SOME TETRANUCLEAR CARBONYL COMPLEXES OF COBALT, RHODIUM AND IRIDIUM CONTAINING TRIFLUOROPHOSPHINE *

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Summary

Syntheses of $Co_2Rh_2(CO)_8(PF_3)_4$ and $Co_2Rh_2(CO)_{10}(PF_3)_2$ are described and their structures are discussed. Evidence is presented for an intermolecular ligand exchange between several tetranuclear cluster complexes. ^{19}F and ^{31}P NMR and mass spectroscopic data are presented and discussed. The complexes $Rh_4(CO)_4$-$(PF_3)_8$ and $Co_2Ir_2(CO)_8(PF_3)_4$ have been identified by their mass spectra.

Introduction

In recent years there has been increasing interest in the study of complexes containing clusters of metal atoms [1—11]. In complexes involving polynuclear metal carbonyls major advances have been made largely because of the application of mass spectrometry and X-ray crystallography while the use of ^{13}C NMR spectroscopy has proved important for studying dynamic behaviour in solution.

In view of the close similarity of trifluorophosphine and carbon monoxide as ligands towards transition metals [12,13] it was of interest to synthesize and study some trifluorophosphine derivatives of tetranuclear metal carbonyls of the type $Rh_4(CO)_{12}$ and $Co_nM_{4-n}(CO)_{12}$ (M = Rh, n = 2, 3; M = Ir, n = 2) and it was hoped that the presence of the ^{19}F and ^{31}P nuclei (both $I = 1/2$, 100% natural abundance) would facilitate structural studies in solution.

At the start of this work no tetranuclear metal complexes containing trifluorophosphine were known. Bennett [14] has reported a dark-red complex formulated as the trinuclear species $Rh_3(PF_2)(PF_3)_8$ or $Rh_3(PF_3)_9$ on the basis of mass spectral data, but the elemental analyses are also consistent with a tetrameric compound $[Rh(PF_3)_3]_4$ which seems more likely in view of the existence of the analogous carbonyl complex. The only other polynuclear metal

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* No reprints available.

complexes containing PF_3 known prior to this work were $Ru_3(PF_3)_n(CO)_{12-n}$ [15] and $PIr_3(PF_3)_9$ [16].

Results and discussion

The tetrasubstituted carbonyltrifluorophosphine complex $Co_2Rh_2(CO)_8(PF_3)_4$ (I), is made using a route similar to that described by Chini et al. [17] for $Co_2Rh_2(CO)_{12}$ by mixing hexane solutions of $[RhCl(PF_3)_2]_2$ [18] and $Co_2(CO)_8$ at room temperature.

$$2[RhCl(PF_3)_2]_2 + 3Co_2(CO)_8 \xrightarrow{\text{hexane}}{\text{RT}} 2Co_2Rh_2(CO)_8(PF_3)_4 + 2CoCl_2 + 8CO$$

(I)

An improved synthesis of I giving up to 80% yields involves treatment of solutions of $[RhCl(PF_3)_2]_2$ with $Tl[Co(CO)_4]$ [19] at room temperature.

$$[RhCl(PF_3)_2]_2 + 2Tl[Co(CO)_4] \xrightarrow{\text{toluene}}{\text{RT}} Co_2Rh_2(CO)_8(PF_3)_4 + 2TlCl$$
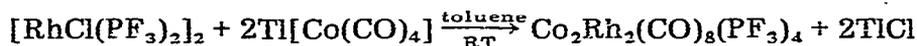
(I)

The bis(trifluorophosphine) compound, $Co_2Rh_2(CO)_{10}(PF_3)_2$ (II), is obtained in a similar way from the reaction of the dinuclear carbonyltrifluorophosphine-chlororhodium complex $[RhCl(CO)(PF_3)]_2$ [20] with $Tl[Co(CO)_4]$.

Both I and II, which are deep brown in colour, are reasonably air stable in the solid state and dissolve in all common organic solvents to give deep red-brown solutions but for long periods are best stored as solids under dinitrogen. Interestingly, complex II is also readily obtained simply by mixing pentane solutions of $Co_2Rh_2(CO)_{12}$ with I at room temperature (vide infra) (eq. 1). This reaction

$$Co_2Rh_2(CO)_{12} + Co_2Rh_2(CO)_8(PF_3)_4 \rightarrow 2Co_2Rh_2(CO)_{10}(PF_3)_2 \qquad (1)$$

(I)   (II)

indicates that a ready intermolecular ligand exchange process is occurring and this appears to be the first observation of this type of behaviour in this class of metal cluster complexes.

A similar intermolecular ligand exchange process between CO and PF_3 has been reported [20] in the dinuclear complexes $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$ while very recently the hetero-bimetallic system $PtPdCl_2L_4$ (L = PBu_3) has been obtained by mixing together $[PtCl_2L]_2$ and $[PdCl_2L]_2$ complexes [21]. Heterobimetallic phosphine complexes containing rhodium(III) and ruthenium-(II) linked by triple chloro bridges have also been reported recently [22].

Although the tetranuclear nature of compounds I and II was confirmed by their mass spectra and satisfactory elemental analytical data were obtained, the mass spectrum of II also revealed the presence of a very small amount of I. The main peaks in the mass spectra of I and II are listed in Fig. 1 and 2 which show the fragmentation patterns. Estimation of the relative peak heights is complicated by the presence of small amounts of impurities which have similar fragmentation patterns.

