CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY,
AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA 2600, AUSTRALIA

Four- and Five-Coordinate Complexes of Rhodium and Iridium Containing Trifluorophosphine

BY M. A. BENNETT* AND D. J. PATMORE

Received February 23, 1971

Trifluorophosphine displaces coordinated cyclooctene from the complex $[RhCl(C_8H_{14})_2]_2$ at room temperature and pressure to give an almost quantitative yield of the dimeric, chloro-bridged complex $[RhCl(PF_3)_2]_2$, which was previously accessible in only 2.6% yield. Trifluorophosphine also reacts with $[IrCl(C_8H_{14})_2]_2$ to give as the final product a five-coordinate complex $IrCl(PF_3)_4$, though there is evidence for intermediate mixed cyclooctene–trifluorophosphine complexes. Both these and $IrCl(PF_3)_4$ readily decompose on warming to give the new compound $[IrCl(PF_3)_2]_2$. Metal–metal bonded structures are proposed for $[MCl(PF_3)_2]_2$ (M = Rh or Ir) *in the solid state*. The preparation of mononuclear complexes such as $M(acac)(PF_3)_2$ and π-$C_5H_5Rh(PF_3)_2$ is also described. Nmr studies indicate that there is rapid exchange between free and coordinated PF_3 at room temperature in planar rhodium(I) complexes but not in π-$C_5H_5Rh(PF_3)_2$. The complexes $[RhCl(PF_3)_2]_2$ (in the presence of PF_3) and $IrCl(PF_3)_4$ are reduced by potassium amalgam in ether giving initially the new metal–mercury bonded complexes $Hg[M(PF_3)_4]_2$ and finally the known salts $K[M(PF_3)_4]$. The latter react with $[RhCl(PF_3)_2]_2$–PF_3 or $IrCl(PF_3)_4$ to give the dimeric metal–metal bonded complexes $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$, which probably are structurally similar to the isomer of $Co_2(CO)_8$ without bridging CO's. Cleavage of $Rh_2(PF_3)_8$ with H_2 (25°, 1 atm) gives $HRh(PF_3)_4$ quantitatively. Five-coordinate metal–metal bonded complexes of general formula $RM(PF_3)_4$ [M = Rh or Ir, R = $(C_6H_5)_3Sn$ or $(C_6H_5)_3PAu$; M = Ir, R = $(C_6H_5)_3Pb$] can be made by reaction of $[M(PF_3)_4]^-$ with RCl. However there is no reaction between $M(PF_3)_4^-$ and $(C_6H_5)_3SiCl$ or $(C_6H_5)_3GeCl$, indicating that $Rh(PF_3)_4^-$ and $Ir(PF_3)_4^-$ are poorer nucleophiles than $Co(CO)_4^-$. A more general route to compounds containing bonds between rhodium or iridium and a group IV element is the reaction between $M_2(PF_3)_8$ and a group IV hydride: $M_2(PF_3)_8 + RH \rightarrow RM(PF_3)_4 + HM(PF_3)_4$ [R = $(C_6H_5)_3Si$, $(C_2H_5O)_3Si$, Cl_3Si, or $(C_6H_5)_3Ge$]. With triphenylgermane there is a subsequent slow reversible reaction $HM(PF_3)_4 + RH \rightleftarrows H_2 + RM(PF_3)_4$, while with $(C_2H_5O)_3SiH$ and $HSiCl_3$, this reaction goes to completion. Kinetic studies indicate both reactions to be bimolecular, the rates depending on the transition element (Rh > Ir), the group IV element (Ge > Si), and the substituents on the group IV atom (Cl $\sim$ C_2H_5O > C_6H_5). The reactions are compared with those believed to occur in the hydrosilation of $Co_2(CO)_8$.

Introduction

Trifluorophosphine (phosphorus trifluoride) resembles carbon monoxide in forming a wide range of stable, low-valent transition metal complexes.[1] The hydrides and anionic species formed by PF_3, such as $HCo(PF_3)_4$ and $Co(PF_3)_4^-$, are considerably more stable thermally and oxidatively than their carbonyl analogs, and spectroscopic evidence[2-6] suggests that the π-acceptor ability of PF_3 is comparable with, and may even exceed, that of CO.

The two methods commonly used to make PF_3 complexes are (1) treatment of a transition metal salt with PF_3, usually in the presence of a reducing agent such as copper,[1] and (2) heating or irradiation of a metal carbonyl or a substituted metal carbonyl with PF_3.[5,7,8] The first method usually requires high pressures of PF_3 and high temperatures, and the second method gives mixtures of randomly substituted products which have to be separated by glc. An alternative approach which has found only occasional application is to displace an organic ligand such as an olefin, arene, or π-cyclopentadienyl group from the metal with PF_3. For example, cycloheptatriene and norbornadiene are readily displaced from their group VI carbonyl complexes, and these provide a convenient route to PF_3 and other fluorophosphine derivatives of the group VI metal carbonyls.[6,9] It has been shown that olefin complexes of rhodium(I) and iridium(I) are convenient intermediates for the preparation of planar complexes of the type MXL_3 (M = Rh or Ir, X = Cl or Br, L = tertiary phosphine or arsine),[10-13] and we now report in detail the atmospheric pressure synthesis of a number of PF_3 complexes of rhodium and iridium by the same method.[14] High-pressure techniques have been used by Kruck and coworkers to prepare $HM(PF_3)_4$ (M = Rh or Ir),[15-17] $Rh_2(PF_3)_8$,[18] and $[RhCl(PF_3)_2]_2$,[18] and the salts $K[M(PF_3)_4]$ have been obtained by reaction of potassium amalgam with the hydrides or with $Rh_2(PF_3)_8$ (in the case of rhodium).[19] The five-coordinate complex $IrI(PF_3)_4$ has been made by treatment of $K[Ir(PF_3)_4]$ with iodine.[19]

Results and Discussion

The cyclooctene complex $[RhCl(C_8H_{14})_2]_2$,[20] suspended in *n*-pentane, reacts with PF_3 (25°, 1 atm) to give $[RhCl(PF_3)_2]_2$ almost quantitatively as volatile, moderately air-stable red crystals which are soluble in *n*-pentane. The complex is dimeric in solution, and the

---

[1] Th. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

[2] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[3] Th. Kruck and A. Prasch, *Z. Naturforsch. B*, **19**, 669 (1964).

[4] Th. Kruck and W. Lang, *Chem. Ber.*, **98**, 3060 (1965).

[5] R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965).

[6] C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc. A*, 2216 (1968).

[7] R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).

[8] R. J. Clark and E. O. Brimm, *ibid.*, **4**, 651 (1965).

[9] R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963).

[10] K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968).

[11] J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1736 (1966).

[12] S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968).

[13] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[14] Preliminary communications: (a) M. A. Bennett and D. J. Patmore, *Chem. Commun.*, 1510 (1969); (b) D. A. Clement, J. F. Nixon, and M. D. Sexton, *ibid.*, 1509 (1969).

[15] Th. Kruck, W. Lang, and N. Derner, *Z. Naturforsch. B*, **20**, 705 (1965).

[16] Th. Kruck and W. Lang, *Angew. Chem., Int. Ed. Engl.*, **4**, 870 (1965).

[17] Th. Kruck, W. Lang, N. Derner, and M. Stadler, *Chem. Ber.*, **101**, 3816 (1968).

[18] Th. Kruck, N. Derner, and W. Lang, *Z. Naturforsch. B*, **21**, 1020 (1966).

[19] Th. Kruck, A. Engelmann, and W. Lang, *Chem. Ber.*, **99**, 2473 (1966).

[20] L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965); the molecularity of this and the analogous iridium complex has not been determined, but the complexes are likely to be dimeric by analogy with $[RhCl(CO)_2]_2$.

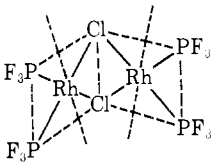
70-eV mass spectrum shows a parent molecular ion $Rh_2Cl_2(PF_3)_4^+$ as well as ions arising from the consecutive loss of PF_3 from this species. The corresponding bromo and iodo complexes can be made by treating $[RhCl(PF_3)_2]_2$ in ether with excess lithium bromide or sodium iodide. They form red crystals which have similar properties to those of the chloro complex. The latter has been obtained as an impure by-product in the high-pressure synthesis of $Rh_2(PF_3)_8$ and could only be obtained pure in 2.6% yield by treating anhydrous $RhCl_3$ and copper powder with PF_3 (80°, 1 atm).[18] The olefin complexes $[RhCl(diene)]_2$ (diene = 1,5-cyclooctadiene or norbornadiene) and $[RhCl(C_2H_4)_2]_2$ can also be used as starting materials for the preparation of $[RhCl(PF_3)_2]_2$,[14b] and the analogous bromo and iodo compounds are also conveniently prepared from $[RhX(1,5\text{-}C_8H_{12})]_2$ (X = Br or I).[21]

The reaction of PF_3 under ambient conditions with the iridium(I)–cyclooctene complex $[IrCl(C_8H_{14})_2]_2$[22] is more complex than that with $[RhCl(C_8H_{14})_2]_2$. The initial product is a yellow crystalline material which is unstable and gives variable analytical data; it is possibly a mixture of $IrCl(C_8H_{14})(PF_3)_2$ and $IrCl(C_8H_{14})(PF_3)_3$, with the latter predominating. Repeated recrystallization from *n*-pentane in the presence of PF_3 gives a second, unstable yellow crystalline substance which contains neither carbon nor hydrogen and which is probably the five-coordinate complex $IrCl(PF_3)_4$ (see below); the analogous iodo complex is known.[19] On heating in *n*-hexane through which a stream of nitrogen is passing or on attempted sublimation, both "$IrCl(C_8H_{14})(PF_3)_3$" and $IrCl(PF_3)_4$ lose PF_3 to give $[IrCl(PF_3)_2]_2$ as deep blue crystals which appear bronze by reflected light. This compound is volatile, very air sensitive, and readily soluble in *n*-pentane and other organic solvents giving yellow-orange solutions. It is dimeric both in solution and in the vapor phase, as shown by molecular weight measurements and the appearance of the molecular ion $Ir_2Cl_2(PF_3)_4^+$ in the mass spectrum. The complex reverts to $IrCl(PF_3)_4$ on treatment with PF_3, and the weight increase accompanying this process agrees with the formula of $IrCl(PF_3)_4$. A similar equilibrium involving the ethylene complexes $IrCl(C_2H_4)_4$ and $[IrCl(C_2H_4)_2]_2$ has recently been reported.[23]

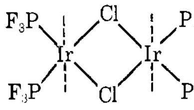
If PF_3 is passed into a suspension of $[IrCl(C_8H_{14})_2]_2$ and the resulting solution is heated with excess $[IrCl(C_8H_{14})_2]_2$ a bright yellow microcrystalline solid $IrCl(C_8H_{14})_2(PF_3)$ is formed, which is monomeric in *n*-hexane. It reacts with 2,4-pentanedionatothallium(I) [Tl(acac)] with loss of cyclooctene giving $Ir(C_8H_{14})(PF_3)(acac)$. Both compounds presumably contain planar-coordinated iridium(I).

