pyramid while the Ni(AA)₂ complex is octahedrally coordinated.[23]

The large variation in the acetylacetonate methyl absorptions previously noted for the Co(AA)₂ complexes can also be explained on the basis of pseudo-contact shifts. Thus for the 2:1 ligand–Co(AA)₂ complex, the geometric factor for these protons is large and negative. For 1:1 complexes in which the (AA) group must take up the sixth coordination site, the positional average of the methyl group has a more positive geometric factor. The effect of this is to produce a more negative pseudo-contact shift as the ratio of (2:1)/(1:1) complexes increases, as is observed.

The chloroform proton absorption provides another example of pseudo-contact shift. Chloroform hydrogen bonds with the amine N-oxides in the absence of M(AA)₂ as evidenced by a downfield shift of this peak with increasing amine N-oxide concentration. (Figure 1 shows a downfield shift of about 10 c.p.s. from the diamagnetic CHCl₃ resonance.) It is also well known for its bonding to chelate compounds[24] with the presently reported chloroform solvate of the α-picoline N-oxide–M(AA)₂ 2:1 complex another example. Figure 1 shows that for increasing Ni(AA)₂ concentration (total ligand concentration being constant) the chloroform peak is shifted downfield as is expected for hydrogen bonding.[25] For the Co(AA)₂ complexes the shift of the chloroform peak is strongly upfield and is due to a positive pseudo-contact contribution. This limits the position of the hydrogen to a cone having $\chi < 54° 44'$. Assuming planar acetylacetonate rings and normal hydrogen bond lengths, the hydrogen bond can be localized to the vicinity of the six oxygen atoms.

(23) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 4, 943 (1965); L. Sacconi, M. Campolini, and G. P. Speroni, *ibid.*, 4, 1116 (1965). In agreement with the octahedral configuration of the Ni(AA)₂ complex, only a green 2:1 2,6-lutidine N-oxide–Ni(DPM)₂ complex was isolated by the addition of an excess of N-oxide to Ni(DPM)₂ in methylcyclohexane. *Anal.* Calcd. for C₈₆H₅₄O₆N₂Ni: C, 64.57; H, 8.13; N, 4.19. Found: C, 64.29; H, 8.41; N, 4.17.

(24) J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, 80, 1838 (1958); J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, 4, 130 (1965).

(25) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

Miscellaneous. Some preliminary data on another interesting system bis(dipivaloylmethido)nickel(II) [Ni-[(CH₃)₃CCOCHCOC(CH₃)₃]₂, Ni(DPM)₂] are also presented in Table II. Ni(DPM)₂ is a red square-planar compound, monomeric in solution,[26] which associates with many ligands in solution particularly at low temperatures to give green and other colored compounds. Coordination of the amine N-oxides with Ni(DPM)₂ which can be observed visually results in spin delocalization in the ligand quite similar to that observed for Ni(AA)₂ although smaller for comparable concentrations. In addition, the effect of axial coordination on the position of the β-diketone C–H proton can be observed. Although at large ligand–Ni(DPM)₂ ratios this peak is not observed owing to broadening, at low ratios this proton is observed to shift from −324 to −279 c.p.s. (relative to TMS) while the chelate *t*-butyl methyl peak shifted from −59.0 to −68.3 c.p.s. For large ligand–Ni(DPM)₂ ratios the *t*-butyl methyl proton resonance is found at about −288 c.p.s. The observed CH shifts lead, by means of linear extrapolation, to the conclusion that at large ratios the CH absorption should be found at +780 c.p.s. (from TMS). This is in reasonable agreement with the analysis of Eaton[27] on the shifts of metal acetylacetonates which would suggest for this complex a ligand to metal β spin transfer with large upfield shift of the CH absorption and a small shift of indeterminant sign for the CH₃ protons. In the system Co(AA)₂–pyridine-N-oxide a broad peak of low intensity at +300 c.p.s. (ligand 0.80 *M*, Co(AA)₂ 0.2 *M*) was observed which may be the acetylacetonate CH proton. The methyl absorption is found at −950 c.p.s. and both of these peaks would be expected to be shifted downfield by a pseudo-contact term. The geometric factors for an acetylacetonate ring are CH = -1.2×10^{-2} and CH₃ = -0.8×10^{-2} Å.$^{-3}$, and therefore the pseudo-contact shift would be greater for the CH group.

(26) G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, 1, 73 (1963); F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 83, 2818 (1961).

