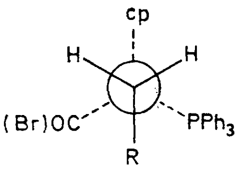
Evidence for Restricted Rotation in Hydrogen-1 and Fluorine-19 Nuclear Magnetic Resonance Spectra of Cyclopentadienylperfluoroalkylcobalt Complexes

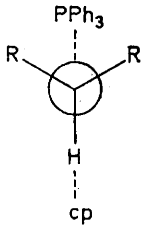
By **Rob J. Burns, Peter B. Bulkowski, Shirley C. V. Stevens,** and **Michael C. Baird,*** Department of Chemistry, Queen's University, Kingston, Ontario, Canada

An extensive series of complexes [(cp)CoI(L)R_F] [L = phosphorus donor; R_F = CF_3, CF_2CF_3, or $CF(CF_3)_2$] and [(cp)CoCO(PPh_3)CF_2CF_3]ClO_4 (cp = π-cyclopentadienyl), many of them hitherto unreported, have been prepared and characterized. Variable-temperature proton and fluorine n.m.r. spectra of several of the complexes provide evidence for hindered rotation about both metal–carbon and phosphorus–aryl bonds, while the i.r. spectrum of the carbonyl complex suggests the presence of diastereoisomers, the co-ordinated phosphine and the cobalt constituting chiral centres.

JUST as proton–proton vicinal coupling constants are extremely useful in elucidating conformations of many complex organic molecules,[1] we have recently presented evidence that phosphorus–hydrogen vicinal coupling constants ($^3J_{PH}$) can be useful in deducing information concerning conformations of alkylmetal complexes containing *cis*-tertiary phosphine ligands.[2] It was suggested, for instance, that primary alkyl complexes containing the pseudotetrahedral moieties (cp)Fe(CO)-(PPh_3) and (cp)RhBr(PPh_3) (cp = π-cyclopentadienyl) exist predominantly as conformation (I) at room temperature, while secondary alkyl complexes containing the (cp)Ni(PPh_3) moiety exist predominantly as conformation (II). The primary alkyl complex [(cp)Ni-(PPh_3)CH_2SiMe_3], which is expected to be less sterically hindered than either of the above two systems, appeared to exist as an equilibrium mixture of conformations; the n.m.r. spectrum was strongly temperature dependent, as expected for a system in which more than one thermally accessible conformation is populated, and hence in which the relative populations are temperature dependent.



(I)



(II)

In all cases, it seemed that the data could be rationalized if it could be assumed that (*a*) for $^3J_{PH}$, $J_{trans} > J_{gauche}$, (*b*) the stereochemical requirements of the 'other' ligands are cp > PPh_3 > CO. The former assumption has both a theoretical basis and experimental precedents in other types of compounds.[1] The latter assumption seemed justified by crystal-structure determinations of the complexes [(cp)Ni(PPh_3)X] (X = CF_3 [3] or $GeCl_3$ [4]), and suggested that similar variable-temperature n.m.r. experiments with different alkyl groups and tertiary phosphine ligands might provide information concerning barriers to rotation of the ligands, together with the stereochemistry of highly crowded complexes.

In an effort to investigate further the generality of the above conclusions, it was decided to work with tertiary phosphine complexes of perfluoroalkyl groups, in part because of the much higher stabilities of complexes of these ligands than their non-fluorinated analogues. It was also expected that the generally larger chemical-shift differences might make the ^{19}F n.m.r. spectra

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[1] W. A. Thomas, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 72.

[2] J. Thomson, W. Keeney, W. F. Reynolds, and M. C. Baird, *J. Organometallic Chem.*, 1972, **40**, 205.

[3] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1970, 161.

[4] F. Glockling, A. McGregor, M. L. Schneider, and H. M. M. Shearer, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3103.

easier to interpret, in contrast to the much more complicated spectra of some simple alkyl complexes.[2,5] It was also hoped, in retrospect naively, that vicinal phosphorus–fluorine coupling constants ($^3J_{\mathrm{PF}}$) would be as easily interpretable in terms of structures as vicinal phosphorus–hydrogen coupling constants had appeared to be. This paper deals with ^{19}F n.m.r. spectra of the perfluoroalkyl complexes $[(cp)CoCO(PPh_3)CF_2CF_3]ClO_4$ and $[(cp)CoI(L)R_F]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OEt)_3$, or $P(OPh)_3$; R_F = CF_3, CF_2CF_3, or $CF(CF_3)_2$]. The series was chosen because of the ease with which quite stable complexes containing a variety of sizes of both alkyl groups and phosphine ligands could be obtained. Subsequent publications will deal with complexes of the types $[(cp)Fe(CO)LR_F]$ and $[(cp)NiLR_F]$.

