–methanol.

TABLE 2

Rhodium-103, ^{31}P, and ^{1}H chemical shifts [a] at 24 °C of some organorhodium and related compounds; 0.2 mol dm^{-3} in benzene unless otherwise stated

Compound	Ξ(^{103}Rh)	δ(^{103}Rh) [b]	δ(^{31}P) [c]	δ(^{1}H)(MeP)	δ(^{1}H)(MeRh or HRh)
trans-$[\mathrm{RhI(CO)(PMe_2Ph)_2}]$ (1)	3 158 346 ± 1	−4 402 ± 1	−7.2 ± 0.2	+1.81 ± 0.02	
trans-$[\mathrm{RhBr(CO)(PMe_2Ph)_2}]$ (2)	3 158 605 ± 2	−4 321 ± 1	−4.1 ± 0.2	+1.71 ± 0.02	
trans-$[\mathrm{RhCl(CO)(PMe_2Ph)_2}]$ (3)	3 158 721 ± 1	−4 284 ± 1 [d]	−2.0 ± 0.2	+1.66 ± 0.02	
$[\mathrm{RhI_2}^{bf}\,\mathrm{Me}^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e}$ (4)	3 160 165 ± 2	−3 828 ± 1	−14.4 ± 0.2	A +2.33 ± 0.02 B +2.04 ± 0.02	+1.08 ± 0.2
$[\mathrm{RhBr_2}^{bf}\,\mathrm{Me}^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]$ (5)	3 161 108 ± 2	−3 531 ± 1	−4.8 ± 0.2	A +2.13 ± 0.02 B +1.87 ± 0.02	+0.91 ± 0.2
$[\mathrm{RhCl_2}^{bf}\,\mathrm{Me}^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]$ (6)	3 161 578 ± 2	−3 383 ± 1	+1.4 ± 0.2	A +2.02 ± 0.02 B +1.77 ± 0.02	+0.81 ± 0.02
$[\mathrm{RhCl}^{b}\,\mathrm{I}^{f}\,\mathrm{Me}^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e}$ (7)	3 160 613 ± 5	−3 687 ± 2	*f*	A +2.19 ± 0.04 B +1.93 ± 0.04	+0.99 ± 0.04
$[\mathrm{RhBr}^{b}\mathrm{I}^{f}\mathrm{Me}^{a}(\mathrm{CO})^{d}(\mathrm{PMe_2Ph})_2{}^{ce}]^{e}$ (8)	3 160 846 ± 2	−3 614 ± 1	−3.95 ± 0.2	A +2.12 ± 0.04 B +1.90 ± 0.04	+0.93 ± 0.04
$[\mathrm{RhCl_3}^{abf}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]$ (9)	3 165 018 ± 8	−2 299 ± 3	−0.9 ± 0.2	+1.95 ± 0.03	
$[\mathrm{RhBr_3}^{abf}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]$ (10)	3 163 395 ± 2	−2 810 ± 1	−9.3 ± 0.3	+2.14 ± 0.03	
$[\mathrm{RhCl_2}^{af}\,\mathrm{H}^{b}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e,g}$ (11)	3 160 757 ± 8	−3 642 ± 3	+5.5 ± 0.8	*f*	*ca.* −13.7
$[\mathrm{RhI_2}^{bf}\,(\mathrm{CF_3})^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e,h,i}$ (12)	3 161 433 ± 17	−3 429 ± 6	−13.9 ± 0.4	A +2.49 ± 0.02 B +2.07 ± 0.02	
$[\mathrm{RhBr}^{b}\,\mathrm{I}^{f}\,(\mathrm{CF_3})^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e,j,k}$ (13)	3 161 975 ± 5	−3 258 ± 2	−7.0 ± 0.6	A +2.33 ± 0.02 B +1.93 ± 0.02	
$[\mathrm{RhCl}^{b}\,\mathrm{I}^{f}\,(\mathrm{CF_3})^{a}\,(\mathrm{CO})^{d}\,(\mathrm{PMe_2Ph})_2{}^{ce}]^{e,i,l}$ (14)	3 162 233 ± 9	−3 177 ± 3	−2.3 ± 0.2	A +2.25 ± 0.02 B +1.86 ± 0.02	
trans-$[\mathrm{RhCl(CO)\{PMe_2(C_6H_4OMe\text{-}}o)\}_2]^{m}$ (15)	3 158 715 ± 5	−4 286 ± 2	*f*	+1.85 ± 0.2 [n]	
$[\mathrm{RhCl}^{b}\,\mathrm{I}^{f}\mathrm{Me}^{a}\,(\mathrm{CO})^{d}\,\{\mathrm{PMe_2(C_6H_4OMe\text{-}}o)\}_2{}^{ce}]^{m}$ (16)	3 160 804 ± 2	−3 627 ± 1	*f*	A +2.45 ± 0.02 [n] B +2.10 ± 0.02 [n]	+0.60 ± 0.02 [n]
mer-$[\mathrm{RhCl_3(SMe_2)_3}]^{o}$ (17)	317 231 0	0			