Co₂Rh₂(CO)₉(PF₃)₄ fragmentation chart:

$Co_2Rh_2(CO)_9(PF_3)_4$
(900)

—CO, —PF₃

$Co_2Rh_2(CO)_8(PF_3)_3^+$ (812) ⟶ $Co_2Rh_2(CO)_8(PF_3)_2^+$ (724)

$Co_2Rh_2(CO)_7(PF_3)_4^+$ (872) ⟶ $Co_2Rh_2(CO)_7(PF_3)_3^+$ (784) ⟶ $Co_2Rh_2(CO)_7(PF_3)_2^+$ (696) ⟶ $Co_2Rh_2(CO)_7(PF_3)^+$ (608)

$Co_2Rh_2(CO)_6(PF_3)_4^+$ (844) ⟶ $Co_2Rh_2(CO)_6(PF_3)_3^+$ (756) ⟶ $Co_2Rh_2(CO)_6(PF_3)_2^+$ (668) ⟶ $Co_2Rh_2(CO)_6(PF_3)^+$ (580)

$Co_2Rh_2(CO)_5(PF_3)_4^+$ (816) ⟶ $Co_2Rh_2(CO)_5(PF_3)_3^+$ (728) ⟶ $Co_2Rh_2(CO)_5(PF_3)_2^+$ (640) ⟶ $Co_2Rh_2(CO)_5(PF_3)^+$ (552) ⟶ $Co_2Rh_2(CO)_5^+$ (464)

$Co_2Rh_2(CO)_4(PF_3)_4^+$ (788) ⟶ $Co_2Rh_2(CO)_4(PF_3)_3^+$ (700) ⟶ $Co_2Rh_2(CO)_4(PF_3)_2^+$ (612) ⟶ $Co_2Rh_2(CO)_4(PF_3)^+$ (524) ⟶ $Co_2Rh_2(CO)_4^+$ (436)

$Co_2Rh_2(CO)_3(PF_3)_4^+$ (760) ⟶ $Co_2Rh_2(CO)_3(PF_3)_3^+$ (672) ⟶ $Co_2Rh_2(CO)_3(PF_3)_2^+$ (584) ⟶ $Co_2Rh_2(CO)_3(PF_3)^+$ (496) ⟶ $Co_2Rh_2(CO)_3^+$ (408)

$Co_2Rh_2(CO)_2(PF_3)_4^+$ (732) ⟶ $Co_2Rh_2(CO)_2(PF_3)_3^+$ (644) ⟶ $Co_2Rh_2(CO)_2(PF_3)_2^+$ (556) ⟶ $Co_2Rh_2(CO)_2(PF_3)^+$ (468) ⟶ $Co_2Rh_2(CO)_2^+$ (380)

$Co_2Rh_2(CO)(PF_3)_4^+$ (704) ⟶ $Co_2Rh_2(CO)(PF_3)_3^+$ (616) ⟶ $Co_2Rh_2(CO)(PF_3)_2^+$ (528) ⟶ $Co_2Rh_2(CO)(PF_3)^+$ (440) ⟶ $Co_2Rh_2(CO)^+$ (352)

$Co_2Rh_2(PF_3)_4^+$ (676) ⟶ $Co_2Rh_2(PF_3)_3^+$ (588) ⟶ $Co_2Rh_2(PF_3)_2^+$ (500) ⟶ $Co_2Rh_2(PF_3)^+$ (412) ⟶ $Co_2Rh_2^+$ (324)

$CoRh_2^+$ (265) Co_2Rh^+ (221)

$CoRh^+$ (162)

Rh^+ (103) Co^+ (59)

Fig. 1. Mass spectroscopic fragmentation pattern of $Co_2Rh_2(CO)_8(PF_3)_4$ (I) (m/e values listed in parentheses).