EXPERIMENTAL

Chemical analyses were undertaken by Schwarzkopf Microanalytical Laboratory, Woodside, New York. I.r. spectra were run on Beckman IR-10 and Perkin-Elmer 180 spectrometers, n.m.r. spectra on a Bruker HX60 spectrometer with internal lock. Fluorine n.m.r. spectra were locked on C_6F_6 or $CFCl_3$ and chemical shifts are reported relative to $CFCl_3$, upfield shifts being positive. M.p.s were determined on a Gallenkamp melting-point apparatus and are uncorrected.

The complexes $[(cp)CoI(CO)CF_3]$,[6] $[(cp)CoI(CO)CF_2CF_3]$,[6] $[(cp)CoI(CO)CF(CF_3)_2]$,[7] $[(cp)CoCO(PPh_3)CF_2CF_3]ClO_4$,[8] and $[(cp)CoI(PPh_3)CF_2CF_3]$ [8] were prepared as described in the literature. The complexes $[(cp)CoI(PPh_3)CF_3]$, $[(cp)CoI(PMePh_2)CF_2CF_3]$, $[(cp)CoI(PMe_2Ph)CF_2CF_3]$, and $[(cp)CoI(L)CF(CF_3)_2]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OEt)_3$, or $P(OPh)_3$] were prepared by treating the corresponding carbonyl derivative with one mol equivalent of the tertiary phosphine in refluxing diethyl ether. In some cases, the desired product precipitated from the reaction mixture, in other cases, the solvent was removed at reduced pressure. All new complexes were recrystallized from methylene chloride–light petroleum (b.p. 30—60 °C). Analytical data and physical properties of the new complexes are listed in Table 1.

TABLE 1

Analytical data (%) and physical properties of the new complexes $[(cp)CoI(L)R_F]$

Complex	Colour	M.p. (t/°C)	Found C	Found H	Calc. C	Calc. H
$[(cp)CoI(PPh_3)CF_3]$	Brown	171—175	49·4	3·65	49·5	3·45
$[(cp)CoI(PMePh_2)CF_2CF_3]$	Brown	145—149	41·35	3·15	42·15	3·20
$[(cp)CoI(PMe_2Ph)CF_2CF_3]$	Brown	118—126	35·95	3·20	35·45	3·20
$[(cp)CoI(PPh_3)CF(CF_3)_2]$	Black	108—110	46·35	3·40	45·75	2·95
$[(cp)CoI(PMePh_2)CF(CF_3)_2]$	Purple	129—130	41·0	3·10	40·65	2·95
$[(cp)CoI(PMe_2Ph)CF(CF_3)_2]$	Brown	127—129	34·55	3·05	34·45	2·90
$[(cp)CoI\{P(OEt)_3\}CF(CF_3)_2]$	Black	90—98	28·5	2·30	28·70	3·45
$[(cp)CoI\{P(OPh)_3\}CF(CF_3)_2]$	Black	140—141	43·05	2·80	42·75	2·75