In the solid state, the complexes $[RhX(PF_3)_2]_2$ (X = Cl, Br, or I) probably have a structure like that of $[RhCl(CO)_2]_2$,[24] *i.e.*, a hinged halogen-bridged dimeric unit with intermolecular and intramolecular Rh–Rh bonds (I). In solution, the intermolecular Rh–Rh bonds are broken, but in the case of the rhodium(I) carbonyl halides there is evidence from dipole moments[25] and infrared spectra[25,26] that the halogen bridges are still nonplanar in solution. The PF_3 complexes are probably similar.

The complex $[IrCl(PF_3)_2]_2$ is unique in having a different stoichiometry from the corresponding carbonyl chloride $[IrCl(CO)_3]$, and it is also far more volatile and more soluble in organic solvents than the carbonyl compound. An attempted preparation of $[IrCl(CO)_2]_2$ by treating $[IrCl(C_8H_{14})_2]_2$ with CO gave $IrCl(CO)_3$ as the only isolable product. The structure of the latter in the solid state, determined by two groups independently,[27,28] consists of infinite chains of planar $IrCl(CO)_3$ units held together by Ir–Ir bonds (2.85 Å in length) so as to complete octahedral coordination about the metal. We therefore suggest that $[IrCl(PF_3)_2]_2$ in the solid state contains dimeric, chlorine-bridged units held together by Ir–Ir bonds (II). We do not know whether the chlorine bridges are planar or nonplanar, but intermetallic bonding is strongly indicated by the color of the solid compound. In solution and in the vapor phase, the metal–metal bonds are probably broken.



I



II

The chlorine bridges of $[RhCl(PF_3)_2]_2$ are readily cleaved by Cl^-, TlC_5H_5, or Tl(acac) to give the expected mononuclear species. The anion $RhCl_2(PF_3)_2^-$ is conveniently isolated as its $(CH_3)_4N^+$ or $(C_6H_5)_4As^+$ salts and probably has a cis configuration like that of the corresponding carbonyl species.[29] The π-cyclopentadienyl derivative $\pi\text{-}C_5H_5Rh(PF_3)_2$ is an orange-red, air-sensitive liquid which appears to be similar to the cobalt(I) complex $C_5H_5Co(PF_3)_2$ made from $Co(C_5H_5)_2$ and PF_3 (170°, 350 atm).[30] Its proton nmr spectrum shows a singlet with multiplet structure at δ 4.95 due to the equivalent protons split by coupling with ^{103}Rh, ^{31}P, and ^{19}F. The 2,4-pentanedionato complex $Rh(acac)(PF_3)_2$ is yellow-orange by both reflected and transmitted light, is not noticeably dichroic, and gives yellow solutions in organic solvents. The complex $Rh(acac)(CO)_2$ is also monomeric and yellow in solution, but it forms dichroic crystals which appear green by reflected light and deep red by transmitted light;[31] the solid consists of chains of monomeric units held together by Rh–Rh bonds 3.27 Å in length.[32] Treatment of $Ir(acac)(C_8H_{14})_2$ (obtained from $[IrCl(C_8H_{14})_2]_2$ and Tl(acac)) with PF_3 gives a good yield of $Ir(acac)(PF_3)_2$, which is pale orange in solution and in the solid state. In contrast, $Ir(acac)(CO)_2$ is greenish red in the solid state and contains Ir–Ir bonds 3.20 Å

---

(21) M. A. Bennett and T. W. Turney, unpublished work.

(22) B. L. Shaw and E. Singleton, *J. Chem. Soc. A*, 1683 (1967).

(23) A. van der Ent and T. C. van Soest, *Chem. Commun.*, 225 (1970).

(24) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, **83**, 1761 (1961).

(25) C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, **36**, 1094 (1962).

(26) B. F. G. Johnson, J. Lewis, P. W. Robinson, and J. R. Miller, *J. Chem. Soc. A*, 2693 (1970).

(27) K. Krogmann, W. Binder, and H. D. Hausen, *Angew. Chem., Int. Ed. Engl.*, **7**, 812 (1968).

(28) H. Vahrenkamp and L. F. Dahl, personal communication.

(29) L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965).

(30) Th. Kruck, W. Hieber, and W. Lang, *Angew. Chem., Int. Ed. Engl.*, **5**, 247 (1966).

(31) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

(32) N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Commun.*, 1041 (1967).

in length.[33] Intermolecular repulsions between PF_3 groups may be responsible for the apparent lack of M–M bonding in $M(acac)(PF_3)_2$ (M = Rh or Ir) and possibly also for the differences in properties and stoichiometry of $[IrCl(PF_3)_2]_2$ and $IrCl(CO)_3$.

The infrared spectra of the rhodium(I) and iridium(I) complexes of PF_3 show bands in the region 950–860 cm^{-1} which are due to P–F stretching modes (Table I).

TABLE I

P–F STRETCHING FREQUENCIES (CM^{-1}) IN PF_3 COMPLEXES OF RHODIUM AND IRIDIUM

Compound	ν(P–F)[a]
$[RhCl(PF_3)_2]_2$	945 m, 926 m, 918 s, 907 s, 871 s
$[RhBr(PF_3)_2]_2$	941 m, 922 m, 913 s, 904 s, 870 s
$[RhI(PF_3)_2]_2$	934 s, 914 m, 903 s, 892 m, 865 s
$[IrCl(PF_3)_2]_2$	955 m, 934 s, 924 m, 910 s, 878 m
$IrCl(PF_3)_4$	960 w, 936 s, 919 s, 913 s, sh, 877 w, sh, 866 s
$IrCl(C_8H_{14})_2(PF_3)$[b]	932 w, 897 s, 883 s
$Rh(acac)(PF_3)_2$	929 s, 916 w, 890 s, 862 s
$Ir(acac)(PF_3)_2$	937 s, 916 w, 890 m, 867 m
π-$C_5H_5Rh(PF_3)_2$	911 s, 867 s, 848 s
$HRh(PF_3)_4$	948 w, 910 s, 895 s, 890 s, sh, 866 w, 856 s
$HIr(PF_3)_4$	958 w, 917 s, 906 s, 894 m, 884 w, sh, 869 m, 862 vs
$Rh_2(PF_3)_8$	922 s, 892 w, sh, 882 m, 874 m, 855 m, 849 m
$Ir_2(PF_3)_8$	932 s, 903 w, sh, 889 s, 863 m, 854 m
$Hg[Rh(PF_3)_4]_2$	909 s, 882 sh, 876 s, 866 w, sh, 857 m, sh, 852 s
$Hg[Ir(PF_3)_4]_2$	923 s, 917 m, 885 s, 874 w, 864 m, sh, 859 s
$Rh_3(PF_3)_9$	905 s, 895 vs, 861 m[c]
$Cl_3SiRh(PF_3)_4$	945 w, 924 m, 902 s, 890 m, sh, 857 s
$(C_6H_5)_3SiRh(PF_3)_4$	934 m, 908 s, 886 sh, 882 s, 868 m, sh, 842 s
$(C_6H_5)_3SiIr(PF_3)_4$	947 m, 919 s, 892 s, 877 m, sh, 851 s
$(C_6H_5)_3GeRh(PF_3)_4$	933 m, 909 m, 886 sh, 881 m, 866 w, sh, 844 s
$(C_6H_5)_3GeIr(PF_3)_4$	944 m, 919 s, 891 s, 876 w, sh, 852 s
$(C_6H_5)_3SnRh(PF_3)_4$	931 s, 908 s, 879 s, 866 w, sh, 845 s
$(C_6H_5)_3SnIr(PF_3)_4$	943 s, 919 s, 888 s, 875 w, sh, 853 s
$(C_6H_5)_3PbIr(PF_3)_4$	940 s, 917 s, 887 s, 862 w, sh, 854 s
$(C_6H_5)_3PAuRh(PF_3)_4$	921 m, 880 m, 857 s, 829 s
$(C_6H_5)_3PAuIr(PF_3)_4$	934 m, 890 m, 868 s, 860 m, 840 s

[a] Measured in dry *n*-hexane solution unless otherwise stated. [b] Measured in CCl_4 solution. [c] Reported values:[18] 905 s, 894 vs, 861 m.