The mass spectra for both I and II exhibit parent ions as expected by analogy with related carbonyl and trifluorophosphine complexes [20,23,24] the fragmentation patterns correspond to successive loss of both PF_3 and CO ligands fol-
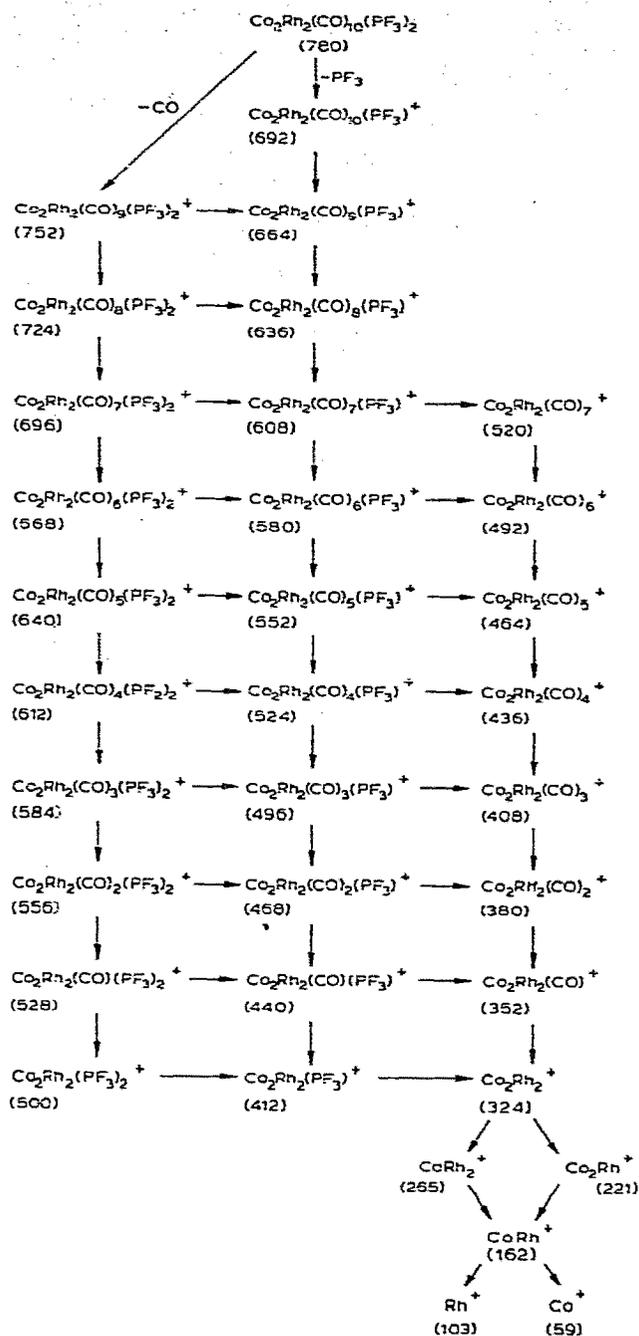
Fig. 2. Mass spectroscopic fragmentation pattern of Co$_2$Rh$_2$(CO)$_{10}$(PF$_3$)$_2$ (II) (m/e values listed in parentheses).

lowed by the ultimate breakdown of the Co$_2$Rh$_2$ cluster to give Co$_2$Rh$^+$, Co$_2$Rh$^+$, CoRh$^+$, Rh$^+$, and Co$^+$ ions.

Some very weak peaks corresponding to the presence of the compounds

$CoRh_3(CO)_4(PF_3)_8$ and $Co_3Rh(CO)_{12}$ detected in the spectrum of I probably arise via a redistribution process (eq. 2), which is similar to observations made

$$2Co_2Rh_2(CO)_8(PF_3)_4 \rightarrow CoRh_3(CO)_4(PF_3)_8 + Co_3Rh(CO)_{12} \qquad (2)$$

by Chini et al. [17] on $Co_2Rh_2(CO)_{12}$. The presence of $Co_2Rh_2(CO)_9(PF_3)_3$ and $Co_2Rh_2(CO)_{11}(PF_3)$ in II can be attributed to small amounts of $Rh_2Cl_2(CO)_3$-(PF_3) and $Rh_2Cl_2(CO)(PF_3)_3$ which were shown by Nixon and Swain to be present in equilibrium with the starting complex $[RhCl(CO)(PF_3)]_2$ [20].

In view of the methods of synthesis it seems likely that the structures of I and II are based on that of the parent complex $Co_2Rh_2(CO)_{12}$ in which some or all of the axial and equatorial carbonyl groups attached to the basal rhodium atoms have been replaced by PF_3 ligands (see Fig. 3) and the three bridging carbonyl groups in the basal plane are retained. This type of structure is widely found in mono-, di-, tri- and tetra-substituted tertiary phosphine complexes of other $M_4(CO)_{12}$ tetranuclear carbonyl compounds (M = Co, Rh, Ir) [25—37].

Poilblanc and Labroue [25] have discussed the IR spectra in the carbonyl region of complexes of the type $Co_4(CO)_{12-n}L_n$ (L = tertiary phosphine, tertiary phosphite). In the parent carbonyl complex eight IR active carbonyl stretching bands are predicted. In the terminal region the C≡O stretching frequencies transform as $3A_1 + 3E$ while the bridging CO modes transform as $A_1 + E$. On substitution of one or more of the terminal CO ligands the E mode of the bridging

Fig. 3. Structure of $Co_2Rh_2(CO)_{12}$ and proposed structures of I and II.

Fig. 4. Infrared spectra in the ν(CO) terminal (A), bridging (B) and P—F (C) stretching regions of $Co_2Rh_2(CO)_8(PF_3)_4$ (i), $Co_2Rh_2(CO)_{10}(PF_3)_2$ (ii) and $CO_2Rh_2(CO)_{12}$ (iii).

Fig. 5. ^{19}F NMR spectrum (at 94.1 MHz) of $Co_2Rh_2(CO)_8(PF_3)_4$ (I) at room temperature (a) and —40°C (b) in CD_2Cl_2 solution.

carbonyl groups splits as a consequence of the lifting of the degeneracy and three bands are observed. The stretching frequencies of both bridging and terminal CO ligands in $Co_4(CO)_{12-n}L_n$ are known to decrease as n increases, the effect being most pronounced for tertiary phosphine compounds. The IR spectra of mono-, di-, and tri-substituted complexes which had been rigorously purified by chromatography exhibited more carbonyl bands than expected, indicating the presence of mixtures of isomers [25].

The IR spectra of I and II in the carbonyl and P—F stretching frequency regions are shown in Fig. 4, which also contains the spectrum of $Co_2Rh_2(CO)_{12}$ for comparison. In the latter because of the presence of two different metals three bands are observed in the bridging carbonyl region and 5 bands can be assigned to terminal carbonyl stretching frequencies [17]. The same number of bridging carbonyl bands are expected for complex I and II and indeed are observed.