TABLE 2

Proton n.m.r. data at **300 K** in $CDCl_3$

Complex	$\tau_{C_5H_5}$	τ_{CH_3} (J/Hz)	Other resonances (τ)
$[(cp)CoI(CO)CF_3]$	4·37		
$[(cp)CoI(PPh_3)CF_3]$	4·96		*ca.* 2·5 (m, Ph)
$[(cp)CoI(CO)CF_2CF_3]$	4·37		
$[(cp)CoI(PPh_3)CF_2CF_3]$	4·97		*ca.* 2·5 (m, Ph)
$[(cp)CoI(PMePh_2)CF_2CF_3]$	4·95	7·80 (dd) (J_{PH} 11·5) (J_{FH} 2)	*ca.* 2·5 (m, Ph)
$[(cp)CoI(PMe_2Ph)CF_2CF_3]$	5·15	8·05 (d) (J_{PH} 11) 7·90 (d) (J_{PH} 11)	*ca.* 2·5 (m, Ph)
$[(cp)CoI(CO)CF(CF_3)_2]$	4·37		
$[(cp)CoI(PPh_3)CF(CF_3)_2]$	4·83		*ca.* 2·75 (m, br, Ph)
$[(cp)CoI(PMePh_2)CF(CF_3)_2]$	4·80	7·90 (dd) (J_{PH} 11·5) (J_{FH} 3)	*ca.* 2·5 (m, Ph)
$[(cp)CoI(PMe_2Ph)CF(CF_3)_2]$	4·91	7·92 (dd) (J_{PH} 11) (J_{FH} 1·5) 8·00 (d, br) (J_{PH} 11) (J_{FH} <1)	*ca.* 2·5 (m, Ph)
$[(cp)CoI\{P(POEt)_3\}CF(CF_3)_2]$	4·82	8·73 (t) (J_{HH} 7)	5·82 (m, CH_2)
$[(cp)CoI\{P(OPh)_3\}CF(CF_3)_2]$	4·85		2·72 (s, br, Ph)
$[(cp)CoCO(PPh_3)CF_2CF_3]ClO_4$ *	4·20		*ca.* 2·5 (m)

m = Multiplet, br = broad, s = singlet, t = triplet, d = doublet, and dd = double doublet.

* In CD_3CN.

RESULTS

Details of the proton n.m.r. spectra are listed in Table 2. In all cases the cyclopentadienyl (cp) resonance was a singlet, albeit broadened somewhat by either the cobalt nuclear quadrupole moment or spin–spin coupling to phosphorus. The methyl resonances of the two methyldi-

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[5] J. Thomson and M. C. Baird, *Canad. J. Chem.*, 1970, **48**, 3443.

[6] P. M. Treichel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3593.

[7] R. B. King, R. N. Kapoor, and L. W. Houk, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2179.

[8] P. M. Treichel and G. Werber, *Inorg. Chem.*, 1965, **4**, 1098.

phenylphosphine complexes were interesting in that coupling to *one* fluorine atom was observed in both cases, presumably five-bond coupling to the single fluorine atom on the α-carbon atom of the isopropyl derivative, and to only one of the fluorine atoms of the ethyl complex. The assignment was verified by fluorine decoupling in the former case. The methyl groups in the dimethylphenylphosphine complexes are diastereotopic because of the chiral cobalt atoms. They thus have different chemical shifts, as has been reported for a similar iron complex.[9] Although no coupling to fluorine was observed in the methyl resonances of the perfluoroethyl complex, the two methyl resonances of the perfluoroisopropyl complex were coupled to the α-fluorine atom, the coupling constants being different. Decoupling the phosphorus resulted in a doublet at τ 7·92 and a broad singlet at τ 8·00, in accord with the assignments of the coupled spectrum.