Comparison of the values for $[RhX(PF_3)_2]_2$ (X = Cl, Br, and I) shows that ν(P–F) falls in the order Cl > Br > I, a trend which is also generally observed for ν(CO) in metal carbonyl halides.[34] The far-infrared spectra of the Rh_I–PF_3 complexes are considerably more complex than those of the analogous carbonyl complexes and will be reported separately.

TABLE II

^{19}F AND ^1H NMR SPECTRA

Compound	$\phi(PF_3)$[a]	Approx J_{P-F},[b] Hz	$\delta(^1H)$[c,d]
$[RhCl(PF_3)_2]_2$	+17.2	1340[e]	...
$Rh(acac)(PF_3)_2$	+20.5	*f*	acac C*H*, 5.18 s (1); C*H*$_3$, 1.72 s (6)
$Rh(acac)(C_8H_{14})_2$	...	...	acac C*H*, 5.02s (1); CH_3, 1.69 s (6); C_8H_{14}, 1.45 m, 1.54 m, 2.38 m (14)
π-$C_5H_5Rh(PF_3)_2$	+1.11	1308[g]	C_5*H*$_5$, 4.95 duodecaplet, spacing 0.6 Hz
$[IrCl(PF_3)_2]_2$	+24.1[h]	1270[i]	
$Ir(acac)(PF_3)_2$	+26.4	1205[j]	
$IrCl(PF_3)_4$	+19.5	1252	
$Rh_2(PF_3)_8$	+2.98[h]	1342	
$Ir_2(PF_3)_8$	+5.2[h]	1230	
$(C_6H_5)_3SiRh(PF_3)_4$	+5.55[h]	1355	

[a] In ppm relative to $CFCl_3$ as internal reference, positive on high-field side; measured in C_6H_6, except where stated. [b] Separation between two main peaks, strictly $|^1J_{P-F} + {}^3J_{P-F}|$. [c] In ppm relative to TMS as internal reference, positive on low-field side, relative intensities in parentheses; measured in C_6D_6. [d] Abbreviations: s, singlet, m, multiplet. [e] $|J_{Rh-F}| = 31.6$ Hz; $|^2J_{P-P}| \approx 61$ Hz. [f] $^1J_{P-F} = -1322 \pm 2$, $^3J_{P-F} = +4$, $|^2J_{P-P}| = 160 \pm 0.4$, $|^4J_{F-F}| = 2.2 \pm 0.2$, $|^2J_{Rh-F}| = 29.8 \pm 0.2$, all in Hz; $^1J_{F-F}$ is assumed to be negative (see R. M. Lynden-Bell, J. F. Nixon, and R. Schmutzler, *J. Chem. Soc. A*, 565 (1970), and references cited therein). [g] $|^2J_{P-P} = 151 \pm 2$ Hz; $|^2J_{Rh-F}| = 32$ Hz. [h] Measured in *n*-hexane. [i] $|^2J_{P-P}| \approx 97$ Hz. [j] $|^2J_{P-P}| = 121$ Hz.

The ^{19}F nmr spectra (Table II) generally consist of two strong lines separated by 1200–1300 Hz arising from ^{31}P–^{19}F coupling; each strong line is surrounded by two weaker signals. The spectra are complex because, in addition to coupling between adjacent phosphorus and fluorine atoms, there is coupling between the phosphorus of one PF_3 group and the fluorine of another, and both phosphorus atoms are themselves strongly coupled. In the case of the Rh(I) complexes, each line is further split into a doublet owing to coupling with ^{103}Rh ($I = ^1/_2$, 100% abundance), $J_{Rh-F} \approx 30$ Hz. The spectrum of $Rh(acac)(PF_3)_2$ (Figure 1) has been analyzed as an $X_3AA'X'_3$ system following the treatment of Harris and Woodman,[35] and the derived values of $^1J_{P-F}$, $^3J_{P-F}$, and $^4J_{F-F}$ are in Table II. The large splitting between the two strong lines is $|^1J_{P-F} + {}^3J_{P-F}|$, although in the case of $Rh(acac)(PF_3)_2$, $^3J_{P-F}$ is very small (+4 Hz). The ^{19}F nmr spectra of $[MCl(PF_3)_2]_2$ appear to be more complex than those of $M(PF_3)_2(acac)$, and they have not been completely analyzed.

When PF_3 is bubbled through a solution of $Rh(acac)(PF_3)_2$, the ^{19}F nmr spectrum collapses to two broad bands without fine structure separated by about 1300 Hz. The original spectrum is reproduced if the dissolved PF_3 is removed by passing nitrogen through the solution. Similar observations have been made with solutions of $[RhCl(PF_3)_2]_2$ and $RhCl(PF_3)[P(C_6H_5)_3]_2$[14b] in the presence of PF_3, and they demonstrate the rapid exchange occurring at ~30° between free and coordinated PF_3 in planar Rh(I) complexes. Likewise there is instantaneous exchange between free and coordinated CO in $[RhCl(CO)_2]_2$[36] and $RhCl(CO)[P(C_6H_5)_3]_2$,[36,37] and between free and coordinated ethylene in $Rh(acac)(C_2H_4)_2$.[38] The rapid intermolecular ligand exchange in the case of $[RhCl(PF_3)_2]_2$ probably proceeds *via* an intermediate five-coordinate complex $RhCl(PF_3)_4$ analogous to the iridium(I) complex already discussed; this compound is formed as an unstable yellow solid when PF_3 is condensed onto $[RhCl(PF_3)_2]_2$.[21] The multiplet structure of the π-C_5H_5 resonance of π-$C_5H_5Rh(PF_3)_2$ is completely unaffected by the presence of PF_3, which indicates that exchange between free and coordinated PF_3 in this compound is slow on the nmr time scale. Similar behavior has been noted for ethylene exchange in π-$C_5H_5Rh(C_2H_4)_2$.[38] As suggested previously,[38] the difference in behavior compared with the planar complexes may arise from

---

(33) C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkü, *J. Amer. Chem. Soc.*, **88**, 4286 (1966).

(34) R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1860 (1956); 2283 (1958); R. S. Nyholm, *Proc. Chem. Soc., London*, 283 (1961).

(35) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1965–1966).

(36) A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, **83**, 525 (1961).

(37) H. B. Gray and A. Wojcicki, *Proc. Chem. Soc., London*, 358 (1960).

(38) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

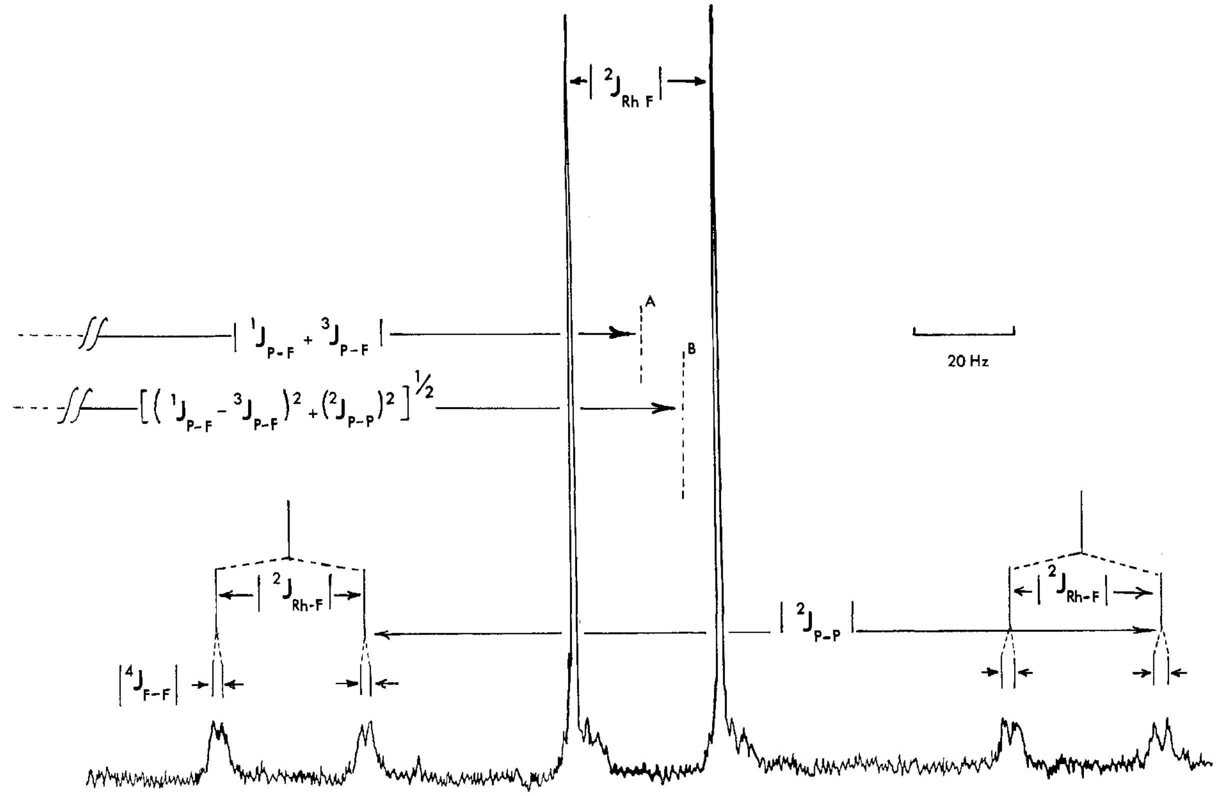


Figure 1.—Half of the ^{19}F nmr spectrum of $Rh(acac)(PF_3)_2$. Dotted line A is the average position of the two strongest peaks; dotted line B is the average position of the four outer peaks.

the fact that the complexes π-$C_5H_5RhL_2$ ($L = C_2H_4$ or PF_3) may be regarded as having an inert-gas configuration, so that an empty orbital is not readily available for an entering ligand. It should be noted, however, that π-$C_5H_5Co(CO)_2$ exchanges rapidly with ^{14}CO,[39] and π-$C_5H_5Rh(CO)_2$ undergoes substitution with ligands by an associative mechanism.[40]

The ^{19}F nmr spectrum of $IrCl(PF_3)_4$ at 30° consists of two complex resonances centered at +19.5 ppm relative to $CFCl_3$ and separated by 1252 Hz. The general outline resembles that of $Ni(PF_3)_4$,[41–43] though the resolution is much poorer. The PF_3 groups are probably in equivalent environments at room temperature owing to rapid intramolecular and/or intermolecular ligand exchange.