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF SOME TETRANUCLEAR CARBONYL COMPLEXES AND THEIR DERIVATIVES CONTAINING Co, Rh, AND Ir

Complex	ν(CO) terminal (cm^{-1})	ν(CO) bridging (cm^{-1})	Ref.
Rh$_4$(CO)$_{12}$ [a]	2089s(sh), 2079s, 2056s(sh), 2043(sh), 2035s, 1919m	1875s	32
Rh$_4$(CO)$_{10}$(PPh$_3$)$_2$ [b]	2069s, 2044s, 2018ms, 2021m, 2002m	1850mw, 1815mw	30
Rh$_4$(CO)$_8$(PPh$_3$)$_4$ [a]	2010m, 1995vs, 1990vs, 1971s, 1965(sh)	1793s, 1790s	29
Rh$_4$(CO)$_4$(PF$_3$)$_8$ [b]	2100w, 2089s, 2074s, 2058s	1929vw, 1880vs(br)	This work
Ir$_4$(CO)$_{10}$(PEt$_3$)$_2$ [c]	2064s, 2036s, 2012m, 2003s(br), 1984(sh)	1823m, 1786	46
Ir$_4$(CO)$_{10}$[P(OPh)$_3$]$_2$ [c]	2076s, 2051s, 2026s, 2012(sh)	1881vw, 1844m, 1826m	46
Ir$_4$(CO)$_8$[P(OPh)$_3$]$_4$ [d]	2054w(sh), 2032m, 2020(sh), 2002vs	1861w, 1806s	35
Co$_2$Rh$_2$(CO)$_{12}$ [e]	2074w, 2064s, 2059s, 2038m, 2030m	1920w, 1910(sh), 1885s, 1871s, 1855w	17
Co$_2$Rh$_2$(CO)$_{10}$(PF$_3$)$_2$ [e]	2104vw, 2096s, 2078(sh), 2070vs, 2062(sh), 2047s	1924w, 1889s, 1878s, 1863(sh)	This work
Co$_2$Rh$_2$(CO)$_8$(PF$_3$)$_4$ [e]	2070vs, 2062vw(sh), 2045s, 2035vw(sh)	1922m, 1887s, 1874s	This work
Co$_2$Ir$_2$(CO)$_{12}$ [e]	2072s, 2061s, 2055s, 2036-2033-2030m	1885w, 1867(sh), 1865s	17
Co$_2$Ir$_2$(CO)$_8$(PF$_3$)$_4$	2090w, 2075s(sh), 2068s, 2044m, 2035(sh), 2018mw	1865s(br), 1872s(br)	This work

[a] Nujol mull. [b] Hexane. [c] Cyclohexane. [d] Chloroform. [e] n-Pentane.

TABLE 2

^{19}F AND ^{31}P NMR CHEMICAL SHIFT AND COUPLING CONSTANT DATA FOR $Co_2Rh_2(CO)_{12-n}(PF_3)_n$ COMPLEXES ($n = 2, 4$)

Complex	Temperature (°C)	$\phi(F)$ [a,b]	$\delta(P)$ [c]	$^1J(PF)$ [d]
$Co_2Rh_2(CO)_8(PF_3)_4$	25	10.3	18.2 [e]	1410
(I)		13.8	29.8	1465
	30 [f]	—	18.2 [g]	—
			29.8	
	90 [f]	—	24.0 [g]	—
$Co_2Rh_2(CO)_{10}(PF_3)_2$ (II) [h]	25	11.9	26.9 [e]	1459
AA'		10.5	—	1416
BB'		13.0	—	1455
DD'		13.6	—	1461
II	−30, −40	12.3	—	1446
AA'		10.5	—	1416
BB'		11.5	—	1431
DD'		13.6	—	1460
EE'		14.7	—	1460

[a] ppm upfield from $CFCl_3$. [b] Dichloromethane solutions. [c] ppm upfield from TMP. [d] Hz. [e] n-Pentane solution. [f] Fluorine decoupled. [g] Toluene solution. [h] Values quoted are independent of synthetic route (see text).

Since it is known that PF_3 and CO have very similar bonding characteristics [12,38,39] (e.g. mass spectroscopic studies [40] show that the $M - CO$ and $M - PF_3$ bond energies are equal and C≡O stretching constants in mixed PF_3—CO complexes are relatively unchanged) frequencies of the terminal and bridging C≡O vibrations in I and II should lie closer to those of $Co_2Rh_2(CO)_{12}$ than other tertiary phosphine compounds of the homonuclear tetra-atomic complexes. Because of the differing symmetries of the complexes a strict comparison of bridging carbonyl group stretching frequencies cannot be made, but inspection of the data in Table 1 for a variety of phosphine-substituted tetranuclear complexes of cobalt, rhodium and iridium shows that substitution of CO by alkyl- or aryl-phosphines invariably leads to greater lowering of the C≡O stretching frequencies of bridging carbonyl ligands than the less basic phosphite ligands. Trifluorophosphine containing complexes on the other hand have the highest C≡O stretching modes which often differ little from the parent carbonyl complex.