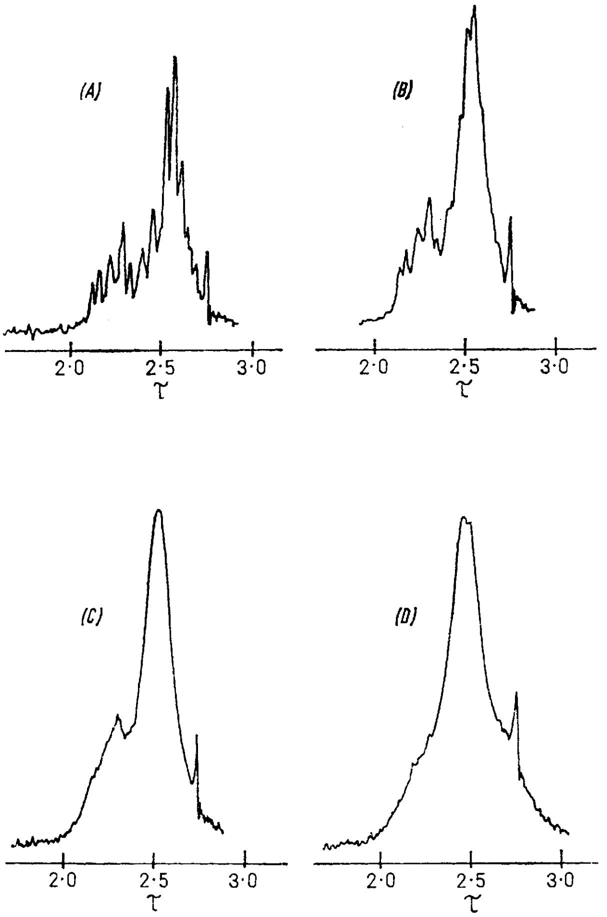

FIGURE 1 ^{1}H N.m.r. spectra of the complex [(cp)CoI(PPh$_3$)CF$_3$] in the phenyl region at (*A*) 300, (*B*) 260, (*C*) 240, and (*D*) 220 K in CDCl$_3$

The phenyl resonances in most cases were broad bands with considerable fine structure from spin–spin coupling. The band contours of the three triphenylphosphine complexes, at least, were strongly temperature dependent. As shown in Figure 1 for the complex [(cp)CoI(PPh$_3$)CF$_3$], the well resolved (at room temperature) multiplet was broadened considerably at 260 K and had coalesced into a broad band at 220 K. As both the residual chloroform line on the high-field side of the band and the cp line remained well resolved, and as the effect was reversible, the broadening cannot be a result of viscosity effects, decomposition or precipitation of solids. Similar effects were observed with the perfluoroethyl and isopropyl complexes. Broadening of the phenyl resonance of the former occurred *ca.* 20 K higher than the corresponding stages in the spectrum of the trifluoromethyl complex, while the phenyl resonance of the latter was almost completely coalesced even at room temperature.

The fluorine resonance of the CF$_3$ group of the complex [(cp)CoI(PPh$_3$)CF$_3$] was a singlet at room temperature, with a linewidth of *ca.* 1·4 Hz. The line broadened somewhat and shifted upfield as the temperature decreased, the chemical shifts being −9·30 (293), −8·88 (250), −8·45 (200), and −8·26 p.p.m. (170 K). The extent of the broadening and the direction of the change in chemical shift are both similar to those observed for the iron complex [(cp)FeCO(PPh$_3$)-CF$_3$].[2] The fluorine n.m.r. spectra of the perfluoroethyl complexes were of the ABM$_3$X type (X = ^{31}P), the two α-fluorine atoms being diastereotopic because of the chiral cobalt atoms. A typical spectrum of the AB region is shown in Figure 2. Coupling of the CF$_2$ fluorines to the CF$_3$ group was in all cases less than 1 Hz.

The chemical shifts and coupling constants were calculated using the usual procedures.[10] As the X part of the spectra (^{31}P) could not be observed because of quadrupolar broadening, two solutions were possible, depending on the assignments of the AB part of the spectrum. Identification of the correct solution was achieved using INDOR procedures based on population transfer.[11] Although in principle use of the method may be criticized in such weakly coupled systems as these, the results were completely

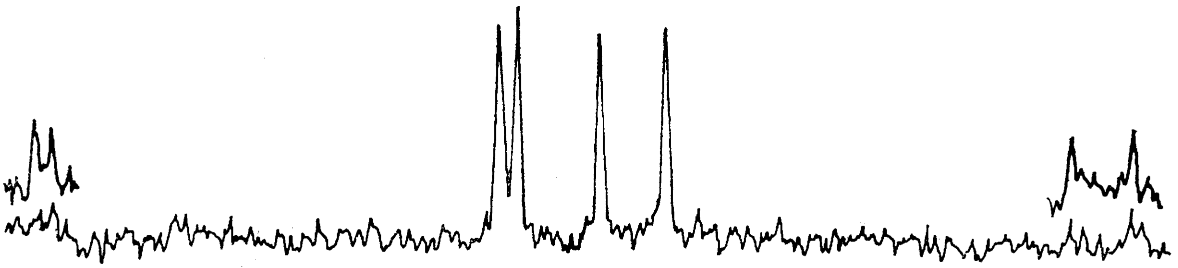

FIGURE 2 Typical ^{19}F n.m.r. spectrum of the perfluoroethyl complexes in the CF$_2$ region

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[9] H. Brunner and E. Schmidt, *Angew. Chem. Internat. Edn.*, 1969, **8**, 616.