[a] Chemical shifts in p.p.m. to low field of reference standards. Ξ(^{103}Rh) in Hz; A and B differentiate the two magnetically inequivalent *P*-methyl groups. [b] Relative to compound (17). [c] Relative to 85% H_3PO_4 (— 40 480 790 Hz). [d] Decrease in shielding with temperature of 0.26 p.p.m. K^{-1}. [e] New compound. [f] Not measured. [g] 0.1 mol dm^{-3} in CH_2Cl_2–C_6H_6. [h] Ξ(^{19}F) 94 094 333 ± 17 Hz. [i] 0.2 mol dm^{-3} in C_6H_6–CF_3I. [j] Ξ(^{19}F) 94 093 950 ± 25 Hz. [k] 0.1 mol dm^{-3} in C_6H_6–CF_3I. [l] Ξ(^{19}F) 94 093 740 Hz. [m] 0.1 mol dm^{-3} in CH_2Cl_2. [n] Ref. 11; benzene solution at 34 °C. [o] Saturated in CH_2Cl_2.

TABLE 3

Rhodium-103, ^{31}P, and ^{1}H coupling constants (in Hz) at 24 °C of compounds (1)—(11), (15), and (16) [a]

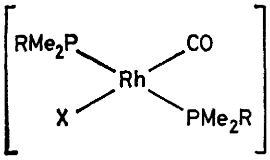
Compound	[^{2}J(^{31}P–^{1}H) + ^{4}J(^{31}P–^{1}H)] [b]	^{1}J(^{103}Rh–^{31}P)	^{3}J(^{103}Rh–^{1}H)	^{2}J(^{103}Rh–^{1}H)	^{2}J(^{31}P–^{31}P)	^{3}J(^{31}P–^{1}H)
(1)	−6.45 ± 0.2	−114.5 ± 0.5	−1.11 ± 0.2		+361 ± 5	
(2)	−6.35 ± 0.2	−116.2 ± 1.0	−1.0 ± 0.2		+368 ± 8	
(3)	−6.63 ± 0.15	−118 ± 1	−1.15 ± 0.2		+376 ± 5	
(4)	A −7.3 ± 0.2 B −7.7 ± 0.2	−82.5 ± 2	*ca.* 0.4	+2.03 ± 0.07	*c*	+5.48 ± 0.07
(5)	A −7.70 ± 0.15 B −8.29 ± 0.15	−84 ± 1	−0.3 ± 0.1	+2.03 ± 0.07	*c*	+5.30 ± 0.07
(6)	A −8.00 ± 0.15 B −8.30 ± 0.15	−84 ± 1	−0.3 ± 0.1	+2.00 ± 0.07	*c*	+5.26 ± 0.07
(7)	A −7.6 ± 0.3 B −8.5 ± 0.3	−85 ± 1	⩽*ca.* 0.3	+2.05 ± 0.07	*c*	+5.46 ± 0.07
(8)	A −8.1 ± 0.3 B −9.1 ± 0.6	−85 ± 5	⩽*ca.* 0.3	+2.05 ± 0.25	*c*	+5.6 ± 0.3
(9)	−9.1 ± 0.2	−70 ± 8	*ca.* 0.4		*c*	
(10)	−8.63 ± 0.08	−73.5 ± 0.5	−0.44 ± 0.08		*c*	
(11)	*c*	−81.5 ± 2	*c*	*d*	*c*	*e*
(15)	−6.7 ± 0.3	−120 ± 5	0.9 ± 0.2		*c*	
(16)	A −7.3 ± 0.2 B −8.3 ± 0.2	−86 ± 1	⩽*ca.* 0.3	+2.2 ± 0.2	*c*	+5.1 ± 0.2

[a] Conditions as in Table 2. [b] *N* (ref. 16). [c] Not measured. [d] ^{1}J(^{103}Rh–^{1}H) = −17.3 ± 0.2 Hz. [e] ^{2}J(^{31}P–Rh–^{1}H) = −12.8 ± 0.2 Hz.