Support for the proposed structure of I also comes from ^{19}F and ^{31}P NMR studies. The room temperature ^{19}F NMR spectrum of I (Fig. 5a) shows two widely spaced doublets ($^1J(PF)$) of roughly equal intensity suggesting two distinct equatorial and axial trifluorophosphine environments. Chemical shift and coupling constant data are listed in Table 2. The ^{19}F chemical shift difference between equatorial and axial ligands is 3.5 ppm while a difference of 47.0 ppm has been observed between the ^{13}C chemical shifts of equatorial and axial carbonyl groups in compound $Rh_4(CO)_{12}$ [41].

On cooling I to −40°C further fine structure is observed (Fig. 5b) and since the PF_3 group is unlikely to bridge, I seems likely to have a rigid structure as far as the PF_3 groups are concerned, although the carbonyl groups may be undergoing an exchange process at this temperature.
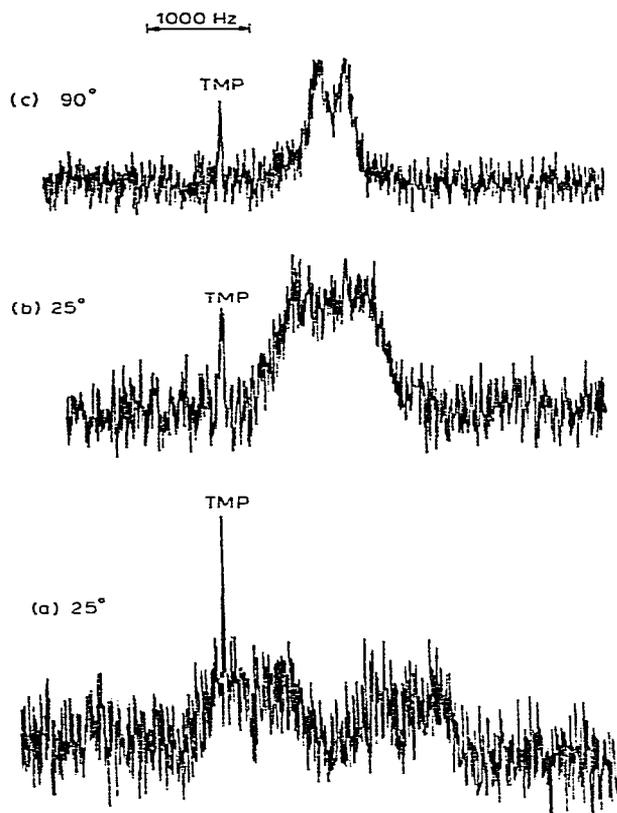
Fig. 6. ^{1}H decoupled ^{31}P NMR spectrum (at 40.49 MHz) of $Co_2Rh_2(CO)_8(PF_3)_4$ (I) in pentane solution (a); ^{19}F decoupled ^{31}P NMR spectrum at 25°C (b), and 90°C (c) in toluene solution.

The room temperature ^{31}P NMR spectrum of I (Fig. 6a) shows the expected two sets of overlapping broad 1/3/3/1 quartets (^1J(PF)) whose chemical shift difference is ~11.6 ppm, which is compatible with the proposed structure in which the PF$_3$ ligands are in two different environments. The coupling constant obtained from the ^{31}P NMR spectrum is in accord with the result obtained from the ^{19}F NMR spectrum (Table 2).

The fluorine decoupled ^{31}P NMR spectrum of I at room temperature exhibits two broad singlets as expected centred at the same position as the midpoint of the two quartets mentioned above (Fig. 6b). At higher temperatures the two singlets broaden and merge to give a doublet pattern at 90°C separated roughly by 270 Hz (Fig. 6c) whose magnitude suggests this could arise from coupling to rhodium. The sample of I was recovered unchanged on recooling to room temperature.

The variable temperature ^{19}F NMR spectra of II obtained from the two independent routes, mentioned earlier which are shown in Fig. 7 exhibit the same number of pairs of lines but the relative intensities are different in the two samples and also vary differently with temperature.