[10] R. A. Hoffman, S. Forsén, and B. Gestblum, *N.M.R., Basic Principles and Progress*, 1971, **5**, 69.

[11] Ref. 10, p. 45.

consistent for the three neutral perfluoroethyl complexes over a range of temperature, and the assignments are believed to be correct. In the case of the only slightly soluble cationic complex, the spectrum of which had a very low signal-to-noise ratio, it was assumed that the AB part of the spectrum could be assigned in the same way as the other complexes. Chemical shifts of the trifluoromethyl group and the two geminal fluorine atoms of the cationic complex (in CD_3CN) are 80·37, 59·51, and 55·02 p.p.m.; the coupling constants of the latter to the phosphorus atom were 35·9 and 8·6 Hz, respectively, while the geminal fluorine–fluorine coupling constant was 238 Hz. Chemical shift and coupling constant data for the other perfluoroethyl complexes are presented in Table 3.

TABLE 3

Fluorine n.m.r. data for the complexes $[(cp)CoI(L)CF_2CF_3]$ in CH_2Cl_2

L = PPh_3

T/K	200	225	250	275	296
δ_A/p.p.m.	66·51	66·16	65·70	65·13	64·58
δ_B/p.p.m.	59·95	59·43	59·01	58·58	58·21
J_{AX}/Hz	17·75	17·95	1875	20·09	20·06
J_{BX}/Hz	11·25	11·80	12·00	12·41	12·39
J_{AB}/Hz	246·8	247·4	246·1	246·8	247·0
δ_{CF_3}/p.p.m.					77·52

L = $PMePh_2$

T/K	200	230	260	296
δ_A/p.p.m.	66·54	66·31	66·01	65·51
δ_B/p.p.m.	63·02	62·60	62·16	61·52
J_{AX}/Hz	8·35	11·93	13·40	14·73
J_{BX}/Hz	17·65	16·82	17·10	16·53
J_{AB}/Hz	250·8	251·1	251·5	250·6
δ_{CF_3}/p.p.m.				78·35

L = PMe_2Ph

T/K	200	225	250	275	300
δ_A/p.p.m.	68·10	67·91	67·65	67·33	66·94
δ_B/p.p.m.	65·80	65·24	64·74	64·23	63·62
J_{AX}/Hz	16·54	17·04	17·50	18·09	17·93
J_{BX}/Hz	14·46	14·71	14·00	13·91	14·32
J_{AB}/Hz	250·5	250·9	250·3	250·5	250·4
δ_{CF_3}/p.p.m.					78·63

The fluorine n.m.r. spectra of the perfluoroisopropyl complexes were of the $AM_3M_3'X$ type, the two trifluoromethyl groups being diastereotopic. In all cases except the carbonyl complex, the CF resonance was a broad band without resolvable fine structure, a result of spin–spin coupling to two non-equivalent trifluoromethyl groups, one phosphorus and, in the cases of the $PMePh_2$ and PMe_2Ph complexes, at least, to protons of the tertiary phosphine ligands. Selective decoupling of the phosphorus atom and each of the trifluoromethyl groups in turn permitted the vicinal phosphorus–fluorine decoupling constants to be obtained in some cases, although the resonances still appeared to be broadened somewhat by quadrupolar coupling to the cobalt. Varying the temperature did little to improve resolution in most cases. The chemical shift and coupling constant data are presented in Table 4.

TABLE 4

Fluorine n.m.r. data for the complexes $[(cp)CoI(L)CF(CF_3)_2]$ at 300 K in CH_2Cl_2

L	δ_{CF}/p.p.m. (J_{PF}/Hz)	δ_{CF_3}/p.p.m. (J_{PF}, J_{CF-CF_3}/Hz)	$J_{CF_3-CF_3}$/Hz
CO	156·9	66·1 (10), 68·4 (10)	10
$P(OEt)_3$	176·8 (*ca.* 14)	64·1 (<1, 8), 67·7 (3·5, 10·5)	10·5
$P(OPh)_3$	172·3 (*ca.* 11)	63·8 (<1, 7·5), 67·7 (3·5, 11)	11
PPh_3	173·6 (*ca.* 10)	62·9 (<1 6·5), 66·6 (5, 14·5)	10·5
$PMePh_2$	174·7 [a]	63·8 (<1, 7·5), 66·9 (5·5, 11)	11
PMe_2Ph	176·9 [a]	63·6 (<1, 8), 66·6 (5·5, 11)	11

[a] Decoupling resulted in a decrease of the band width only.