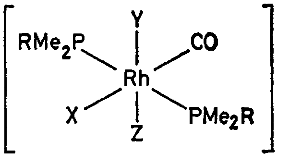
there a reasonably large body of data in the literature.[1–7] By contrast, for ^{103}Rh, which also has $I = \frac{1}{2}$, but a natural abundance of 100%, chemical shifts have been reported for less than ten compounds,[8,9] and sign information on coupling constants is very limited.[3,4]

Much of this neglect can be attributed to the very low sensitivity to n.m.r. detection of the ^{103}Rh nucleus which is only 0.003% of that of the proton, so that even with pulsed Fourier transform spectrometry there is a very large time penalty. The alternative approach adopted here is to use heteronuclear double-resonance methods [8] rather than direct observation. The experiments have the additional advantage that the relative signs of various coupling constants involving rhodium can also be obtained.

We report here the results of ^{1}H-{^{19}F}, ^{1}H-{^{31}P}, ^{1}H-{^{103}Rh}, ^{19}F-{^{31}P}, and ^{19}F-{^{103}Rh} heteronuclear double-resonance experiments on 16 selected derivatives of Rh$^{\mathrm{I}}$ and Rh$^{\mathrm{III}}$. The compounds have structures (I) or (II) (R = aryl). They all have mutually *trans* aryldimethylphosphine ligands, and all have at least one rhodium–carbon bond. Several of the compounds have not been reported previously.



(I)



(II)

EXPERIMENTAL

Compounds are numbered according to Tables 1 and 2. The rhodium(I) compounds (1)—(3) and (15) were prepared by standard methods,[10–12] and the rhodium(III) compounds (4)—(14) and (16) were made from these [11,12] by oxidative addition of alkyl halide, hydrogen chloride, or halogen as appropriate. Of these the new compounds (4), (7), and (8) are trivial variants of known species.[10–13] The new trifluoromethyl derivatives (12)—(14) were prepared by passing CF_3I through *ca.* 0.2 mol dm^{-3} solutions in benzene of the precursors (1)—(3) for 30 min at 24 °C; the more volatile components were then removed under reduced pressure and the products recrystallised. Analytical data for compounds (4), (7), (8), and (12)—(14) are in Table 1. Although hydrogen analyses were satisfactory, the carbon analyses were consistently higher than expected for samples recrystallised from benzene–light petroleum (b.p. 40—60 °C) and lower than expected for those recrystallised from dichloromethane–methanol; this suggests that solvent of crystallisation was present. Each compound was therefore additionally characterised by its i.r. (Table 1) and comprehensive n.m.r. (Tables 2—4) spectra, and the absence of spurious peaks in the latter was also used as a criterion of purity. The hydride (11) was prepared by the addition of HCl in diethyl ether to a benzene solution of compound (3),[14] and the resulting crystals were rapidly filtered off, dried, and examined without further purification. The ready decomposition of this compound at room temperature precluded satisfactory analysis, and made rapid working essential; the necessary ^{1}H-{^{31}P} and ^{1}H-{^{103}Rh} n.m.r. experiments were carried out in less than 30 min of instrument time.

TABLE 4

Coupling constants (in Hz) at 24 °C for the trifluoromethyl compounds (13)—(15), $[\mathrm{RhX(I)(CF_3)(CO)(PMe_2Ph)_2}]$ [a]

Coupling constant		Compound		
		(13; X = I)	(14; X = Br)	(15; X = Cl)
$^1J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$		*ca.* −85	−84.7 ± 2.0	−83 ± 2
$^3J(^{103}\mathrm{Rh}-^{1}\mathrm{H})$		⩽ 0.3	⩽ 0.3	−0.2 ± 0.1
N [b]	A	−8.65 ± 0.2	−8.6 ± 0.2	−8.85 ± 0.15
	B	−7.75 ± 0.2	−8.0 ± 0.3	−8.15 ± 0.15
$^2J(^{103}\mathrm{Rh}-^{19}\mathrm{F})$		−14.5 ± 0.8	−14.1 ± 0.5	−14.2 ± 0.2
$^3J(^{31}\mathrm{P}-^{19}\mathrm{F})$		+17.8 ± 1.4	+16.8 ± 0.8	+18.0 ± 0.2
$^5J(^{19}\mathrm{F}-^{1}\mathrm{H})$	A	⩽ 0.1	⩽ 0.1	⩽ 0.1
	B	*ca.* 0.2	*ca.* 0.2	*ca.* 0.2