In the absence of complete intermolecular scrambling of PF$_3$ and CO ligands
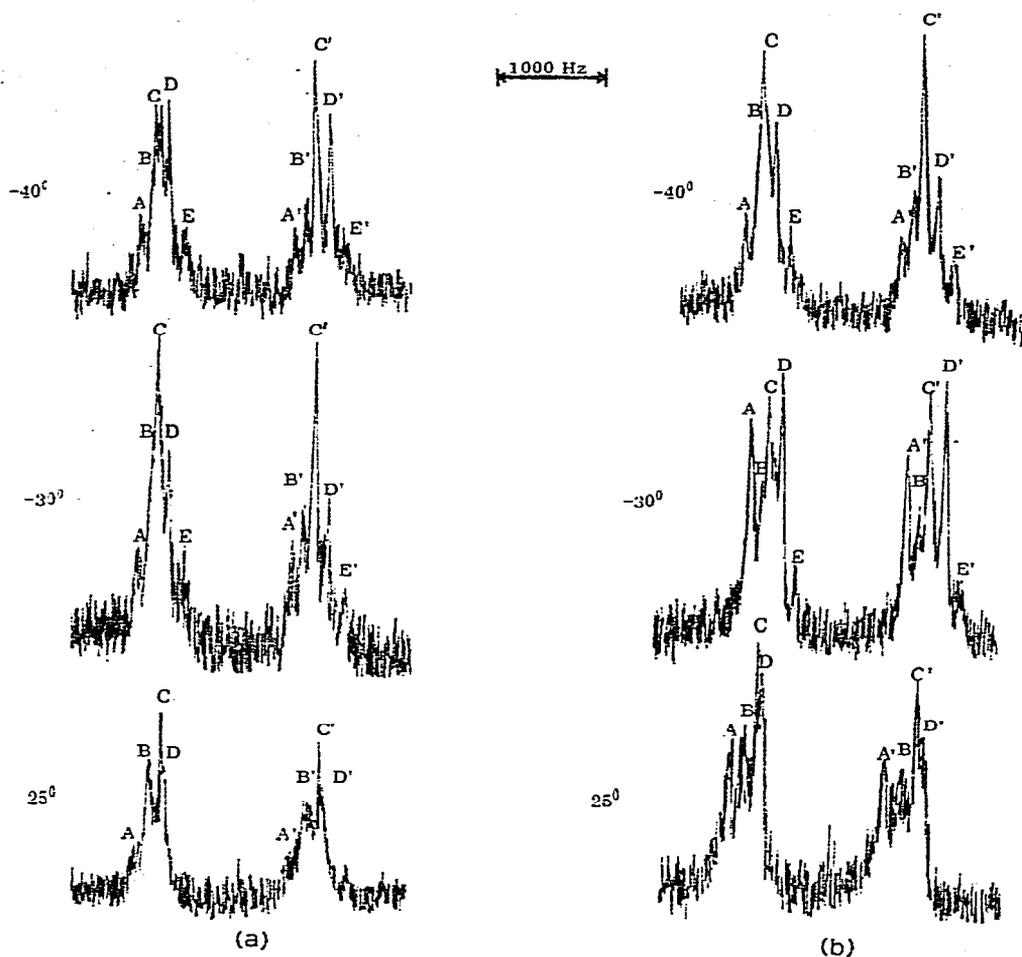
Fig. 7. ^{19}F NMR spectra (at 94.1 MHz) of $Co_2Rh_2(CO)_{10}(PF_3)_2$ (II) obtained from $Tl[Co(CO)_4]$ + $[RhCl(CO)(PF_3)]_2$ (a), and from $Co_2Rh_2(CO)_{12}$ ÷ $Co_2Rh_2(CO)_8(PF_3)_4$ (b) in CD_2Cl_2 solutions at different temperatures.

the expected stereochemistry of II obtained from the reaction of $[RhCl(CO)-(PF_3)]_2$ and $Tl[Co(CO)_4]$ would be [II(i)], [II(ii)] or [II(iii)], i.e. isomers in which each rhodium atom is bonded to one CO and one PF_3 ligand which can occupy axial (a) or equatorial (e) positions (see Fig. 8). Isomer [II(iv)] is also likely to be formed in the reaction between $Co_2Rh_2(CO)_{12}$ and $Co_2Rh_2(CO)_8-(PF_3)_4$. Further scrambling between II and I or $Co_2Rh_2(CO)_{12}$ would give complexes of the type $Co_2Rh_2(CO)_{11}(PF_3)$ and $Co_2Rh_2(CO)_9(PF_3)_3$ and these could exist as a total of four isomers. This behaviour is new for polynuclear complexes but is known to occur in $Ni(CO)_4$ and $Ni(PF_3)_4$ mixtures where the statistical distribution of $Ni(CO)_n(PF_3)_{4-n}$ are found [42].

The ^{19}F NMR spectrum of II, formed by either route, on cooling to $-40°C$ shows at least five doublet patterns AA', BB', CC', DD', and EE'. The most predominant new doublet CC' appearing in both spectra is assigned to a major isomer of II. The chemical shifts of AA' and DD' lie very close to those observed

Fig. 8. Proposed structures for $Co_2Rh_2(CO)_{10}(PF_3)_2$ (CO ligands have been omitted for clarity).

in I but their relative intensities differ in the two samples.

Because of the complexity of the spectra, definite assignments of the resonances to specific isomers cannot be made and the possibility of BB' and EE' arising from species such as $Co_2Rh_2(CO)_{11}(PF_3)$ and $Co_2Rh_2(CO)_9(PF_3)_3$ cannot be ruled out particularly in view of the mass-spectroscopic evidence. The differing behaviour of the ^{19}F NMR spectra of II on cooling to —40°C could be a result of either intramolecular interconversions of the various isomers or simply reflect differences in the relative solubilities of the different complexes present in the mixture.

The room temperature ^{31}P NMR spectrum of II in contrast to the ^{19}F NMR spectrum shows the expected broad quartet 1/3/3/1 pattern. The phosphorus chemical shift is similar to the high field resonance of complex I which may suggest that in the major isomer the PF_3 ligands occupy axial positions as in the previously known complex $Ir_4(CO)_8(PMePh_2)_4$, in which the phosphorus chemical shifts of the axial phosphines appeared at highest field [37].

Surprisingly, coupling between rhodium and phosphorus or fluorine in I and II cannot readily be resolved and the broad resonances observed presumably arise from quadrupole interaction with the cobalt nuclei ($I = 7/2$). Interestingly, the magnitude of (^1J(PF) $\simeq$ 1450 Hz) is close to the free ligand value and is much higher than that observed in most PF_3 transition metal complexes [12].

High values of ($^1J(PF)$) have also recently been reported for mercury(I) and silver(I) complexes of PF_3 [43].