DISCUSSION

The temperature dependences of the spectra of the perfluoroethyl derivatives exhibited marked differences. In all cases, the CF_2 chemical shifts decreased linearly as the temperature increased, the rates of decrease all being approximately the same. The vicinal phosphorus–fluorine coupling constants of the non-ionic complexes were all temperature dependent to varying degrees, as illustrated in Figure 3. In the cases of complexes of the largest (PPh_3) and smallest (PMe_2Ph) phosphine, the changes in J are regular and small, although significant. In the case of the $PMePh_2$ complex, the change in J_{AX} is relatively large.

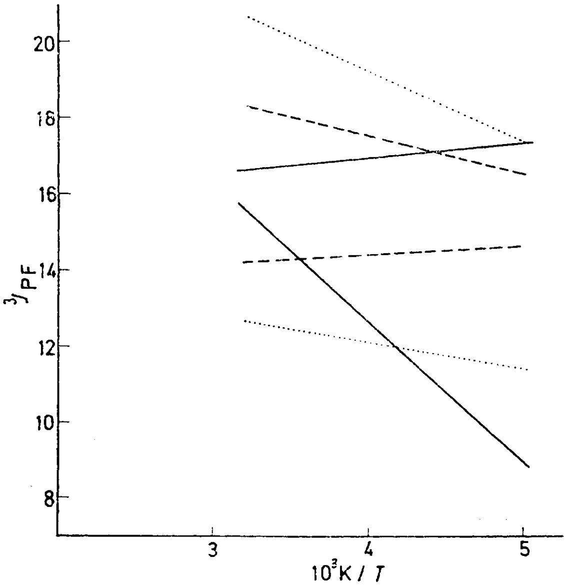
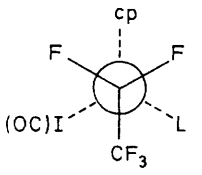
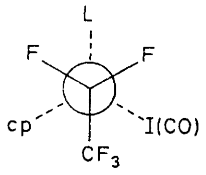


FIGURE 3 Plots of J_{AX} and J_{BX} against T^{-1} for the complexes $[(cp)CoI(PPh_3)CF_2CF_3]$ (· · · ·), $[(cp)CoI(PMePh_2)CF_2CF_3]$ (——), and $[(cp)CoI(PMe_2Ph)CF_2CF_3]$ (– – –)

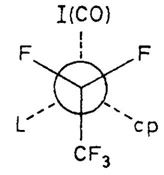
Three staggered conformations are possible for these complexes, (III), (IV), and (V). By analogy with



(III)



(IV)



(V)

previously studied systems,[2] when L = PPh_3 the order of relative stabilities is expected to be (III) < (IV) < (V), and thus rotamer (III) is expected to be the highest populated. The large differences between J_{AX} and J_{BX} in the spectra of the complexes $[(cp)CoI(PPh_3)CF_2CF_3]$ and $[(cp)CoCO(PPh_3)CF_2CF_3]ClO_4$ are in accord with this conclusion; it seems probable that *gauche* and *trans* coupling constants would be different, although unequivocal assignments cannot be made. Although variable-temperature studies of the carbonyl complex could not be made, preliminary studies of the isostructural iron complex, $[(cp)FeCO(PPh_3)CF_2CF_3]$, for which J_{AX} and J_{BX} are 43·3 ± 0·5 and 1·2 ± 0·4 Hz, respectively, over a temperature range of 108 K,[12] are in accord with the suggestion that (III) is significantly more stable than the other rotamers. On this basis the somewhat larger temperature dependence of J_{AX} and J_{BX} of the complex $[(cp)CoI(PPh_3)CF_2CF_3]$ may then indicate changing populations of the rotational isomers, although $^3J_{PF}$ may be inherently temperature dependent. Vicinal fluorine–fluorine coupling constants do exhibit temperature dependence,[13] for instance, while the variation in $^3J_{PF}$ of the complex $[(cp)FeCO(PPh_3)CF_3]$ [2] cannot be a result of conformational changes. The very large change in J_{AX} of the complex of $PMePh_2$, a phosphine of intermediate steric requirements, probably indicates major changes in the relative populations of the rotamers, although which rotamers are being significantly populated cannot be determined. The relatively small changes in vicinal coupling constants of the complex of dimethylphenylphosphine, the smallest of the three phosphines, may indicate that energy differences between the populated rotamers are relatively small, and thus that the two or three rotamers which are significantly populated are populated almost equally over the temperature range studied. As expected, on this basis, J_{AX} and J_{BX} are much closer together for this complex than for that of triphenylphosphine.