[a] Conditions as in Table 2. [b] $N = [^2J(^{31}\mathrm{P}-^{1}\mathrm{H}) + {}^4J(^{31}\mathrm{P}-^{1}\mathrm{H})]$ (ref. 16).

The n.m.r. experiments were performed at 24 °C; compounds (1)—(10) were examined as *ca.* 0.2 mol dm^{-3} solutions in benzene, (12)—(14) at a similar concentration in benzene saturated with CF_3I, (11) as a *ca.* 0.1 mol dm^{-3} solution in benzene–dichloromethane (1 : 1), and (15) and (16) as *ca.* 0.1 mol dm^{-3} solutions in dichloromethane. Compound (14) was also examined in pure benzene solution and showed a negligible difference in the measured parameters.

The spectra were obtained on a JEOL C-60 H instrument operating at 60 (^{1}H) and 56.4 (^{19}F) MHz which was modified by the addition of a second radiofrequency (r.f.) coil in the probe for double-resonance experiments. For these, r.f. power at frequencies of 1.89, 24.28, and 56.4 MHz for ^{103}Rh, ^{31}P, and ^{19}F respectively was provided by a Schlumberger FS-30 frequency synthesiser and tuned amplifier together with a frequency-doubling facility for ^{19}F. The frequency synthesiser was also used to drive the main spectrometer oscillator at 60 MHz, and the method used to control the ^{19}F observing frequency at 56.4 MHz was such as to reduce the relative frequency drift to a negligible level.[15] Spectra recorded in the field-sweep mode were calibrated by the generation of side-bands at known audio frequencies, and those in the frequency-sweep mode by use of a frequency counter to determine the frequency of the audiomodulated side-band used to excite the resonance.

[1] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, and I. R. H. Marshall, *J.C.S. Dalton*, 1976, 459 and refs. therein.

[2] J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J.C.S. Dalton*, 1976, 874 and refs. therein.

[3] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[4] J. F. Nixon, in ‘ NMR Spectroscopy of Nuclei other than Protons,’ eds. T. Axenrod and G. A. Webb, Wiley, 1974, p. 389.

[5] M. A. Bennett, R. Bramley, and I. B. Tomkins, *J.C.S. Dalton*, 1973, 166.

[6] R. Bramley, J. R. Hall, G. A. Swile, and I. B. Tomkins, *Austral. J. Chem.*, 1974, **27**, 2491.

[7] J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, *J.C.S. Dalton*, 1976, 745.

[8] W. McFarlane, *Chem. Comm.*, 1969, 700.

[9] J. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 1970, **92**, 2359.

[10] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437.

[11] H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Dalton*, 1974, 1980.

[12] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.

[13] R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2796.

[14] A. J. Deeming and B. L. Shaw, unpublished work (A. J. Deeming, Thesis, University of Leeds, 1968).

[15] W. McFarlane, *Mol. Phys.*, 1970, **18**, 817.