(27) D. R. Eaton, *ibid.*, 87, 3097 (1965).

Fluoroolefin Complexes of Transition Metals

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Contribution No. 1103 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware. Received June 8, 1965

The tetrafluoroethylene complexes (AcAc)Rh(C₂F₄)(C₂H₄) (1), (Ph₃P)₂IrCl(CO)(C₂F₄) (4), and (Ph₃P)₃Ni(C₂F₄) (6) have been prepared and characterized. Various Lewis bases (L) displace ethylene from 1 to give complexes of the types (AcAc)Rh(C₂F₄)L₂ (2) and [(AcAc)Rh(C₂F₄)L]₂ (3). The dimeric complexes contain tridentate bridging acetonylacetotonate (AcAc) ligands. The spectra indicate that the C₂F₄–metal link in complexes 2–4 approaches the form of a σ-bonded three-membered ring. In complexes 1 and 6, the metal-olefin bond appears to have considerable π character.

Attempts to prepare fluoroolefin π complexes of transition metals analogous to the complexes formed by simple olefins have usually given σ-bonded fluoro-

alkyl compounds. The first such reaction to be reported was that of tetrafluoroethylene (TFE) with $Fe_3(CO)_{12}$ to give $C_4F_8Fe(CO)_4$. This stable compound was found to contain an octafluorotetramethyleneiron ring rather than two fluoroolefin molecules π-bonded to the iron atom.[1] Other organometallic compounds derived from TFE have been reported,[2] but none appear to be simple π complexes.

A recent communication[3] reported the isolation of some tetrafluoroethylene complexes of rhodium, iridium, and nickel in which the lability of the fluoroolefin approaches that of π-bonded ethylene. We now describe some chemistry of these compounds and spectral properties which relate to the nature of the metal–olefin bond.

Rhodium Complexes. Yellow tetrafluoroethylene complex 1[3] was prepared by treatment of acetylacetonatobis(ethylene)rhodium(I)[4] with TFE. This complex reacted with Lewis bases to give two new and distinctly different types of TFE complexes. Phosphines, amines, and dimethyl sulfoxide displaced ethylene to give soluble monomeric complexes (2) which contained two of these ligands per rhodium atom. Nitriles and dimethylformamide likewise displaced ethylene but gave insoluble binuclear compounds (3) with only one nitrile ligand coordinated to each rhodium. The structure proposed for the nitrile and amide complexes involves bridging by a tridentate acetylacetonate ligand similar to that shown to exist in platinum(IV) diketonate compounds.[5]

1
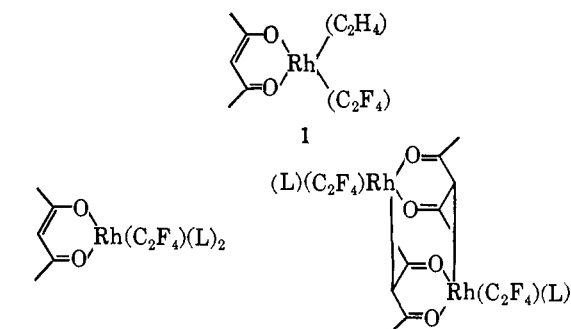
Complex	L	Complex	L
2a	(n-C$_4$H$_9$)$_3$P (*trans*)	3a	CH$_3$CN
2b	Ph$_3$P (*trans*)	3b	PhCN
2c	(CH$_3$)$_2$SO (*cis*)	3c	HOCH$_2$CH$_2$CN
2d	C$_5$H$_5$N (*cis*)	3d	n-C$_5$H$_{11}$CN
2e	½ (Me$_2$NCH$_2$–)$_2$ (*cis*)	3e	n-C$_6$H$_{13}$CN
2f	½[(C$_6$H$_5$)$_2$PCH–]$_2$ (*cis*)	3f	HCON(CH$_3$)$_2$

The two types of complex were distinguished by their infrared spectra (see below) and elemental analyses. When solubility permitted, n.m.r. and molecular weight data confirmed the structures.

All these complexes are pale yellow solids except for $2a$, which is colorless. They are stable to air but decompose on heating between 100 and 200°. The dimethyl sulfoxide (DMSO) in complex $2c$ exchanges readily in DMSO-d_6 solution or in acetonitrile-d_3

solution, as shown by n.m.r. The half-lives for the exchange reactions are slightly less than 10 min. at 25°. No mononuclear nitrile complex could be isolated from treatment of the DMSO complex with acetonitrile, but binuclear complex $3a$ was not formed.