The complexes $[RhCl(PF_3)_2]_2$ and $IrCl(PF_3)_4$, dissolved in ether in the presence of PF_3, can be reduced with potassium amalgam at 0° to give ultimately the anionic species $M(PF_3)_4^-$ (M = Rh or Ir) in ~70% yield, isolated as their potassium salts; they are identical with those obtained by Kruck, *et al.*[19] The initial reduction products are the colorless, crystalline monomeric Hg–M bonded derivatives $Hg[M(PF_3)_4]_2$, which are soluble in *n*-pentane and show parent ion peaks in their mass spectra. The rhodium compound can be isolated, together with $K[Rh(PF_3)_4]$, after treatment of $[RhCl(PF_3)_2]_2$–PF_3 with potassium amalgam for 30 min but is formed in better yield either by reducing $[RhI(PF_3)_2]_2$ under the same conditions or by treating $K[Rh(PF_3)_4]$ with mercuric chloride. Reduction of $IrCl(PF_3)_4$ with potassium amalgam gives only $Hg[Ir(PF_3)_4]_2$ after 30 min, and 4–5 hr is required for complete conversion to $K[Ir(PF_3)_4]$.

The anions $M(PF_3)_4^-$ (M = Rh or Ir) resemble $Co(CO)_4^-$ in undergoing nucleophilic substitutions with organometallic halides such as $(C_6H_5)_3SnCl$, $(C_6H_5)_3PbCl$, and $(C_6H_5)_3PAuCl$ to give the metal–metal bonded complexes $(C_6H_5)_3SnM(PF_3)_4$, $(C_6H_5)_3PbIr(PF_3)_4$, and $(C_6H_5)_3PAuM(PF_3)_4$ as stable, colorless, crystalline solids. However, the anions fail to react with $(C_6H_5)_3SiCl$ or $(C_6H_5)_3GeCl$ to give the analogous silicon or germanium complexes. This is not because the latter are particularly unstable (see below), and it presumably implies that the $M(PF_3)_4^-$ anions are poorer nucleophiles than $Co(CO)_4^-$, which is known to react with $(C_6H_5)_3GeCl$ to give $(C_6H_5)_3GeCo(CO)_4$.[44] Further evidence for this conclusion is the fact that $Rh(PF_3)_4^-$ is oxidized by $SnCl_4$ and by $TlCl_3$ to give $[RhCl(PF_3)_2]_2$, the other products being $SnCl_2$ and TlCl, respectively; in contrast, $TlCl_3$ reacts with $Co(CO)_4^-$ to give $Tl[Co(CO)_4]_3$,[45] and $SnCl_4$ gives a mixture of $Cl_2Sn[Co(CO)_4]_2$ and $ClSn[Co(CO_4]_3$.[46] We assume that the structures of $Hg[M(PF_3)_4]_2$ and $(C_6H_5)_3PAuM(PF_3)_4$ (M = Rh or Ir) resemble those of $Hg[Co(CO)_4]_2$[47] and $(C_6H_5)_3PAuCo(CO)_4$[48] in having a trigonal-bipyramidal arrangement of ligands about rhodium or iridium, with the directly bonded metal atom in an axial position. X-Ray structural analysis of $HCo(PF_3)_4$ suggests that the hydrogen atom also

---

(39) A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

(40) H. G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 1657 (1966).

(41) G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967).

(42) J. F. Nixon, *J. Chem. Soc. A*, 1136 (1967).

(43) R. M. Lynden-Bell, J. F. Nixon, and R. Schmutzler, *ibid.*, *A*, 565 (1970).

(44) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

(45) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1586 (1966).

(46) D. J. Patmore and W. A. G. Graham, *ibid.*, **7**, 771 (1968).

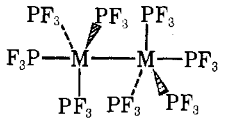
(47) G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1005 (1968).

(48) B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Commun.*, 444 (1965).

occupies an axial site of a distorted trigonal bipyramid.[49] For reasons discussed below it is unlikely that ^{19}F nmr spectra measured at room temperature will provide any structural information.

Reaction of $[RhCl(PF_3)_2]_2$ with $K[Rh(PF_3)_4]$ in ether in the presence of PF_3 gives the dimeric orange, crystalline complex $Rh_2(PF_3)_8$ in good yield, and the yellow iridium compound can be made analogously from $IrCl(PF_3)_4$ and $K[Ir(PF_3)_4]$. The rhodium compound, which was characterized by analysis, infrared spectrum, and reactions, is identical with that obtained in 30% yield by the reaction of PF_3 (250 atm) with $RhCl_3$ and copper powder,[18] but the present preparation is clearly more convenient. The iridium compound is new. Both compounds can be sublimed at 20° (10^{-3} mm), are air-sensitive, and are readily soluble in *n*-pentane and other organic solvents. The iridium compound is dimeric in *n*-hexane (vapor pressure osmometer), and its mass spectrum shows a parent ion peak at *m/e* 1088 in addition to ions arising from the loss of PF_3 and F. In contrast, the mass spectrum of $Rh_2(PF_3)_8$ shows only the peaks of its thermal decomposition product (see below). Osmometry on *n*-hexane solutions of $Rh_2(PF_3)_8$ gives apparent molecular weights which are considerably higher than the calculated value (see Experimental Section), though the value obtained by cryoscopy in cyclohexane[18] agrees reasonably well with the calculated value. Possibly the osmometric method is vitiated in this case by the volatility of $Rh_2(PF_3)_8$ at 25°. The ^{19}F nmr spectrum of $Rh_2(PF_3)_8$ at 30° consists of two broad resonances separated by 1342 Hz (width at half-height ~200 and 280 Hz, respectively, for the low- and high-field resonances). There is no discernible Rh–F coupling. The spectrum of $Ir_2(PF_3)_8$ is similar, though the separation is smaller (1230 Hz) and the peaks are somewhat less broad (~100 Hz at half-height).

The structures of $M_2(PF_3)_8$ (M = Rh or Ir) presumably consist of $M(PF_3)_4$ units held together by a metal–metal bond; the presence of bridging PF_3 groups is considered unlikely. A closely related molecule is the non-CO-bridged isomer of $Co_2(CO)_8$, which is in equilibrium with the CO-bridged isomer in solution.[50–52] Noack[50,52] favored a structure containing two staggered trigonal-bipyramidal $Co(CO)_4$ groups joined by a metal–metal bond, whereas Bor[51] preferred structures containing linked square-pyramidal $Co(CO)_4$ groups. The first possibility seems preferable in view of the known structures of $Co(CO)_4$ derivatives[47,48] and we suggest it also for $M_2(PF_3)_8$ (III). One would then have expected to see two sets of ^{19}F resonances in a 3:1 intensity ratio. The broadness of the two peaks at room temperature may be due to stereochemical nonrigidity, similar to that occurring in $Fe(CO)_5$, PF_5, and other five-coordinate compounds containing monodentate ligands.[53] Low-temperature ^{19}F nmr studies suggest that compounds such as (butadiene)$Fe(PF_3)_3$[54] and $CF_3Co(CO)_3(PF_3)$[55] are fluxional, and we are currently examining the variable-temperature ^{19}F nmr spectra of all the five-coordinate complexes prepared in this work.



III, M = Rh o Ir

It is worth noting that, whereas PF_3 forms $M_2(PF_3)_8$ and $HM(PF_3)_4$ (M = Co, Rh, or Ir), there is no evidence for the existence of $M_2(CO)_8$ and $HM(CO)_4$ (M = Rh or Ir) at atmospheric pressure,[56] though these compounds may exist in equilibrium with $M_4(CO)_{12}$ under high CO pressures.[57] The reduced tendency of PF_3 compared with CO to form polynuclear complexes is well illustrated by the behavior of $Rh_2(PF_3)_8$ on thermal decomposition. On heating to 170°, it evolves 2 mol of PF_3 per mole of dimer, giving a dark red, volatile crystalline solid which is more soluble in *n*-pentane than its precursor. Analytical data are consistent with the formula $Rh(PF_3)_3$, and the mass spectrum suggests that the molecule is trimeric, since the highest mass fragment observed is $Rh_3(PF_2)(PF_3)_8^+$. The ^{19}F nmr spectrum shows only two very broad resonances at room temperature, and the infrared spectrum (Table I) is identical with that of a deep red crystalline compound obtained by thermal decomposition of $HRh(PF_3)_4$.[15,18] At present we do not know whether the complex is $Rh_3(PF_2)(PF_3)_8$ or $Rh_3(PF_3)_9$, since compositions are not very different and the latter could easily lose F^- in the mass spectrometer. In contrast, thermal decomposition of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ gives $Co_4(CO)_{12}$ and $Rh_6(CO)_{16}$, respectively. $Ir_2(PF_3)_8$ is thermally stable up to 200°.