RESULTS

The compounds (Table 2) all had mutually *trans* aryldimethylphosphine ligands. In these the 12 *P*-methyl protons and the two phosphorus nuclei constitute $AA'X_6X'_6$ (or $[AX_6]_2$) spin systems in which $J(AA') \gg L$, where $L = [J(A\text{–}X) - J(A\text{–}X')]$.[16] The resonances of the *P*-methyl protons were therefore 'deceptively simple' triplets,[16] in which the separation of the outer components is N, where $N = [^2J(^{31}P\text{–}^1H) + {}^4J(^{31}P\text{–}^1H)]$. Additional splitting due to coupling $^3J(^{103}Rh\text{–}^1H)$ was well resolved in compounds (1)—(3) (*ca.* 1 Hz) [12] and (9) and (10) (*ca.* 0.4 Hz), and so for each of these $^1H\text{-}\{^{103}Rh\}$ selective-decoupling experiments (*e.g.* Figure 1) readily yielded the rhodium resonance frequency $\nu(^{103}Rh)$ and the magnitude of the rhodium–phosphorus coupling constant $^1J(^{103}Rh\text{–}^{31}P)$. These experiments also showed that the sign of N was the same as that of $^1J(^{103}Rh\text{–}^{31}P)$ which can thus be presumed to be negative. (Note that γ, the magnetogyric ratio, for ^{103}Rh has a negative sign.) In addition $^1H\text{-}\{^{31}P\}$ experiments gave the ^{31}P resonance frequency, $\nu(^{31}P)$, and also confirmed the magnitude of $^1J(^{103}Rh\text{–}^{31}P)$ and gave its sign relative to that of $^3J(^{103}Rh\text{–}^1H)$ which was therefore also shown to be negative (*e.g.* Figure 2). The larger magnitude of $^3J(^{103}Rh\text{–}^1H)$ in compounds (1)—(3) permitted a reasonable resolution of the two *P*-methyl proton triplets arising from the two spin states of ^{103}Rh, and in these cases the $^1H\text{-}\{^{31}P\}$ experiments on the outer components of the triplets [2,7,17,18] gave the magnitude of $^2J(^{31}P\text{–}^{31}P)$ and its sign relative to N (Figure 2).

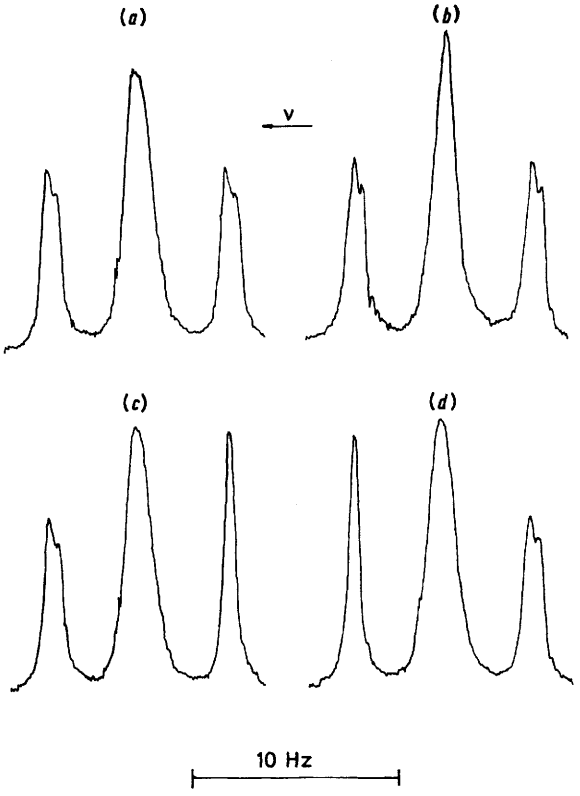


FIGURE 1 60-MHz ^1H and $^1H\text{-}\{^{103}Rh\}$ n.m.r. spectra for the *P*-methyl group of $[RhBr_3(CO)(PMe_2Ph)_2]$ (10): (*a*) normal ^1H spectrum, (*b*) with simultaneous irradiation at $\nu(^{103}Rh)$, (*c*) with simultaneous irradiation at $[\nu(^{103}Rh) + |^1J(^{103}Rh\text{–}^{31}P)|]$, and (*d*) with simultaneous irradiation at $[\nu(^{103}Rh) - |^1J(^{103}Rh\text{–}^{31}P)|]$. This shows that $^1J(^{103}Rh\text{–}^{31}P)$ is of the same sign as N, where $N = [^2J(^{31}P\text{–}^1H) + {}^4J(^{31}P\text{–}^1H)]$ (Note that γ for ^{103}Rh is negative.)