Although the coordinated TFE in 1 was stable to σ bases as described above, it was displaced from the rhodium by 1,5-cyclooctadiene and by carbon monoxide.[3] The products were the known cyclooctadiene and dicarbonylrhodium(I) acetylacetonates.[6] The TFE was also displaced from 2 and 3 by treatment with carbon monoxide or nitric oxide.

Solvolysis of the TFE complex 1 in protonic solvents led to displacement of fluoride ion from the coordinated olefin to give difluoroacetic acid or carbon monoxide. In acetic acid, the solvolysis appeared to be catalytic because 1 mole of complex sufficed to convert several moles of tetrafluoroethylene to carbon monoxide. Hexafluoropropylene was converted to a mixture of trifluoroacetic and 2,3,3,3-tetrafluoropropionic acids by acetylacetonatobis(ethylene)rhodium(I) in acetic acid.

Iridium Complexes. Treatment of a toluene suspension of chlorocarbonylbis(triphenylphosphine)iridium(I)[7] with TFE at 25° and about 3 atm. pressure gave the pale yellow TFE complex 4. The formation of 4 reversed at low pressure. Purification was effected by recrystallization under TFE pressure, but, once isolated, the crystalline complex was stable for 18 months at room temperature. Pyrolysis of the solid at 100° gave TFE and (Ph$_3$P)$_2$Ir(CO)Cl.

4   5
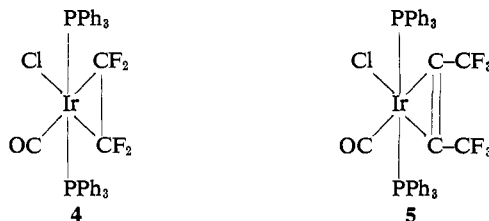
Hexafluoro-2-butyne reacted with (Ph$_3$P)$_2$Ir(CO)Cl at atmospheric pressure to give the colorless complex 5. This product was somewhat more stable than the analogous TFE compound but, like 4, could be pyrolyzed to give (Ph$_3$P)$_2$Ir(CO)Cl and unchanged butyne. Remarkably, however, when the pyrolysis products were cooled to room temperature in contact with one another, the hexafluorobutyne was reabsorbed to give 5. The pyrolysis and reabsorption processes were repeated three times without extensive degradation.

Nickel Complex. Treatment of a xylene solution of (Ph$_3$P)$_2$Ni(C$_2$H$_4$)[8] with TFE gave bright yellow crystals of tetrafluoroethylenetris(triphenylphosphine)nickel(0) (6). No other products of this unusual displacement–disproportionation reaction were isolated. The yield was at least 40% based on the amount of triphenylphosphine present. This yellow complex was thermally stable below 150° but was very sensitive to air.

$$(Ph_3P)_2Ni(C_2H_4) + C_2F_4 \longrightarrow (Ph_3P)_3Ni(C_2F_4)$$
$$6$$

Infrared Spectra (Table I). The spectra of the mononuclear rhodium acetylacetonate complexes 1 and 2 contain peaks at about 1515 and about 1590 cm.$^{-1}$

(1) K. F. Watterson and G. Wilkinson, *Chem. Ind.* (London), 991 (1959); 1358 (1960); H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).
(2) For a review on fluorocarbon derivatives of metals, see P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.* 1, 143 (1964).
(3) R. Cramer and G. W. Parshall, *J. Am. Chem. Soc.*, 87, 1392 (1965).
(4) R. Cramer, *ibid.*, 86, 217 (1964).
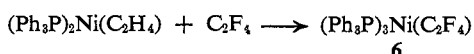(5) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), A254, 205 (1960).
(6) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).
(7) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 83, 2784 (1961).
(8) G. Wilke and G. Hermann, *Angew. Chem.*, 74, 693 (1962).