The reactions of $M_2(PF_3)_8$ with hydrogen and with group IV hydrides show interesting similarities and differences compared with the corresponding reactions of $Co_2(CO)_8$. The rhodium compound, both in solution and in the solid state, reacts instantaneously with hydrogen (25°, 1 atm) to give $HRh(PF_3)_4$. The reaction of the iridium compound in solution with hydrogen to give $HIr(PF_3)_4$ is very slow; only a weak peak at 2090 cm^{-1} due to ν(Ir–H) is detectable after 10 min. The hydrogenation of $M_2(PF_3)_8$ is irreversible, unlike that of $Co_2(CO)_8$.[58]

Silanes react rapidly at room temperature with $Co_2(CO)_8$ giving silylcobalt carbonyls according to the idealized equation[59]

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2$$

There is good evidence that this reaction proceeds in two steps involving $HCo(CO)_4$ as an intermediate[60,61]

$$Co_2(CO)_8 + R_3SiH \longrightarrow HCo(CO)_4 + R_3SiCo(CO)_4$$

$$HCo(CO)_4 + R_3SiH \longrightarrow R_3SiCo(CO)_4 + H_2$$

Triphenylsilane, $(C_6H_5)_3SiH$, and $Rh_2(PF_3)_8$ dissolved in *n*-hexane in a 1:1 mole ratio react to give $(C_6H_5)_3SiRh(PF_3)_4$ as a colorless crystalline solid which is unstable in solution and cannot be recrystallized

---

(49) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).
(50) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).
(51) G. Bor, *ibid.*, 2065 (1963).
(52) K. Noack, *Helv. Chim. Acta*, **47**, 1555 (1963).
(53) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 251 (1966); E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).
(54) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).
(55) C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, **91**, 526 (1969).
(56) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
(57) R. Whyman, *Chem. Commun.*, 1381 (1969); 1194 (1970).
(58) M. Orchin, L. Kirch, and I. Goldfarb, *J. Amer. Chem. Soc.*, **78**, 5450 (1956).
(59) A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 1133 (1965).
(60) A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1640 (1967).
(61) Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, **8**, 986 (1969).

without decomposition. The other reaction product is $HRh(PF_3)_4$ which has a characteristic infrared band at 1960 cm^{-1} due to ν(Rh–H). The course of the reaction is readily followed by measuring the rate of disappearance of the band due to ν(Si–H) in $(C_6H_5)_3SiH$ at 2140 cm^{-1} and the rate of appearance of the band at 1960 cm^{-1}. With both reactants initially 0.066 *M* (c_0), a good second-order rate plot [$(c_0/c) - 1$ *vs. t*, where *c* is the concentration of each reactant remaining after time *t*] is obtained up to 19 min, corresponding to about 30% reaction (k_2 = 3.79 l. mol^{-1} min^{-1}). Thereafter a large positive deviation appears in the second-order plot, and reaction is over after 43 min. In this subsequent period, a plot of *c vs. t* is practically linear; *i.e.*, the reaction is apparently zero order. The reaction of 0.0308 *M* triphenylsilane with 0.015 *M* $Rh_2(PF_3)_8$ also shows second-order behavior initially; thus, if *x* is the concentration of triphenylsilane reacted after time *t*, a plot of ln $[(c_0 - x)/(c_0 - 2x)]$ *vs. t* is linear up to about 3 min (k_2 = 8.5 l. mol^{-1} min^{-1}), but thereafter apparent zero-order behavior is again observed, and reaction is complete after about 8 min, when half the silane has reacted. There is no further reaction between $(C_6H_5)_3SiH$ and $HRh(PF_3)_4$ under the conditions used, in contrast with the corresponding $HCo(CO)_4$ reaction;[60,61] indeed, the reverse reaction of hydrogen (25°, 1 atm) with $(C_6H_5)_3SiRh(PF_3)_4$ to give $(C_6H_5)_3SiH$ and $HRh(PF_3)_4$ occurs quantitatively, as shown by the appearance of the characteristic infrared bands at 2140 and 1960 cm^{-1}, respectively. The reason for the deviation from second-order behavior in the reaction of $Rh_2(PF_3)_8$ with $(C_6H_5)_3SiH$ is not known, though it may be due to product decomposition in solution and a competing reaction $(C_6H_5)_3SiRh(PF_3)_4 + (C_6H_5)_3SiH \rightarrow (C_6H_5)_3Si\text{–}Si(C_6H_5)_3 + HRh(PF_3)_4$. These factors may also account for the poor agreement between the two values of k_2.

The reaction of $Ir_2(PF_3)_8$ with triphenylsilane in *n*-hexane to give $(C_6H_5)_3SiIr(PF_3)_4$ occurs more slowly than the corresponding $Rh_2(PF_3)_8$ reaction, and the colorless, crystalline Ir–Si bonded complex is more stable than its rhodium analog. The appearance of an infrared band at 2090 cm^{-1} as reaction proceeds confirms that $HIr(PF_3)_4$ is also formed. With both reactants initially 0.033 *M*, a good second-order rate plot is obtained for about 2 hr, corresponding to 70% reaction (k_2 = 0.768 l. mol^{-1} min^{-1}). Reaction is complete after about 10 hr.

Both trichlorosilane and triethoxysilane react with $Rh_2(PF_3)_8$ to give $R_3SiRh(PF_3)_4$ (R = Cl or C_2H_5O) as volatile oils, although on a preparative scale we have been unable to separate the ethoxy derivative from unreacted triethoxysilane. The initial reactions are too rapid to follow by conventional techniques, but preliminary studies indicate that there is a slower second-stage reaction of these silanes with $HRh(PF_3)_4$ to give $R_3SiRh(PF_3)_4$ and hydrogen.

The reaction of triphenylgermane, $(C_6H_5)_3GeH$, with $Rh_2(PF_3)_8$ to give $(C_6H_5)_3GeRh(PF_3)_4$ and $HRh(PF_3)_4$ is also too rapid to follow by conventional techniques, and in contrast with the triphenylsilane case, there is a subsequent, relatively slow reaction of triphenylgermane with $HRh(PF_3)_4$ to give $(C_6H_5)_3GeRh(PF_3)_4$ and hydrogen. This second step can be followed by starting with $(C_6H_5)_3GeH$ and $Rh_2(PF_3)_8$ in a 2:1 mole ratio and after a few minutes monitoring the peaks at 1960 and 2055 cm^{-1} due to ν(Rh–H) and ν(Ge–H), respectively. With $HRh(PF_3)_4$ and $(C_6H_5)_3GeH$ initially 0.04 *M*, a good second-order rate plot is obtained for about 30 min, corresponding to ~35% reaction (k_2 = 0.41 l. mol^{-1} min^{-1}). Subsequent negative deviation in the plot of $(c_0/c) - 1$ *vs. t* is undoubtedly due to the reversibility of the reaction, which is only 60% complete after 4–6 hr at 30°. Indeed, hydrogen reacts with pure $(C_6H_5)_3GeRh(PF_3)_4$ in *n*-hexane to give detectable amounts of $(C_6H_5)_3GeH$ and $HRh(PF_3)_4$. Reversible hydrogenolysis of Pt–Ge bonds has also been observed.[62]

The reaction of $(C_6H_5)_3GeH$ with $Ir_2(PF_3)_8$ is, as expected, slower than that with $Rh_2(PF_3)_8$. The formation of the products $(C_6H_5)_3GeIr(PF_3)_4$ and $HIr(PF_3)_4$ is complete after 30 min, but there is no observable reaction of $(C_6H_5)_3GeH$ with $HIr(PF_3)_4$ in a period of 20 hr. Kinetic studies have not been attempted owing to the proximity of the infrared bands due to ν(Ge–H) and ν(Ir–H) at 2055 and 2090 cm^{-1}, respectively.

Although more work is obviously needed to clarify the kinetic behavior, it is clear that the rates of reaction of group IV hydrides with $M_2(PF_3)_8$ and $HM(PF_3)_4$ are in the order Ge > Si and Rh > Ir and that the rates increase with increasing electronegativity of the substituent on the group IV atom. A recent observation[21] that $(n\text{-}C_4H_9)_3SnH$ and $Rh_2(PF_3)_8$ react very rapidly at room temperature giving $(n\text{-}C_4H_9)_3SnRh(PF_3)_4$ and H_2 follows the expected trend. Our work also provides additional support for the two-step mechanism suggested for the hydrosilation of $Co_2(CO)_8$,[59–61] though $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ are clearly less reactive than $Co_2(CO)_8$.

Finally, we note an incomplete experimental finding which emphasizes the similarity of $M_2(PF_3)_8$ and $Co_2(CO)_8$. When $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ are sublimed *in vacuo* on to a Dry Ice cooled probe, very deep green and pale green crystalline sublimates, respectively, are obtained, which revert to the original dimers, together with some decomposition products, on warming to room temperature. The green products are not formed simply by cooling either $Rh_2(PF_3)_8$ or $Ir_2(PF_3)_8$ to Dry Ice or liquid nitrogen temperature. The formation of $Co(CO)_4$ radicals from $Co_2(CO)_8$ under similar experimental conditions has been reported,[63] so that the green sublimates may well contain the corresponding $M(PF_3)_4$ radicals, but attempts to obtain their esr spectra have so far been unsuccessful.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Ether and tetrahydrofuran were distilled from lithium aluminum hydride and stored over sodium–lead alloy. All other solvents used were dried over anhydrous calcium chloride. Trifluorophosphine was obtained commercially and was passed through Dry Ice traps before use.

Microanalyses (Table III) were carried out by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates), and by the Australian Microanalytical Service, Melbourne. Molecular weights were measured in ~0.02 *M* hexane solutions at 25° in a nitrogen atmosphere on a vapor pressure osmometer (Model 301A, Mechrolab). Melting

---

[62] F. Glockling and K. A. Hooton, *J. Chem. Soc. A*, 826 (1968).

[63] H. J. Keller and H. Wawersik, *Z. Naturforsch. B*, **20**, 938 (1965).