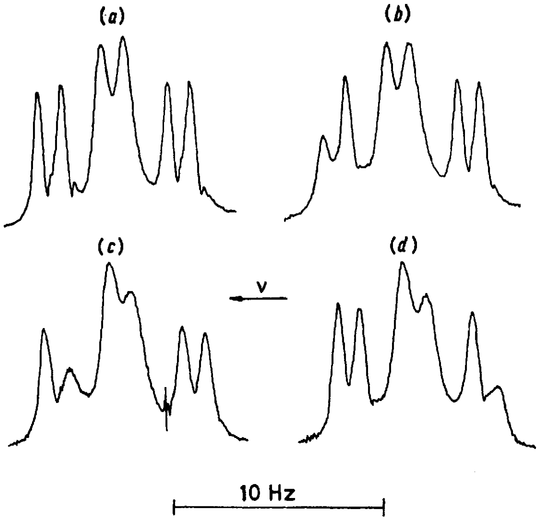


FIGURE 2 60-MHz ^1H and $^1H\text{-}\{^{31}P\}$ n.m.r. spectra for the *P*-methyl group of $[RhCl(CO)(PMe_2Ph)_2]$: (*a*) normal ^1H spectrum, (*b*) with simultaneous irradiation at $[\nu(^{31}P) + \tfrac{1}{2}|^1J(^{103}Rh\text{–}^{31}P)| - |^2J(^{31}P\text{–}^{31}P)|]$, (*c*) with simultaneous irradiation at $[\nu(^{31}P) - \tfrac{1}{2}|^1J(^{103}Rh\text{–}^{31}P)| - |^2J(^{31}P\text{–}^{31}P)|]$, and (*d*) with simultaneous irradiation at $[\nu(^{31}P) - \tfrac{1}{2}|^1J(^{103}Rh\text{–}^{31}P)| + |^2J(^{31}P\text{–}^{31}P)|]$. This shows that $^3J(^{103}Rh\text{–}^1H)$ is negative and $^2J(^{31}P\text{–}^{31}P)$ positive relative to $^1J(^{103}Rh\text{–}^{31}P)$ and N both negative (Note that γ for ^{103}Rh is negative.)

In compounds (4)—(8), (11), and (16) it was more convenient to obtain $\nu(^{103}Rh)$, $\nu(^{31}P)$, and $^1J(^{103}Rh\text{–}^{31}P)$ by double irradiation experiments on the *Rh*-methyl proton resonances [compounds (4)—(8) and (16)] [which also gave the signs of $^3J(^{31}P\text{–}^1H)$ and $^2J(^{103}Rh\text{–}^1H)$] or from the rhodium hydride proton resonance [compound (11)] [which also gave the signs of $^2J(^{31}P\text{–}Rh\text{–}^1H)$ and $^1J(^{103}Rh\text{–}^1H)$]. The values of $\nu(^{103}Rh)$, $\nu(^{31}P)$, and $^1J(^{103}Rh\text{–}^{31}P)$ thus obtained were used to confirm the signs of N and $^3J(^{103}Rh\text{–}^1H)$ by observation of the *P*-methyl proton resonance. In the trifluoromethyl compounds (12)—(14), $^3J(^{103}Rh\text{–}^1H)$ was not well resolved, but the heights of the components of the *P*-methyl proton triplets could be increased by *ca.* 10% by irradiation at $\nu(^{103}Rh)$ and the experiments were otherwise straightforward. The magnitudes of $^2J(^{103}Rh\text{–}^{19}F)$ and $^3J(^{31}P\text{–}^{19}F)$ were obtained from the ^{19}F spectra directly, and $^{19}F\text{-}\{^{31}P\}$ and $^{19}F\text{-}\{^{103}Rh\}$ experiments determined the signs.

In compounds (4)—(8) and (12)—(14) the methyl groups on the phosphorus atoms are inequivalent in pairs due to the effective dissymmetry at rhodium,[12] and their proton resonances were generally well separated.

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[16] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[17] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

[18] I. J. Colquhoun, J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1975, 638.

This can be attributed to the anisotropy of the adjacent carbonyl ligand. It was noted that coupling constants involving these protons were different for each of the two dissimilar pairs of groups: specifically, N was different, and in compounds (12)—(14) the couplings ^5J-($^{19}F-^1H$) were larger for the more shielded *P*-methyl group. The presence of the latter coupling permitted the determination of $\nu(^{19}F)$ without reference to an internal fluorine standard and also gave confirmation of the sign of $^3J(^{31}P-^{19}F)$ by selective sharpening of the three components of the proton triplet in $^1H-\{^{19}F\}$ experiments.