Table I. Infrared Spectra[a]

Complex	AcAc	Selected infrared peaks,[b] cm.$^{-1}$ C–F	Others
1		785, 1118, 1234	
2a	1517, 1612	830, 1027, 1072	
2b	1517, 1595	811, 1042, 1105(b)	694, 718
2c	1515, 1603	814, 1047, 1105	1144 (m), 1030 (m)
2d	1515, 1580	823(b), 1033, 1064, 1090	690, 700, 763
2e	1520, 1600	827, 1030, 1075	802, 773 (m)
2f	1504, 1592	805, 1041, 1095(b)	
3a	1657	821, 1028, 1043, 1102	2293, 2315
3b	1660	819, 1020–1050, 1095, 1111	2258, 2216 (w)
3c		819, 1080, 1109	2299, 3425
3d	1642, 1653 (sh), 1660	815, 827, 1040, 1099	2288 (w)
3e	1647, 1667	815, 827, 1041, 1100	2294
3f	1667	823(b), 1033, 1087	1642
4		803, 1052, 1094, 1122	2040, 1724, 1626, 1595, 1575 (w)
5			2025, 1773 (m)
6		1075–1100, 1190, 1224	

[a] A Perkin-Elmer Model 21 was used to produce spectra of 1–4 as KBr pellets. Complexes 5 and 6 were examined as Nujol mulls using a Perkin-Elmer 237 Grating Infracord. [b] Peaks are strong except when designated medium (m) or weak (w); b means broad.

assignable to the bidentate acetylacetonate function. These frequencies agree with data reported for bidentate acetylacetonate in which the carbonyl bond order is 1.5.[9,10] In contrast, each of the binuclear complexes (3a–f) gives a sharp, strong peak or peaks near 1660 cm.$^{-1}$ assignable to the acetylacetonate function. This frequency could be anticipated for a coordinated ketone having a bond order of two and is shorter than that reported for ordinary acetylacetonate chelates. The infrared spectrum of complex 3d has a strong sharp peak at 1660 cm.$^{-1}$, a shoulder at 1653 cm.$^{-1}$, and a weaker, sharp peak at 1642 cm.$^{-1}$. The spectrum of complex 3e is similar. The relative intensities of these peaks are markedly changed by repeated recrystallization of the complexes. This change shows that these complexes are mixtures of at least three isomers. This is not surprising as the proposed structures have four possible isomers. The complexes 3d and 3e have sharp, irreversible melting points which are unchanged by recrystallization.

Three (sometimes four) intense peaks seem characteristic of the TFE in all these complexes although the vibration modes of the other ligands sometimes render assignments uncertain. In $(C_2F_4)(C_2H_4)RhAcAc$ (1) these peaks are at 785, 1118, and 1234 cm.$^{-1}$. The character of the TFE in complexes 2–4 is apparently somewhat different; the corresponding peaks occur at roughly 810, 1040, and 1100 cm.$^{-1}$. The 1224-cm.$^{-1}$ peak of $(Ph_3P)_3Ni(C_2F_4)$ (6) suggests that this complex is similar to 1; the other peaks of 6 are unassignable.

The metal CO stretching frequencies of the iridium complexes 4 and 5 appear at 2040 and 2025 cm.$^{-1}$, respectively. This shift relative to $(Ph_3P)_2(CO)IrCl$ (1949 cm.$^{-1}$) is ascribable to the strong electron-withdrawing nature of the fluoroolefin ligands. The shift is even more pronounced than in the analogous molecular oxygen complex, $(Ph_3P)_2(CO)IrCl(O_2)$, which has a metal CO stretching frequency at 2000 cm.$^{-1}$.[11]

(9) F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 379–386.
(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 216–223.
(11) L. Vaska, Science, 140, 809 (1963).

The hexafluorobutyne complex 5 has a band at 1773 cm.$^{-1}$ which is assignable to coordinated multiple bond absorption. The actual bond order is probably two or a little less by analogy with the C=C stretching frequencies of 1820 and 1715 cm.$^{-1}$ found, respectively, for[12]

$$CF_3C\!\!=\!\!=\!\!=\!\!CCF_3 \quad \text{and} \quad CF_3C\!\!=\!\!=\!\!CCF_3$$
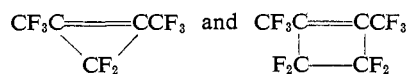
A similar absorption was reported for the hexafluoro-2-butyne in $(Ph_3P)_2Pt(CF_3CCCF_3)$.[13]

Other features of the infrared spectra of these compounds are consistent with the structures assigned.