Because of the broadness and/or complexity of the CF resonances of the perfluoroisopropyl complexes, the vicinal phosphorus–fluorine coupling could not in all cases be resolved. In addition, temperature dependences of $^3J_{PF}$ could not be determined for these complexes, and little stereochemical information can be obtained. The large differences in couplings between the phosphorus and the trifluoromethyl groups in each complex, however, may indicate a four-bond stereochemical dependence of the phosphorus–fluorine coupling constants. Such dependences have been observed for fluorine–fluorine couplings.[14] Attempts to relate magnitudes of observed $^3J_{PF}$ of the perfluoro-methyl, -ethyl, and -isopropyl complexes with expected dihedral angles, as is apparently possible for vicinal phosphorus–hydrogen coupling constants,[2] met with little success. The possibility of temperature dependences of the coupling constants has already been discussed and, as has been reported for vicinal fluorine–fluorine coupling constants,[13] substituent effects are also clearly important.

By analogy with fluorine–fluorine couplings,[13] substitution of fluorine atoms on the α-carbon atoms by the less electronegative trifluoromethyl groups should increase the vicinal coupling constants (contrast $^3J_{FF}$ of the pentafluoroethyl complexes, <1 Hz, with $^3J_{FF}$ of the perfluoroisopropyl complexes, *ca.* 10 Hz). Although the averaged vicinal phosphorus–hydrogen coupling constants of the complexes $[(cp)Fe(CO)(PPh_3)Me]$ and $[(cp)RhBr(PPh_3)Me]$ agree closely with the average of two *gauche* and one *trans* coupling constant obtained from spectra of similar primary alkyl complexes,[2] the very small averaged $^3J_{PF}$ of $[(cp)CoI(PPh_3)CF_3]$ cannot be an average of the apparent *gauche* and *trans* coupling constants observed in spectra of $[(cp)CoCO(PPh_3)CF_2CF_3]ClO_4$ or $[(cp)CoI(PPh_3)CF_2CF_3]$. Nor is there even any apparent correlation between the observed coupling constants of the four perfluoroethyl complexes. Thus it seems probable that vicinal fluorine–phosphorus coupling constants will show no clear tendency as a function of the dihedral angle, as has been observed for vicinal fluorine–fluorine coupling constants,[14] rather than as has been demonstrated for couplings of several nuclei to hydrogen.[1] In this connection, it may be noted that both *gauche* and *trans* $^3J_{FF}$ can vary between rotamers of the same compound.[15]

The i.r. spectra of all the complexes discussed are consistent with the formulations and in most cases do not merit discussion here. In the case of the carbonyl complex, however, two carbonyl stretching bands of almost equal intensity were observed at 2 106 and 2 094 cm^{-1} in chloroform solution. Similar doubling is also observed in cyclohexane solution spectra of the complexes $[(cp)FeCO(PPh_3)CF_2CF_3]$ [12] [ν(CO) 1 959, 1 956 cm^{-1}] and $[(cp)FeCO(PPh_3)CF(CF_3)_2]$ [14,16] [ν(CO) 1 972, 1 956 cm^{-1}]. Although similar observations on these and other complexes have been interpreted in terms of rotational isomerism,[16,17] such an explanation is inconsistent with the n.m.r. spectra of the iron complexes,[12] which strongly suggest the presence of only one rotamer in each case. Thus one rotamer is presumably favoured in the case of the cobalt carbonyl cation as well. However, a co-ordinated triphenylphosphine is known to assume two propeller-like chiral conformations, the difference between the conformations being the sense of the twist about the phosphorus–aryl bonds.[18–20] Thus the phosphine ligands in these complexes constitute second chiral centres and the molecules should exist as diastereoisomers, explaining the presence of two ν(CO)

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[12] M. C. Baird, unpublished work.