The results are summarised in Tables 2—4. The signs of coupling constants, J, are given relative to the sign of N [$= {}^2J(^{31}P-^1H) + {}^4J(^{31}P-^1H)$], which is assumed to be negative. The basis of this is that ^4J-($^{31}P-^1H$) will be small, and that $^2J(^{31}P-^1H)$, although small ($\leqslant$*ca.* 3 Hz) and positive in the free phosphine, is known to become larger and negative on co-ordination to a metal.[19] The assumption is further justified in that it leads to a positive sign for $^1K(^{103}Rh-^{31}P)$ which is to be expected by comparison with the positive sign of $^1K(^{195}Pt-^{31}P)$ in analogous compounds of platinum-(II) and -(IV).[2] The absence of a sign in the Tables indicates that it has not been determined. Chemical shifts, δ, are quoted in the convention high field negative–low field positive and are given relative to $SiMe_4$ for ^1H, 85% H_3PO_4 for ^{31}P (Ξ 40 480 790 Hz), and *mer*-[$RhCl_3$-$(SMe_2)_3$] for ^{103}Rh (Ξ 3 172 310 Hz). Ξ(X) is the resonance frequency of nucleus X corrected to the field strength at which the $SiMe_4$ protons resonate at exactly 100 MHz. Since it may be some time before a generally accepted reference standard for ^{103}Rh chemical shifts is agreed upon, $\Xi(^{103}Rh)$ values are also given in Table 2.

The variation of $\delta(^{103}Rh)$ with temperature was measured for compound (3) and found to be 0.26 ± 0.04 p.p.m. K^{-1} which is within the ranges previously established for ^{103}Rh.[8,9] Temperature variations will therefore lead to $\delta(^{103}Rh)$ values outside the error limits quoted in Table 2 but these discrepancies will not be serious. All our compounds were examined at 24 °C.

DISCUSSION

Coupling Constants.—Electron-mediated one-bond coupling constants are generally dominated by the Fermi-contact interaction,[20] and when the bond is strong [21] and neither element has *s*-electron lone pairs a mean electronic excitation-energy approximation may be used to yield equation (1).[20] In this expression, which requires

$$^1K(X-Y) = \frac{4e^2h^2}{9m^2c^2} \cdot \frac{1}{\Delta E} \cdot \psi_X{}^2(0)\psi_Y{}^2(0) \, . \, \alpha_X{}^2\alpha_Y{}^2 \qquad (1)$$

all $^1K(X-Y)$ to be positive, ΔE is an average energy of excitation, $\psi^2(0)$ is the valence *s*-electron density at the nucleus, and α^2 is the *s* character of the orbital used to form the relevant bond. It should be noted that the magnetogyric ratio for ^{103}Rh is negative, and therefore the signs of $^nK(Rh-P)$, $^nK(Rh-F)$, and $^nK(Rh-H)$ are opposite to those for the corresponding J values given in Tables 3 and 4.

The observation that $^1J(^{103}Rh-^{31}P)$ and $^1J(^{103}Rh-^1H)$ are both negative thus indicates that equation (1) is valid for the compounds examined here. This is further supported by the observed ratios of corresponding couplings involving Rh^{III} and Rh^I. This should be 0.67 : 1 owing to the different atomic hybridisations of d^2sp^3 and dsp^2 respectively,[22] and is in reasonable agreement with the ratios of 0.59—0.73 : 1 obtained from our data. A dependence on the *s*-electron density is shown by the values of $^1J(^{103}Rh-^{31}P)$ in compounds (1)—(3), which change with the variations in $\psi_{Rh}{}^2(0)$ expected with changing effective nuclear charge. However, the small magnitude of this coupling in compounds (9) and (10) compared to the other Rh^{III} compounds implies that changes in ΔE can also be significant or that there are differences in the distribution of *s* character within the formal d^2sp^3 hybridisation framework. The latter effect is well known, for example in organic derivatives of tin, in which a change in formal hybridisation from sp^3 to sp^3d^2 can be associated with an *increase* in $^1K(Sn-C)$ by a factor of up to 2.0.[23,24]