Proton N.m.r. Spectra (Table II). The H^1 n.m.r. spectrum of each of the mononuclear rhodium complexes (1 and 2a–e) has a singlet assignable to the vinylic C–H of the acetylacetonate ligand at −5.0 to −5.5 p.p.m. (vs. Me$_4$Si). In contrast, the binuclear complexes 3d and 3e have doublets (J = 4 c.p.s.) assignable to the methinyl C–H at −3.20 and −3.30 p.p.m. This large difference provides powerful evidence for the structures proposed. In the monomeric complexes, the vinyl proton is attached to a ring having delocalized π electrons, while in the dimer it is attached to a saturated carbon. The splitting observed in 3d and 3e is assignable to Rh^{103}–H coupling. Such coupling is absent in the spectrum of rhodium(III) acetylacetonate[14] in which there is no C–Rh bond.

In the mononuclear complexes, the methyl protons of the acetonylacetonate ligand give rise to peaks in the −1.7- to −2.1-p.p.m. region. In the chelate diamine and diphosphine complexes 2e and 2f, which necessarily have the cis configuration, the two sharp peaks assignable to the methyl groups are separated by 14–17 c.p.s. Complexes 2c and 2d also have two methyl peaks separated by 11–12 c.p.s., while complexes 2a and 2b have a single sharp methyl peak. This result indicates that the two ligands L in complexes 2c–f are cis to one another and those in 2a and 2b are trans.

(12) W. Mahler, J. Am. Chem. Soc., 84, 4600 (1962).
(13) J. L. Boston, S. O. Grim, and G. Wilkinson, J. Chem. Soc., 3468 (1963).
(14) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1963.

Table II. Proton Magnetic Resonance Spectra

Complex	Probable config.	Solvent[b]	Chemical shift[a] (−δ, p.p.m.) and integral ratio		
			Methynyl CH	Methyl CH₃	Ligand
1	...	CDCl₃ (i)	5.55	2.08	4.20, 4.23
2a	trans	CCl₄ (e)	5.07	1.78	1.13, 1.47 (broad)
2b	trans	CD₃COCD₃ (i)	5.38 (1.0)	1.68 (6.5)	7.33 (broad)
2c	cis	(CD₃)₂SO (e)	5.47 (1.0)	1.86, 2.05 (6.9)	3.17,[c] 2.62[d]
2d	cis	CDCl₃ (i)	5.22 (1.0)	1.80, 2.00 (6.6)	8.60, 7.74, 7.32
2e	cis	CDCl₃ (i)	5.49 (1.0)	1.85, 2.08 (6.5)	3.05, 2.77, 2.25
2f	cis	CDCl₃ (i)	4.73 (1.0)	1.40, 1.67 (6.5)	8.3 to 7.1, 2.9 to 2.2
3d	Mixed	CDCl₃ (i)	3.20[e] (1.0)	2.32 (6.6)	2.44, 1.40, 0.88
3e	Mixed	CDCl₃ (e)	3.34[e] (1.0)	2.43	2.57, 1.38, 0.98
4	...	CDCl₃ (i)	...	...	4.5 to 4.2

[a] Spectra were recorded at 60 Mc./sec. with a Varian A-60 spectrometer vs. (CH₃)₄Si as a reference. [b] i = internal, e = external. [c] Coordinated (CH₃)₂SO. [d] Free (CH₃)₂SO. [e] Doublets, J = 4 c.p.s.

The $-CH_3$ singlets of binuclear complexes **3d** and **3e** fall at -2.32 and -2.46 p.p.m. This downfield shift is consistent with a change in bond order of the adjacent carbonyl from 1.5 to 2.

Fluorine N.m.r. Spectra (Table III). The chemical shifts of the TFE complexes **1–4** show substantial deshielding of the F^{19} nucleus relative to that in tetrafluoroethylene. However, all of the peaks are at much higher fields than those (+5 ppm.[1]) assignable to the α fluorines in $C_4F_8Fe(CO)_4$. The hexafluorobutyne complex **5** and the TFE–nickel complex **6** show only small shifts relative to hexafluoro-2-butyne and TFE, respectively.

Table III. F^{19} N.m.r. Spectra

Compound	Solvent	Chemical shift, p.p.m.[a]	Form
1	CDCl₃	+49.3 e	Complex
2b	Me₂SO	49.9 i	AB
		57.7 i	AB
2f	THF	41.7 i	AB
		51.1 i	AB
3d	CHCl₃	46.9 e	AB
		56.4 e	AB
4	CH₂Cl₂	46 e	Pair of triplets[b]
		64 e	Pair of quartets[c]
5	CH₂Cl₂	−14.2 e	Singlet
		−16.7 e	Singlet
6	CH₂Cl₂	64.0 e	Complex
TFE	THF	65.7 e	Sharp

[a] Spectra were measured at 56.4 Mc./sec. vs. FCCl₂CCl₂F as a reference; i = internal, e = external. [b] J = 154, J′ = 41 c.p.s. [c] J = 159, J′ = 50, J″ = 37 c.p.s.