TABLE III

ANALYTICAL DATA, MELTING POINTS, AND COLORS[a]

Compound	Mp, °C	Color	% calcd					% found				
			C	H	X	F	P	C	H	X	F	P
$[RhCl(PF_3)_2]_2$[b]	67–68.5	Red	0.0	0.0	11.3	36.2	19.8	0.0	0.0	11.5	35.2	18.8
$[RhBr(PF_3)_2]_2$	62–63	Red	0.0	0.0	22.2	31.8	17.2	0.0	0.0	21.7	31.9	17.8
$[RhI(PF_3)_2]_2$	58–60	Red	0.0	0.0	31.1	28.1	15.3	0.0	0.0	28.7	25.4	15.7
$Rh(acac)(C_8H_{14})_2$	136–138	Orange-yellow	59.7	8.3	...	...	...	60.5	8.2	...	...	...
$Rh(acac)(PF_3)_2$[c]	75–77	Orange	15.9	1.8	0.0	30.2		16.2	2.3		29.5	
π-$C_5H_5Rh(PF_3)_2$	−8	Orange	17.5	1.5	0.0	33.2		18.2	1.7	0.0	32.2	
$[(CH_3)_4N][RhCl_2(PF_3)_2]$[d]	Nm	Pale yellow	11.3	2.8	16.7	24.9		12.1	3.1	17.5	26.3	
$[(C_6H_5)_4As][RhCl_2(PF_3)_2]$	Nm	Pale yellow	39.3	2.7	9.7	15.6		39.8	3.4	9.4	13.9	
$Rh_2(PF_3)_8$[e]	100 dec	Orange	...	...	0.0	50.2	27.2	...	...	<0.4	49.2	26.8
$Hg[Rh(PF_3)_4]_2$[f]	105–106	White	...	...	0.0	41.4	21.7	...	...	0.0	41.6	21.7
$Cl_3SiRh(PF_3)_4$	20–22.5	Yellow	0.0	0.0	18.0		21.0	0.0	0.0	17.3		20.4
$(C_6H_5)_3SiRh(PF_3)_4$[g]	105 dec	White	30.3	2.1		31.9	17.4	32.5	2.5		25.8	15.7
$(C_6H_5)_3GeRh(PF_3)_4$	105–108 dec	White	28.5	2.0	...	30.1	16.3	29.3	2.2		30.2	14.6
$(C_6H_5)_3SnRh(PF_3)_4$	100 dec	White	27.0	1.8	0.0	28.5		28.0	2.0	0.8	25.9	
$(C_6H_5)_3PAuRh(PF_3)_4$	158–159	White	23.7	1.7	0.0		17.0	24.1	1.7	0.0		16.8
$Rh_3(PF_3)_9$[h]	Nm	Red	...	...	...	46.6	25.3				46.3	25.6
$IrCl(PF_3)_4$[g]	32–35	Pale yellow	0.0	0.0	6.1	39.4	21.4	0.0	0.0	6.6	34.8	20.1
$[IrCl(PF_3)_2]_2$[i]	76–78	Dark blue	0.0	0.0	8.8	28.2		0.0	0.0	8.95	28.0	
$Ir(acac)(C_8H_{14})_2$	Nm	Yellow	49.3	6.8	...	...	...	48.8	6.7	...	...	
$IrCl(C_8H_{14})_2(PF_3)$[j]	106–109	Yellow	35.9	5.2	6.6	10.6	...	36.4	5.7	6.8	10.8	
$Ir(acac)(C_8H_{14})(PF_3)$	Nm	Yellow	31.9	4.3	0.0	11.6	...	32.4	4.8	0.0	11.5	
$Ir(acac)(PF_3)_2$	Nm	Orange	12.8	1.5	...	24.4	...	13.2	1.8	...	24.5	
$Ir_2(PF_3)_8$[k]	113–116	Yellow	...	...	0.0	41.6	22.6	...	...	<0.2	43.5	22.0
$Hg[Ir(PF_3)_4]_2$[l]	111–113	White	0.0	0.0		35.4		<0.3	<0.3		34.6	
$(C_6H_5)_3SiIr(PF_3)_4$	98–101	White	26.9	1.7				27.2	2.7			
$(C_6H_5)_3SnIr(PF_3)_4$	113–114	White	24.2	1.7		25.5		24.2	1.6		26.2	
$(C_6H_5)_3PbIr(PF_3)_4$	117–118	White	22.0	1.5	0.0	23.2	12.6	22.3	1.6	<0.2	22.2	12.6
$(C_6H_5)_3PAuIr(PF_3)_4$	161–162	White	21.5	1.5			15.4	21.8	1.6			13.9

[a] Abbreviations: X = Cl, Br, or I; nm, not measured. [b] Mol wt: calcd, 627; found, 684. [c] Mol wt: calcd, 422; found, 412. [d] Per cent N: calcd, 3.3; found, 3.6. [e] Mol wt: calcd, 910; found, 1510 (see text). [f] Per cent Hg: calcd, 18.0; found, 17.6. [g] Compound is unstable and decomposes on attempted recrystallization. [h] Calcd for $Rh_3(PF_2)(PF_3)_8$: F, 45.6; P, 25.8. [i] Mol wt: calcd, 807; found, 900. [j] Mol wt: calcd, 536; found, 550. [k] Mol wt: calcd, 1098; found, 1330. [l] Mol wt: calcd, 1289; found, 1437. Per cent Hg: calcd, 15.6; found, 15.5.

points were measured on a Gallenkamp melting point apparatus, the samples having been sealed under nitrogen. Mass spectra were measured on an AEI MS9 instrument by Mr. K. W. Goggin, the solid samples being introduced directly. Infrared spectra were recorded on a Perkin-Elmer 457 instrument which was calibrated in the ν(P–F) region by reference to the spectrum of gaseous NH_3.[64] Proton nmr spectra were measured at 100 MHz on a Varian HA-100 instrument using TMS as internal reference, and ^{19}F nmr spectra were recorded at 56.45 MHz on a JEOL C60 HL instrument using $CFCl_3$ as internal reference (Dr. R. Bramley and Mr. C. Arandjelovic).

Di-μ-chloro-tetrakis(trifluorophosphine)dirhodium(I), $[RhCl(PF_3)_2]_2$.—Trifluorophosphine (PF_3) was bubbled into a stirred suspension of $[RhCl(C_8H_{14})_2]_2$[20] (3.0 g, 8.4 mmol) in 50 ml of *n*-pentane at room temperature. When all the starting material had dissolved (about 20 min), the solution was filtered and evaporated to about 10 ml in a stream of nitrogen. The solution was cooled slowly to −80°, and the dark red needles were recrystallized from *n*-pentane at −80° to give 2.30 g (88%) of product.

Di-μ-bromo-tetrakis(trifluorophosphine)dirhodium(I), $[RhBr(PF_3)_2]_2$.—A solution of $[RhCl(PF_3)_2]_2$ (0.42 g, 0.67 mmol) in 20 ml of diethyl ether was stirred at room temperature with anhydrous lithium bromide (0.5 g, 5.7 mmol) for 2 hr. The solution was evaporated to dryness and extracted with 20 ml of *n*-pentane. The extract was evaporated to a few milliliters and cooled to −80°, giving 0.4 g (83%) of dark red crystals of product, which were recrystallized from *n*-pentane at −80°.

Di-μ-iodo-tetrakis(trifluorophosphine)dirhodium(I), $[RhI(PF_3)_2]_2$.—Sodium iodide (1.0 g, 6.7 mmol) was added to a solution of $[RhCl(PF_3)_2]_2$ (0.60 g, 0.96 mmol) in 15 ml of diethyl ether which had been cooled to −20°. After the solution had been stirred for 30 min, it was evaporated to dryness and the residue was extracted with 20 ml of *n*-pentane. The extract was evaporated to a few milliliters and cooled to −80° to give a 76% yield of dark red crystals, which were purified by recrystallization from *n*-pentane.

Tetramethylammonium Dichlorobis(trifluorophosphine)rhodate(I), $[(CH_3)_4N][RhCl_2(PF_3)_2]$.—A solution of $[RhCl(PF_3)_2]_2$ (0.10 g, 0.16 mmol) in 5 ml of dichloromethane was stirred at room temperature with tetramethylammonium chloride (0.1 g, excess) for 15 min. The solution was filtered, evaporated to dryness, and washed with 10 ml of *n*-pentane. The residue was recrystallized from dichloromethane by cautious addition of *n*-pentane to give a 59% yield of yellow crystals.

Tetraphenylarsonium Dichlorobis(trifluorophosphine)rhodate(I), $[(C_6H_5)_4As][RhCl_2(PF_3)_2]$.—A mixture of $[RhCl(PF_3)_2]_2$ (0.15 g, 0.24 mmol) and tetraphenylarsonium chloride (0.20 g, 0.48 mmol) in 10 ml of dichloromethane was stirred at room temperature for 10 min and then evaporated to dryness under reduced pressure. The residual oil was redissolved in ~50 ml of dichloromethane and *n*-pentane was added slowly. The initially deposited brown solid was centrifuged off and *n*-pentane was added to the supernatant liquid. Cooling to −20° gave yellow-brown crystals, which were recrystallized from dichloromethane–pentane to give a 36% yield of yellow crystals.

2,4-Pentanedionatobis(cyclooctene)rhodium(I), $Rh(acac)(C_8H_{14})_2$.—A suspension of $[RhCl(C_8H_{14})_2]_2$ (0.36 g, 1.0 mmol) in THF (10 ml) was treated with a solution of Tl(acac) 0.36 g, 1.19 mmol). After stirring for 5 min at room temperature, the solution was centrifuged and evaporated to dryness under reduced pressure. The residue was extracted with two 10-ml portions of *n*-pentane, evaporated to ~2 ml, and cooled to −20°. The solid was recrystallized from *n*-pentane to give the product (0.31 g, 71%) as orange-yellow needles.