For geminal coupling constants $^2J(X-A-Y)$ involving strongly localised X–A and A–Y bonds in which the bonding orbitals used by X and Y both have substantial *s* character, an equation similar to (1) may be used with the inclusion of a factor F which depends on additional excitations involving the intermediate atom A. For sp^3-hybridised carbon F appears to be negative and thus $^2K(Rh-C-H)$ should be of opposite sign to the product of $^1K(C-H)$ (positive) and $^1K(Rh-C)$ (expected to be positive), *i.e.* it should be negative as is observed. Similarly, $^2K(Rh-F)$ should be of opposite sign to the product of the signs of $^1K(Rh-C)$ and $^1K(C-F)$ (negative); *i.e.* it should be positive, again in agreement with observation. [It may be noted that $^1K(C-F)$ is believed to be negative owing to an incompatability with the mean excitation approximation used to derive equation (1),[20] but this will not seriously affect arguments concerned with the transmission of spin information through the carbon atom.] When the intermediate atom A is a transition metal, there is a marked dependence of F on the symmetry of the available electronic excitations. Thus the large positive values of $^2J(^{31}P-^{31}P)$ measured here arise because the symmetry of favourable transitions in the molecular orbitals arising from the metal *p* and *d* orbitals is such as to be able to make dominant positive contributions to *trans*- but not *cis*-coupling paths;[3,7,22,25] *cis*-coupling constants between geminal four-co-ordinate

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[19] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Comm.*, 1966, 89; W. McFarlane, *ibid.*, 1967, 772.

[20] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[21] J. D. Kennedy and W. McFarlane, *J. Organometallic Chem.*, 1974, **80**, C47.

[22] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[23] T. N. Mitchell, *J. Organometallic Chem.*, 1973, **59**, 189.

[24] J. D. Kennedy and W. McFarlane, *J.C.S. Chem. Comm.*, 1974, 983.

[25] R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

phosphorus atoms are generally small and negative in orthogonal transition-metal compounds.[22]

These excitations will also contribute to vicinal couplings involving phosphorus, and it has been suggested that the resulting differences in sign for *cis*- and *trans*-$^3J(^{31}P-M-C-^1H)$ in methyl derivatives of Pt^{II},[5] Pt^{IV},[6] and Au^{III} [7] are diagnostic of the stereochemistries. Our present results suggest that this generalisation may also apply to compounds of Rh^{III}, since the magnitudes (and signs of K) for *cis*-$^3J(^{31}P-Rh-C-^1H)$ [compounds (4)—(8)] are within the ranges established for the platinum and gold compounds. Similar conclusions apply to the vicinal three-bond phosphorus–fluorine couplings in compounds (13)—(15), since these are also within the range observed for trifluoromethyl-platinum and -gold compounds.[7]

Rhodium Chemical Shifts.—It is generally thought that changes in the magnetic shielding of heavier nuclei can be accounted for by variations in the ' paramagnetic ' term defined by Ramsey.[26] This is a summation of terms related to the changes in electronic angular momentum about the nucleus which are associated with the electronic excitations of the molecule, and the temperature dependence of the nuclear shielding in transition elements such as cobalt and platinum suggests that those excitations associated with the ligand-field splitting ΔE may make contributions to this summation.[27-29] The decrease in shielding of *ca.* 0.25 p.p.m. K^{-1} observed here for ^{103}Rh is also in accord with this, and arises from the decrease in ΔE resulting from the increase in population of higher vibrational levels. However, this effect is not a dominant one, since it would predict a decrease in ^{103}Rh shielding on increasing the atomic number of a halogen substituent on rhodium, which is contrary to observation [*e.g.* compounds (1)—(3), (4)—(8), and (12)—(14)]. This increase in shielding with the atomic number of the substituent atom is difficult to rationalise. Similar shielding increases have been observed for the other heavy elements tin,[30] mercury,[31] platinum,[1,2] and lead,[32] but the neighbouring-atom diamagnetism [33] is too small to account for the observed increments. For platinum, the effect has been tentatively ascribed [1] to an increase in covalency in the sequence $Cl < Br < I$, but it may be unwise to generalise from this conclusion. In the main an increase in shielding appears to be associated with polarisable substituents on the metal atom, and thus may involve metal–ligand charge-transfer excitations. Clearly there is scope here for further theoretical development.

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[26] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.

[27] S. M. Cohen and T. H. Brown, *J. Chem. Phys.*, 1974, **61**, 2985.

[28] R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc.*, 1957, **A242**, 455.

[29] S. S. Dharmatti and G. R. Kanekar, *J. Chem. Phys.*, 1960, **31**, 1436.

[30] J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin, and Lead Compounds*, 1974, **1**, 235.

[31] J. D. Kennedy and W. McFarlane, *J.C.S. Faraday II*, 1976, 1653.

[32] J. D. Kennedy, W. McFarlane, and B. Wrackmeyer, *Inorg. Chem.*, 1976, **15**, 1299.

[33] W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, 1968, **49**, 3122.