A study was made of the effect of mixing two tetranuclear complexes containing different numbers of cobalt and rhodium atoms. The ^{19}F NMR spectrum of a solution of a 1/1 mixture of $Co_2Rh_2(CO)_8(PF_3)_4$ and $Co_3Rh(CO)_{12}$ showed evidence for the immediate exchange of PF_3 and CO between the two clusters. The resulting spectrum was essentially identical to that obtained by mixing $Co_2Rh_2(CO)_8(PF_3)_4$ with $Co_2Rh_2(CO)_{12}$ suggesting that the mechanism of the intermolecular ligand exchange process is independent of the nature of the tetranuclear metal cluster.

Attempts were made to synthesise tetranuclear rhodium complexes of the type $Rh_4(CO)_n(PF_3)_{12-n}$ ($n = 0, 4, 8$) by treating the appropriate $MRhL_4$ and $(RhClL_2)_2$ complexes (M = Na, K; L = CO or PF_3). Although no evidence was either found for $Rh_4(PF_3)_{12}$ or $Rh_4(CO)_8(PF_3)_4$ a brown solid, sublimable in vacuo at 60°C obtained from $[RhCl(CO)_2]_2$ and $K[Rh(PF_3)_4]$ is formulated as $Rh_4(CO)_4(PF_3)_8$ (III) on the basis of its mass spectrum which showed a parent ion peak at m/e 1225 and the expected fragmentation pattern for the consesutive loss of eight PF_3 and four CO groups. As expected the IR spectrum of III shows stronger broad bands in the P—F stretching region than complex I and a very strong broad band at 1880 cm^{-1} is attributable to the bridging carbonyls while three weaker bands at 2089, 2074 and 2058 cm^{-1} arise from terminal carbonyl vibrations. The ^{19}F and ^{31}P NMR spectra of III were recorded but proved inconclusive.

The dark brown iridium analogue of I, $Co_2Ir_2(CO)_8(PF_3)_4$ (IV), was prepared by mixing a toluene solution of $[IrCl(PF_3)_2]_2$ and $Tl[Co(CO)_4]$ at room temperature and was identified by its characteristic mass spectrum which showed a parent ion peak at m/e 1078 and successive loss of CO and PF_3 group. The IR spectrum is similar in appearance to $Co_2Rh_2(CO)_8(PF_3)_4$, but was less well resolved.

Experimental

All manipulations were performed under dry nitrogen gas. Solvents were dried using standard methods and distilled under a nitrogen atmosphere prior to use. The following starting materials were prepared as described in the literature: $Tl[Co(CO)_4]$ [19], $[RhCl(CO)(PF_3)]_2$ [20], $[IrCl(PF_3)_2]_2$ [14], $[RhCl(PF_3)_2]_2$ [18], $Co_3Rh(CO)_{12}$ [17], $Na[Rh(CO)_4]$ [44], and $K[Rh(PF_3)_4]$ [14]. $Co_2Rh_2(CO)_{12}$ was prepared from $[RhCl(CO)_2]_2$ according to the literature method using $Tl[Co(CO)_4]$ instead of $Zn[Co(CO)_4]_2$ [17].

Di-μ-chlorotetracarbonyldirhodium was prepared by a slightly different procedure from that of Powell and Shaw [45]. Carbon monoxide was bubbled through a refluxing solution of rhodium trichloride trihydrate in ethanol for 4 h. After evaporating the resulting yellow solution to dryness, the solid residue was sublimed under high vacuum at 80°C to give large red crystals of the product (80—90%). The infrared spectrum was identical with a known sample. ^{19}F and ^{31}P NMR spectra were recorded on a Jeol PFT spectrometer operating at 94.1 and 40.49 MHz, respectively, with ^1H noise decoupling. ^{19}F chemical shifts were measured relative to CCl_3F and ^{31}P shifts relative to $P(OMe)_3$. IR spectra were

recorded in the 4000—400 cm^{-1} range on a Perkin—Elmer 457 spectrometer. Elemental analyses were carried out by Mrs. A. Olney of this department. Mass spectra were recorded on an AEI MS9 spectrometer.

Preparation of $Co_2Rh_2(CO)_8(PF_3)_4$ (I)

(i) Reaction of $[RhCl(PF_3)_2]_2$ with $Tl[Co(CO)_4]$. A solution of $Tl[Co(CO)_4]$ (0.310 g, 0.82 mmol) in toluene (7 ml) was added to a solution of $[RhCl(PF_3)_2]_2$ (0.260 g, 0.41 mmol) in toluene (7 ml) and the mixture stirred at room temperature for 2 h. After filtering off the resulting greyish precipitate of TlCl the dark-brown filtrate was concentrated and cooled to —78°C. The crude product was washed with n-pentane at the same temperature to give the fine crystalline brown-black product. An analytical sample was recrystallised further from n-pentane at —78°C to give deep-brown crystals of I (0.297 g, 0.33 mmol; 80%), (Found: C, 10.7; H, 0.0. $C_8Co_2F_{12}O_8P_4Rh_2$ calcd.: C, 10.66; H, 0.0%). IR spectrum: 2094s, 2086vw(sh), 2070vs, 2062vw(sh), 2045s, 2035vw(sh), 1922m, 1887s, 1874s, 927w(sh), 918s, 905s, 898(sh), 888vw, 878w, 867s cm^{-1} (n-pentane solution).