[13] R. J. Abraham and L. Cavalli, *Mol. Phys.*, 1965, **9**, 67.

[14] K. Hirao, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.

[15] R. R. Dean and J. Lee, *Trans. Faraday Soc.*, 1969, **65**, 1.

[16] W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 1971, **10**, 843 and references therein.

[17] R. B. King, R. N. Kapoor, and K. H. Pannell, *J. Organometallic Chem.*, 1969, **20**, 187.

[18] V. G. Albano, P. L. Bellon, and M. Sansoni, *Chem. Comm.*, 1969, 899.

[19] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc. (A)*, 1971, 2420.

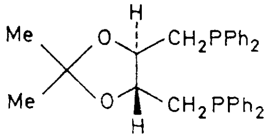
[20] D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, 1973, **95**, 1535.

bands in the i.r. spectra. The asymmetry of the tertiary phosphine which we postulate is not without precedent, having been observed in crystal structures of the highly hindered complexes [$PtCO(PPh_3)_3$] [18] and [IrNO-$(PPh_3)_3$].[19] The probability of diastereoisomers also offers an alternative explanation for the presence of two ν(CO) bands in the i.r. spectrum of the complex [(cp)-$FeCO(PPh_3)SnPh_3$] to that which has been suggested,[17] in that a partially eclipsed rotamer is significantly populated.

The suggestion that restricted rotation about the phosphorus–aryl bonds provides an explanation for the line-broadening phenomena reported in our previous paper [2] has been made in a recent note by Brown and Mertis.[21] Although slow interconversion between the enantiomeric conformations of co-ordinated triphenylphosphine may be a factor affecting linewidths of the resonances of co-ordinated alkyl groups, it does not satisfactorily explain the temperature dependences of the vicinal coupling constants in some of the complexes. Thus we believe that criticism of our suggestions concerning restricted rotation about metal–carbon σ-bonds is unwarranted. On the other hand, the temperature dependences of the band shapes of the aryl resonances of the triphenylphosphine complexes are in accord with restricted rotation about the phosphorus–aryl and/or the phosphorus–metal bonds. In all three cases, the high-temperature spectra show well-resolved time-averaged multiplets; on cooling, the multiplet structures broaden and eventually coalesce into broad bands long before the cp resonances broaden significantly. The relative coalescence temperatures correlate well with the bulk of the perfluoroalkyl group, $CF(CF_3)_2 > CF_2CF_3 > CF_3$, as expected.

Whether the broadening is caused by restricted rotation about the phosphorus–aryl or the phosphorus–metal bonds cannot be determined in this system. Molecular models suggest that the molecules are very crowded, however, and it may be tentatively suggested that a perfluoroalkyl group and a phosphine ligand in a molecule might rotate synchronously. On this basis, as there is no obvious correlation between the time scales of the hindered rotation observed in the fluorine and proton spectra, it seems probable that the broadening observed in the latter is a result of hindered rotation about the phosphorus–aryl bonds rather than the phosphorus–metal bonds.

Somewhat similar effects have been observed in methyl resonances of the complexes [$MNO(PMePh_2)_3$] (M = Co or Rh).[22] Although the observed broadening was interpreted only in terms of restricted rotation about the phosphorus–metal bonds, the origin is probably the same, severe crowding in the molecule. The efficiency with which rhodium(I) complexes of the optically active diphosphine (A) catalyse asymmetric reduction of olefins is also undoubtedly a result of steric requirements of the ligand.[23] As well as the two chiral carbon atoms, the two phosphorus atoms could also become chiral on co-ordination to the rhodium atom. The presence of such chirality may possibly be observable in the phenyl region of the proton n.m.r. spectra of complexes of the ligand.



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[21] J. M. Brown and K. Mertis, *J. Organometallic Chem.*, 1973, **47**, C5.

[22] G. Dolcetti, N. W. Hoffman, and J. P. Collman, *Inorg. Chim. Acta*, 1972, **6**, 531.

[23] T. P. Dang and H. B. Kagan, *Chem. Comm.*, 1971, 481.