2,4-Pentanedionatobis(trifluorophosphine)rhodium(I), $Rh(acac)(PF_3)_2$.—(i) A solution of $[RhCl(PF_3)_2]_2$ (0.10 g, 0.16 mmol) in 10 ml of tetrahydrofuran was stirred at room temperature with Tl(acac) (0.12 g, 0.40 mmol) for 30 min. The solution was evaporated to dryness (0.1 mm) and the residue was extracted with three 5-ml portions of *n*-pentane. The extract was evaporated to a few milliliters and cooled to −80° to give an 80% yield of orange crystalline product, which was purified by recrystallization from *n*-pentane.

(ii) A solution of $Rh(acac)(C_8H_{14})_2$ (0.30 g, 0.71 mmol) in *n*-pentane was treated with a stream of PF_3 for 5 min. The solution was evaporated to small volume, centrifuged, and cooled to −80° to give orange crystals (0.23 g, 85%) which were recrystallized from *n*-pentane.

---

[64] International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, London, 1961, p 589.

π-Cyclopentadienylbis(trifluorophosphine)rhodium(I), π-$C_5H_5Rh(PF_3)_2$.—A solution of $[RhCl(PF_3)_2]_2$ (0.72 g, 1.15 mmol) in 20 ml of ether was stirred with TlC_5H_5 (1.2 g, excess) at room temperature for 30 min. Solvent was removed in a stream of nitrogen and the residue was extracted with three 20-ml portions of *n*-pentane. The extract was evaporated to ~5 ml and cooled to −80° to give impure crystals which melted on being allowed to warm to room temperature. The product was purified by sublimation at 25° (10^{-3} mm) onto a −80° probe and was an orange oil at room temperature (yield 58%).

Chlorotetrakis(trifluorophosphine)iridium(I), $IrCl(PF_3)_4$.—PF_3 was bubbled through a suspension of pure, dry $[IrCl(C_8H_{14})_2]_2$[22] (2.0 g, 1.12 mmol) in 25 ml of *n*-pentane which was stirred at room temperature. Reaction was complete when all the starting material had dissolved and the solution had turned yellow. It was then evaporated to ~10 ml in a stream of dry nitrogen, saturated with PF_3, and slowly cooled to −80°. The yellow crystals so formed were recrystallized twice from *n*-pentane by cooling to −80°, after the solution had been saturated with PF_3 (yield 75%).

If the reaction mixture was cooled to −80° and the product was recrystallized in the absence of PF_3, a different yellow crystalline substance was obtained. This was unstable and gave variable analytical data, but the presence of cyclooctene was indicated by the C and H figures and by the infrared spectrum. *Anal.* Calcd for $IrCl(C_8H_{14})(PF_3)_2$: C, 18.7; H, 2.7; Cl, 6.9; F, 22.1. Calcd for $IrCl(C_8H_{14})(PF_3)_3$: C, 16.0; H, 2.3; Cl, 5.9; F, 28.4. Found: C, 14.2, 14.0, 17.4; H, 2.4, 2.1, 2.7 (different preparations); Cl, 5.8; F, 25.9.

Di-μ-chloro-tetrakis(trifluorophosphine)diiridium(I), $[IrCl(PF_3)_2]_2$.—(i) A sample of $IrCl(PF_3)_4$, prepared as above, was sublimed at 25° (10^{-3} mm) onto a water-cooled probe. Material which did not condense was trapped at −80° and resublimed. The product was obtained in 40% yield as very dark blue crystals with a bright copper-colored reflection.

(ii) A solution of $IrCl(PF_3)_4$ (1.9 g, 3.28 mmol) in 20 ml of *n*-hexane was heated under reflux for 1.5 hr in a slow stream of nitrogen. The solution was evaporated to ~5 ml and cooled to −80° to give dark blue crystals, which were purified either by sublimation or by recrystallization from *n*-pentane at −80° (yield 65%).

Reaction of $[IrCl(PF_3)_2]_2$ with PF_3 to Give $IrCl(PF_3)_4$.—Approximately 0.05–0.10 g of $[IrCl(PF_3)_2]_2$ was introduced into a weighed 100-ml flask, which was then evacuated and cooled to −80°. After warming to room temperature, about 400 mm of pure PF_3 was added, and the flask was alternately cooled in liquid nitrogen and warmed to 0° two or three times. The dark blue crystals turned yellow. After cooling to −80°, excess PF_3 was pumped off; the flask was allowed to come to room temperature and was reweighed. For 0.07114 g of $[IrCl(PF_3)_2]_2$, the weight increase was 0.0330 g (calcd for 4 mol of PF_3 reacting with 1 mol of $[IrCl(PF_3)_2]_2$ giving 2 mol of $IrCl(PF_3)_4$: 0.0310 g). In a duplicate experiment using 0.05022 g of $[IrCl(PF_3)_2]_2$, the weight increase was 0.0219 g (calcd 0.0219 g).

Chlorobis(cyclooctene)(trifluorophosphine)iridium(I), $IrCl(C_8H_{14})_2(PF_3)$.—PF_3 was bubbled into a suspension of $[IrCl(C_8H_{14})_2]_2$ (0.40 g, 0.90 mmol) in 20 ml of *n*-pentane until a clear solution was obtained. This was then heated under reflux for 30 min with $[IrCl(C_8H_{14})_2]_2$ (0.80 g, 1.80 mmol). After removing unreacted $[IrCl(C_8H_{14})_2]_2$ by filtration, the solution was evaporated to ~10 ml and cooled to −80°, giving a yellow microcrystalline solid. More solid was obtained by further evaporation of the mother liquor and cooling to −80°. The product was recrystallized from *n*-pentane (yield 70%).

2,4-Pentanedionato(cyclooctene)(trifluorophosphine)iridium(I), $Ir(acac)(C_8H_{14})(PF_3)$.—A solution of $IrCl(C_8H_{14})_2(PF_3)$ (0.10 g, 0.19 mmol) in THF (25 ml) was stirred at room temperature with Tl(acac)(0.08 g, 0.26 mmol) for 15 min. The solution was centrifuged, evaporated to dryness, and extracted with three 5-ml portions of *n*-pentane. Yellow crystals were obtained by evaporating the solvent and cooling to −80° and were purified by slow crystallization from *n*-pentane.

2,4-Pentanedionatobis(trifluorophosphine)iridium(I), $Ir(acac)(PF_3)_2$.—A suspension of $[IrCl(C_8H_{14})_2]_2$ (0.46 g, 1.02 mmol) in 25 ml of THF was stirred at room temperature with Tl(acac) (0.46 g, 1.52 mmol) for 15 min. The solution was centrifuged and evaporated to dryness. Extraction of the residue with *n*-pentane and evaporation of the solution to dryness gave 0.46 g (88%) of $Ir(acac)(C_8H_{14})_2$. This was redissolved in *n*-pentane to give an orange solution and PF_3 was bubbled through until the color was very pale yellow. Evaporation to ~5 ml and cooling to −80° gave an 88% yield of orange crystals, which were purified by recrystallization from *n*-pentane.

Potassium Tetrakis(trifluorophosphine)rhodate(−I), $K[Rh(PF_3)_4]$.—A solution of $[RhCl(PF_3)_2]_2$ (2.2 g, 7.0 mmol) in 70 ml of diethyl ether was cooled to 0°, saturated with PF_3, and stirred with 1% potassium amalgam. PF_3 was passed into the solution during the reduction. After 1 hr the solution was allowed to warm to room temperature, stirred for a further 15 min, and evaporated to dryness in a stream of nitrogen. The residue was washed with *n*-pentane to give a 70% yield of colorless crystalline solid. If the ether used in this preparation is not freshly distilled from $LiAlH_4$, brown decomposition products tend to be formed.

Reduction of $[RhI(PF_3)_2]_2$ under the same conditions gave a 50% yield of $K[Rh(PF_3)_4]$.

Bis[tetrakis(trifluorophosphine)rhodium]mercury(II), $Hg[Rh(PF_3)_4]_2$.—(i) A solution of $[RhI(PF_3)_2]_2$ (0.30 g, 0.32 mmol) in ether was reduced with 1% potassium amalgam in the presence of PF_3 at 0° for 30 min, centrifuged, and evaporated to dryness. The residual white solid was recrystallized from *n*-pentane to give 0.13 g (35%) of colorless crystals.

(ii) A solution of $K[Rh(PF_3)_4]$ (0.20 g, 0.45 mmol) in 10 ml of ether was stirred at room temperature with mercuric chloride (0.06 g, 0.22 mmol) for 30 min. The solution was centrifuged and evaporated to dryness. The residue was recrystallized from *n*-pentane to give 0.17 g (76%) of product. An analytically pure sample was obtained after two recrystallizations from *n*-pentane.

Octakis(trifluorophosphine)dirhodium(0), $Rh_2(PF_3)_8$.—PF_3 was bubbled through a solution of $[RhCl(PF_3)_2]_2$ (0.29 g, 0.46 mmol) and $K[Rh(PF_3)_4]$ (0.51 g, 1.03 mmol) in 5 ml of ether for 10 min. After centrifuging to remove KCl and cooling to −80°, the orange solution deposited a mass of orange platelets. The mother liquor was evaporated to dryness in a stream of nitrogen and extracted with two 10-ml portions of *n*-pentane. Evaporation to dryness gave a more crude product. The combined solids were recrystallized from *n*-pentane at −80° giving 0.49 g (57%) of pure product.