The spectra of the substituted TFE–rhodium complexes **2** and **3** seem consistent with the distorted octahedral structures postulated in the discussion section. The two CF_2 groups of the coordinated TFE are in nonequivalent environments and the two F's on each carbon are also nonequivalent and give rise to an AB pattern.

In the hexafluorobutyne complex **5**, the nonequivalence of the CF_3 groups suggests a structure such as **5a**

or **5b** in which the two phosphorus atoms are not coplanar with the acetylene ligand. A structure analogous

5a   5b
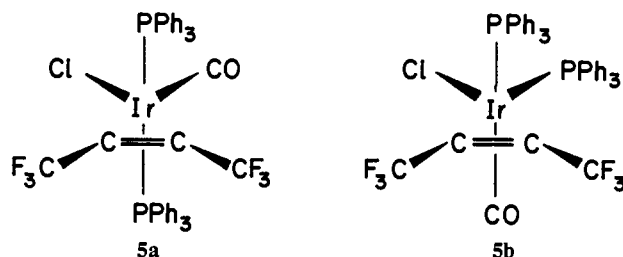
to **5a** has been established for the oxygen complex, $(Ph_3P)_2(CO)IrCl(O_2)$.[15] The spectrum of the TFE–iridium complex **4** has much more fine structure owing to PF and FF coupling. However, the spectrum is not completely compatible with the structures analogous to **5a** or **5b** nor with the structure having both phosphine ligands and the fluoroolefin in the same plane.

Discussion

The gross structures of the complexes described here seem well established, but the mode of bonding of TFE to the metals remains uncertain. Two extreme situations can be visualized: (1) the TFE–metal bond might resemble the ordinary olefin–metal π bond, deriving a large part of its stability from bonding of the filled metal d orbitals to the antibonding π orbitals of the olefin (Figure 1a); (2) the bonding might involve formation of a σ-bonded three-membered ring in which electrons from two σ orbitals of the metal are paired with sp^3 electrons of carbon (Figure 1b). In the latter situation the oxidation state of the metal is formally greater by two than in the former. Bonding situations intermediate between these extremes seem more probable than either limiting case.

Our data are insufficient for a full description of the TFE–metal bonding in these compounds, but certain observations can be made. The infrared spectra suggest that the TFE ligands in complexes **1** and **6** are bound in a somewhat different way from those in complexes **2–4**. The F^{19} n.m.r. spectra of **1** and **6** have fine structure involving relatively small internal chemical shifts

(15) J. A. Ibers and S. J. LaPlaca, *Science*, **145**, 920 (1964).

Table IV. Data for Complexes

Com-plex	Ligand	Yield, %	M.p., °C.[a]	Empirical formula	— Mol. wt. — Calcd.	Found	— % C — Calcd.	Found	— % H — Calcd.	Found		— % other — Calcd.	Found
1	C2H4	76	78–79	C9H11F4O2Rh	330.05	350[b]	32.75	33.3	3.36	3.65	..	...	...
2a	(n-C4H9)3P	36	111–113	C31H61F4O2P2Rh	706.67	650[b]	52.56	52.86	8.71	8.80	P	8.76	8.84
2b	(C6H5)3P	55	148–149	C43H31F4O2P2Rh	826.63	500[b]	62.47	62.73	4.51	4.50	P	7.50	7.25
2c	(CH3)2SO	55	130–170 dec.	C11H19F4O4RhS2	458.28	380[c]	28.83	29.22	4.13	4.40	S	13.99	13.96
2d	C5H5N	Good	138–155 dec.	C17H17F4N2O2Rh			44.36	45.06	3.72	3.96	N	6.99	6.23
2e	(Me2NCH2 CH2NMe2)1/2	28	151.5–152.5	C13H23F4N2O2Rh			37.33	37.95	5.54	5.68	N	6.70	7.04
2f	[(C6H5)3PCH2CH2-P(C6H5)2]1/2	83	153–159 dec.	C33H31F4O2P2Rh			56.58	56.37	4.46	4.62	P	8.85	8.89
3a	CH3CN	83	185–225 dec.	C18H20F8N2O4Rh2			31.51	31.71	2.93	3.17	N	4.17	4.14
3b	C6H5CN	66	170–200 dec.	C28H24F8N2O4Rh2			41.50	42.77	2.99	2.98	N	3.46	3.76
3c	HOCH2CH2CN	Good	135–180 dec.	C20H24F8N2O6Rh2			32.19	32.51	3.24	3.35	N	3.76	3.53
3d	C5H11CN	72	125.5–126 dec.	C26H36F8N2O4Rh2	798.37	650[b]	39.02	39.27	4.53	4.71	N	3.50	3.51
3e	C6H13CN	66	127–127.5 dec.	C28H40F8N2O4Rh2	826.43	760[b]	40.69	40.78	4.88	4.99	N	3.39	3.34
3f	HCON(CH3)2	68	190 dec.	C20H28F8N2O6Rh2			32.02	32.35	3.76	3.87	N	3.73	3.71
4		Good	Dec.	C39H30ClF4IrOP2			53.22	53.63	3.44	3.73	F	8.63	8.85
5		Good	Dec.	C41H30ClF6IrOP2			52.26	54.59	3.21	3.76	F	12.09	12.58
6		Ca. 40	Dec.	C56H45F4NiP3			71.13	70.90	4.80	5.43	F	8.03	8.14
											P	9.83	9.67