(ii) Reaction of $Co_2(CO)_8$ with $[RhCl(PF_3)_2]$. A solution of $Co_2(CO)_8$ (0.243 g, 0.71 mmol) in hexane (25 ml) was stirred at room temperature with [RhCl-$(PF_3)_2]_2$ (0.299 g, 0.47 mmol). After three days all the $Co_2(CO)_8$ had reacted as shown by IR spectroscopy. The resulting deep-brown solution was filtered and the insoluble cobalt chloride extracted with n-pentane until the extracts were colourless. The original and extracted solutions were combined and cooled to —78°C giving the dark-brown crystalline product I, (0.340 g, 0.37 mmol; 79%), (Found: C, 10.6; H, 0.0. $C_8Co_2F_{12}O_8P_4Rh_2$ calcd.: C, 10.66; H, 0.00%).

The IR and mass spectra were identical to those of the product obtained by route (i).

Preparation of $Co_2Rh_2(CO)_{10}(PF_3)_2$ (II)

(i) Reaction of $[RhCl(CO)(PF_3)]_2$ with $Tl[Co(CO)_4]$. In a similar way to the above, a mixture of $Tl[Co(CO)_4]$ (0.117 g, 0.31 mmol) in toluene (3 ml) and $[RhCl(CO)(PF_3)]_2$ (0.080 g, 0.16 mmol) in toluene (2 ml) gave the complex $Co_2Rh_2(CO)_{10}(PF_3)_2$ (II) as a deep-brown solid (0.079 g, 0.10 mmol; 65%) (Found: C, 15.8; H, 0.0. $C_{10}Co_2F_6O_{10}P_2Rh_2$ calcd.: C, 15.38; H, 0.00%). IR spectrum: 2104vw, 2096s, 2078(sh), 2070vs, 2062(sh), 2047s, 1924w, 1889s, 1878s, 1863(sh), 919m, 906s(br), 900(sh), 888s, 880m, 867s cm^{-1} (n-pentane solution). The mass spectrum and ^{19}F and ^{31}P NMR spectra are discussed in the text.

(ii) Reaction of $Co_2Rh_2(CO)_8(PF_3)_4$ with $Co_2Rh_2(CO)_{12}$. A mixture of Co_2Rh_2-$(CO)_8(PF_3)_4$ (0.131 g, 0.14 mmol) in n-pentane (10 ml) and $Co_2Rh_2(CO)_{12}$ (0.096 g, 0.14 mmol) in n-pentane (10 ml) was stirred in a Schlenk tube for 4 h at room temperature. The resulting dark-brown solution was filtered and the filtrate evaporated to dryness to give II as a deep-brown solid (0.90 g, 0.11 mmol; 80%). The IR and ^{19}F NMR spectrum were similar to those of the product obtained by route (i).

Preparation of $Rh_4(CO)_4(PF_3)_8$ (III)

A solution of $[RhCl(CO)_2]_2$ (0.56 g, 0.14 mmol) in ether (10 ml) was stirred

with a solution of $K[Rh(PF_3)_4]$ (0.14 g, 0.28 mmol) in ether (8 ml) for 3 h. The reaction mixture was filtered and the filtrate concentrated to give the dark-red product which was recrystallised from ether/hexane. Although the mass spectrum showed the parent ion peak at m/e 1228, a satisfactory analysis was not obtained. (Found: C, 5.9; H, 1.2. $C_4F_{24}O_4P_8Rh_4$ calcd.: C, 3.90; H, 0.00%). IR spectrum: 2100m, 2089s, 2074s, 2058s, 1929w, 1880vs(br), 870vs(br), 740w, 725w, 535m(sh), 520m, 493w, 464w, 453w cm^{-1} (Nujol mull). The complex could be sublimed unchanged at 60°C/10^{-3} mmHg.

Attempted preparation of $Rh_4(PF_3)_{12}$

A solution of $[RhCl(PF_3)_2]_2$ (0.691 g, 0.14 mmol) in ether (10 ml) was stirred with $K[Rh(PF_3)_4]$ (0.144 g, 0.29 mmol) in ether (8 ml). After 30 min the orange coloured solution changed gradually to red and then deepened. Removal of ether followed by sublimation only led to the recovery of substantial amounts of unreacted $[RhCl(PF_3)_2]_2$ identified by its IR spectrum.

Preparation of $Co_2Ir_2(CO)_8(PF_3)_4$ (IV)

A solution of $Tl[Co(CO)_4]$ (0.102 g, 0.27 mmol) in toluene (7 ml) was added to a solution of $[IrCl(PF_3)_2]_2$ (0.109 g, 0.13 mmol) in toluene (7 ml). An immediate colour change from yellow to brown-red was observed and thallous chloride was precipitated. After 2 h the solution was filtered and cooled to —78°C, but no separation of crystalline product occurred. After removal of solvent the dark-brown solid complex was recrystallised from hexane at —78°C (0.093 g, 0.69 mmol; 64%) and characterised by mass spectroscopy (see text). IR spectrum: 2090w(sh), 2075s(sh), 2068s, 2044m, 2035(sh), 2018m w, 1872s(br), 1865s(br), 925w, 915w, 900(sh), 889s(br), 878(sh) cm^{-1} (n-pentane solution).

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