Potassium Tetrakis(trifluorophosphine)iridate(−I), $K[Ir(PF_3)_4]$.—(i) A solution of $IrCl(PF_3)_4$ (1.0 g, 1.73 mmol) or an equivalent amount of $[IrCl(PF_3)_2]_2$ in 50 ml of ether was cooled to 0° and saturated with PF_3. About 200 g (excess) of 1% potassium amalgam was added, and the solution was stirred for 30 min at 0° and then for 3.5 hr at room temperature. Ether was removed at 0.1 mm and the white crystalline product was washed with *n*-pentane. Yields in different preparations varied from 30 to 65%, apparently depending on the purity of the $IrCl(PF_3)_4$ and on the dryness of the ether.

(ii) A solution of $Hg[Ir(PF_3)_4]_2$ (1.0 g) (see below) in 60 ml of ether was saturated with PF_3 and was reduced with potassium amalgam at room temperature for 3 hr. Evaporation of the filtered solution gave white crystals of the product in 80% yield.

Bis[tetrakis(trifluorophosphine)iridium]mercury(II), $Hg[Ir(PF_3)_4]_2$.—(i) A solution of $IrCl(PF_3)_4$ (1.5 g) in 80 ml of ether was stirred at 0° with excess 1% potassium amalgam for 15 min and then at room temperature for 30 min. The almost colorless solution was filtered and evaporated to dryness at 0.1 mm. The residue was recrystallized from *n*-pentane giving the white crystalline product in 35% yield.

(ii) A solution of $Ir_2(PF_3)_8$ (0.08 g, 0.07 mmol) (see below) was stirred with excess mercury for 2 days. Evaporation of the solution followed by recrystallization from *n*-pentane gave 0.02 g (20%) of product.

Octakis(trifluorophosphine)diiridium(0), $Ir_2(PF_3)_8$.—A solution of $K[Ir(PF_3)_4]$ (1.10 g, 1.89 mmol) in 50 ml of ether was treated with $IrCl(PF_3)_4$ (1.04 g, 1.80 mmol) in an atmosphere of PF_3, and the mixture was stirred at room temperature for 15 min. The solution was centrifuged to remove KCl and evaporated to dryness to give the crude yellow, crystalline product. It was purified by recrystallization from *n*-pentane (yield 73%).

Triphenylsilyltetrakis(trifluorophosphine)rhodium(−I), $(C_6H_5)_3SiRh(PF_3)_4$.—A mixture of $Rh_2(PF_3)_8$ (0.25 g, 0.27 mmol) and triphenylsilane (0.05 g, 0.19 mmol) in 10 ml of *n*-pentane was stirred at room temperature for 2 hr. The solution was evaporated to dryness and recrystallized from *n*-pentane to give an almost colorless solid. Owing to decomposition in solution, an analytically pure product could not be obtained.

Triphenylsilyltetrakis(trifluorophosphine)iridium(−I), $(C_6H_5)_3SiIr(PF_3)_4$.—A mixture of $Ir_2(PF_3)_8$ (0.10 g, 0.09 mmol) and triphenylsilane (0.05 g, 0.19 mmol) was heated in a nitrogen atmosphere at 125° for 1 hr. After cooling to room temperature, the crude product was recrystallized from *n*-pentane. The yield was 0.03 g (20%).

Trichlorosilyltetrakis(trifluorophosphine)rhodium(−I), $Cl_3SiRh(PF_3)_4$.—A solution of $Rh_2(PF_3)_8$ (0.30 g, 0.33 mmol) in 10 ml of *n*-pentane was stirred with trichlorosilane (0.09 g, 0.66 mmol) at room temperature for 20 hr. The solution was evaporated in a stream of nitrogen, and the residual oil was sublimed twice at 25° (10^{-3} mm) onto a −80° cold finger. A yield of 0.25 g (64%) of pale yellow liquid was obtained. It turned red reversibly below −50°.

Triethoxysilyltetrakis(trifluorophosphine)rhodium(−I), $(C_2H_5O)_3SiRh(PF_3)_4$.—A solution of $Rh_2(PF_3)_8$ (0.55 mmol) in 10 ml of *n*-pentane was stirred at room temperature and a solution of triethoxysilane (0.18 g, 1.10 mmol) in 10 ml of *n*-pentane was added slowly. The course of the reaction was monitored by infrared spectroscopy (see below) in an effort to avoid the presence of excess triethoxysilane, and addition was stopped when there was still some $HRh(PF_3)_4$ in the solution. After being stirred for 30 min at room temperature, *n*-pentane was removed in a stream of nitrogen. The dark oily residue was sublimed at 25° (10^{-3} mm) onto a −80° probe to give white crystals which melted at $\sim -20°$ to a yellow liquid. Analytical data suggested that the product was contaminated with triethoxysilane, but it could not be purified further.

Triphenylgermyltetrakis(trifluorophosphine)rhodium(−I), $(C_6H_5)_3GeRh(PF_3)_4$.—This was prepared similarly to $(C_6H_5)_3SiRh(PF_3)_4$, from $Rh_2(PF_3)_8$ (0.2 g, 0.22 mmol) and triphenylgermane (0.13 g, 0.43 mmol) in 5 ml of *n*-pentane for 24 hr. The yield was 0.24 g (73%) after one recrystallization from *n*-pentane at −80°. Though more stable than $(C_6H_5)_3SiRh(PF_3)_4$, the compound decomposes slowly in solution.

Triphenylstannyltetrakis(trifluorophosphine)rhodium(−I), $(C_6H_5)_3SnRh(PF_3)_4$.—A solution of $K[Rh(PF_3)_4]$ (0.20 g, 0.40 mmol) in 10 ml of ether was treated with triphenyltin chloride (0.16 g, 0.42 mmol) and the mixture was stirred at room temperature for 10 min. The solvent was removed at 15 mm and the residue was extracted with 20 ml of *n*-pentane. The extract was evaporated to ~0.5 ml and cooled to −78°, yielding 0.18 g (55%) of crude product, which was purified by another crystallization from *n*-pentane at −78°.

The following were prepared similarly: $(C_6H_5)_3SnIr(PF_3)_4$, from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3SnCl$ (yield 57%); $(C_6H_5)_3PbIr(PF_3)_4$ from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3PbCl$ (yield 80%); $(C_6H_5)_3PAuRh(PF_3)_4$ from $K[Rh(PF_3)_4]$ and $(C_6H_5)_3PAuCl$ (yield 60%); $(C_6H_5)_3PAuIr(PF_3)_4$ from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3PAuCl$ (yield 50%, after three recrystallizations from *n*-pentane at −80°).

Kinetics.—The kinetics of the reactions of triphenylsilane and triphenylgermane with $M_2(PF_3)_8$ in *n*-hexane were studied by mixing known concentrations of the reactants (~0.03–0.07 *M*) and transferring the solution rapidly to a 1-mm path length infrared liquid cell with KBr windows. The peak heights of the bands due to ν(Si–H) at 2140 cm^{-1}, ν(Ge–H) at 2055 cm^{-1}, ν(Rh–H) at 1960 cm^{-1}, and ν(Ir–H) at 2090 cm^{-1} were then followed as a function of time using the PE 457 spectrometer; the cell temperature was 30°. The peak heights were converted to concentrations by means of calibration curves obtained from standard solutions of the compounds.

Acknowledgments.—We thank the National Research Council of Canada for the award of a postdoctoral fellowship to D. J. P. and the Johnson Matthey Co. for its generous loan of rhodium and iridium salts. We also thank Dr. R. Bramley for helpful discussions of the ^{19}F nmr spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

Charge-Transfer Spectra of Ruthenium(II) Complexes

BY A. M. ZWICKEL* AND CAROL CREUTZ

Received March 9, 1970

The charge-transfer spectra of four series of ruthenium(II) complexes—$(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2{}^{2+}$, where L represents a nitrogen heterocycle—have been analyzed. The molecular orbital parameters thus obtained allow back-bonding, metal to ligand, in these compounds to be quantitatively assessed.

Ford, Rudd, Gaunder, and Taube[1] have reported the syntheses and spectra of pentaammineruthenium(II) complexes containing aromatic nitrogen heterocycles such as pyridine and pyrazine. They found that, in addition to essentially unperturbed internal ligand transitions at *ca.* 40 kK (250 nm), these compounds shown an intense (ϵ *ca.* 10^4) band at roughly 20 kK (400–500 nm). This band, analogous to Jørgensen's iridium–pyridine bands,[2] was assigned to metal–ligand charge transfer.

They reported[1] that the basicity of the pyrazine complex is some 2 powers of 10 greater than that of free ligand, thus proving that back-bonding, metal to π^*, is significant in these species. The charge-transfer band gives information about the states involved in this interaction, and it is therefore of interest to evaluate the relevant molecular orbital parameters.

To do so, we analyze the spectra of the complexes $(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2{}^{2+}$, where L represents a nitrogen heterocycle—pyridine, isonicotinamide, methyl isonicotinate, or pyrazine. This series allows us to evaluate semiempirically the various interactions without recourse to assumed matrix elements. We shall proceed to show, first, that symmetry and/or overlap arguments exclude all but one metal 5d orbital and one π^* ligand orbital from consideration and, next, that a simple molecular orbital treatment using only these states can give semiquantitative agreement with experiment (each of our four series of compounds has four spectral bands, two of which serve to fix our two parameters leaving two bands as tests) We then show that one additional small interaction parameter for all compounds suffices to bring all the data into agreement. Using these parameters, we compute back-bonding energies.

Experimental Section

***cis*-$(NH_3)_4(NC_4H_4N)_2{}^{2+}$, *trans*-$(NH_3)_4Ru(NC_5H_4CO_2CH_3)_2{}^{2+}$, and *trans*-$(NH_3)_4Ru(NC_5H_4CONH_2)_2{}^{2+}$.**—These ions were pre-

---

* Address correspondence to this author at Clark University, Worcester, Mass. 01610, from which he is on sabbatical leave.

(1) P. Ford, D F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

(2) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1966 (1957).