[a] Corrected; a Fisher-Johns melting point block was used. [b] Cryoscopic in benzene. [c] Cryoscopic in $(CH_3)_2SO$.

(ca. 1 p.p.m.) in contrast to the shifts of 7–18 p.p.m. for 2–4. These differences, taken together with the stoichiometry of the complexes, suggest that the metal–TFE bonds in 1 and 6 more closely approach that of Figure 1a than do those of 2–4.
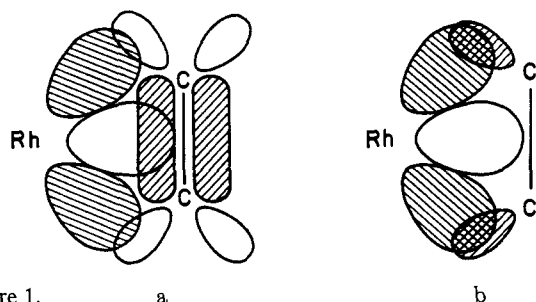

Figure 1.   a   b

The TFE–iridium complex 4, on the basis of its infrared and F^{19} n.m.r. spectra, seems to be structurally similar to $(Ph_3P)_2(CO)IrCl(O_2)$ for which a near-octahedral[16] structure has been demonstrated.[15] Hence, the TFE–iridium bond may approach that of Figure 1b and could be regarded as a $[C_2F_4]^{-2}$ anion coordinated to Ir(III). Similarly, the rhodium compounds of types 2 and 3 might be regarded as distorted octahedral Rh(III) complexes with two coordination sites occupied by the carbon atoms of TFE.

Experimental Section

Analytical and physical data for all compounds are given in Table IV. Molecular weights were determined when solubility and stability permitted.

Acetylacetonato(ethylene)(tetrafluoroethylene)rhodium(I) (1).[17] In a 500-ml., three-necked flask equipped with a magnetic stirrer, a −78° condenser, and a gas inlet was placed 10.0 g. (0.039 mole) of acetylacetonatobis(ethylene)rhodium(I)[4] and 100 ml. of ether. TFE was bubbled in rapidly; the resulting heat loss was re-

(16) These structures may be considered to be trigonal bipyramidal if the O2 and TFE ligands are assigned single coordination sites.
(17) This complex was first prepared by Cramer.[3]

placed by intermittent warming to 10–20° to dissolve most of the solids. The orange color of the starting material was gradually replaced by the yellow color of the product; yellow crystals began to appear. After 1 hr. the mixture was cooled to −78° and filtered. The solid was recrystallized from ether (filtered while warm, then cooled to −78°) to give 9.8 g. (76%) of complex 1, m.p. 78–79°. A second crop of 1.2 g. of less pure material was also obtained.

Complex 1 was sublimable at 40–50° (10⁻³ mm.) and was soluble in common polar organic solvents. Solutions of 1 decomposed gradually on exposure to air, but the solid reacted only very slowly with air.

Acetylacetonatobis(donor)tetrafluoroethylenerhodium Complexes 2a–f. The bis(tributylphosphine) complex 2a was prepared by treating acetylacetonato(ethylene)-(tetrafluoroethylene)rhodium(I) with excess tri-n-butylphosphine in vacuo. The product precipitated; it was recrystallized three times by cooling hexane solutions to −78°. The analogous bis(triphenylphosphine) complex 2b was prepared by treating ether solutions of complex 1 with 2 molar equiv. of triphenylphosphine.

Complexes 2c and 2d were prepared by dissolving complex 1 in excess dimethyl sulfoxide and pyridine, respectively. After 1 hr. or more, the product was precipitated by addition of ether (2c) or hexane (2d). Complex 2c was recrystallized from a dimethyl sulfoxide–ether mixture.

The chelate diamine complex 2e was prepared from complex 1 and excess tetramethylethylenediamine in ether. The product was recrystallized by cooling an ether solution to −78°. The chelate diphosphine complex 2f was prepared similarly using 1 molar equiv. of tetraphenylethylenediphosphine.

Binuclear Complexes 3a–f. The nitrile complexes 3a–c precipitated from solutions of complex 1 in a large excess of the appropriate nitrile on standing overnight. These complexes were insoluble in all common solvents.

Complexes 3d–f were prepared similarly except that precipitation of the products was completed by addi-

tion of hexane. Nitrile complexes **3d** and **3e** were recrystallized from tetrahydrofuran–ether. The melting points of these substances were not changed by repeated recrystallization, but the relative intensities of the three closely spaced infrared peaks in the 1660-cm.$^{-1}$ region changed decidedly.

Chlorocarbonylbis(triphenylphosphine)(tetrafluoroethylene)iridium(I) (**4**). A 200-ml. Carius tube containing 4.0 g. of tetrafluoroethylene and 95 ml. of a saturated solution of chlorocarbonylbis(triphenylphosphine)-iridium(I)[7] in toluene was agitated at 25° for 1 week. The brilliant yellow solution slowly became colorless. The solvent was removed at reduced pressure to leave a faintly yellow solid. Recrystallization from toluene under TFE pressure (3 atm.) gave white crystals of the TFE complex **4**. The P^{31} n.m.r. spectrum of a saturated benzene solution contained a single broad peak at +16.4 p.p.m. (*vs.* 85% H$_3$PO$_4$ external reference).

Pyrolysis of Complex **4**. In a system of known volume attached to a manometer, 0.0903 g. (0.111 mmole) of the above product was slowly heated. Gas evolution was slow at 100°; equilibrium was quickly reached at 130°. The gas (0.08 mmole) was characterized by its infrared and mass spectra as TFE. The bright yellow residual solid appeared to be pure chlorocarbonylbis-(triphenylphosphine)iridium(I) on the basis of its infrared spectrum; it weighed 0.084 g. (97%). The solid did not reabsorb TFE as it cooled.

Chlorocarbonylbis(triphenylphosphine)(hexafluoro-2-butyne)iridium (**5**). A suspension of 0.78 g. of chloro-carbonylbis(triphenylphosphine)iridium(I)[7] in 20 ml. of toluene was stirred under 700 mm. pressure of hexa-fluoro-2-butyne for 16 hr. The brilliant yellow starting material dissolved, and a pale yellow solid crystallized. The solid was collected and dried for 4 hr. at 25° at a pressure of 10^{-3} mm. Some toluene remained in the crystal lattice as indicated by the elemental analyses and the pyrolysis experiment below.

Reversible Pyrolysis of Complex **5**. An 0.816-g. (0.867 mmole) sample of the hexafluorobutyne complex (**5**) was pyrolyzed under high vacuum in a test tube sealed to a vacuum manifold. No gas evolution was noted below 85°. At 110° a rapid pressure increase occurred and equilibrium was reached at 110 mm. (corrected to 25°) within 2 hr. The mixture was allowed to stand at room temperature overnight. The pressure fell to 30 mm. Heating to 110° caused a pressure rise to 110 mm. The gas evolution by weight and volume change was 0.87 mmole. The gas was characterized by its infrared and mass spectra as hexafluoro-2-butyne containing a small amount of toluene. During the pyrolysis the color of the solid changed from off-white to bright yellow. The infrared spectrum of the yellow residue was identical with that of chlorocarbon-ylbis(triphenylphosphine)iridium(I); 0.663 g. (98%) was recovered. Exposure of the recovered solid to oxygen did not lead to gas absorption. However, re-exposure to hexafluoro-2-butyne resulted in absorption of 0.56 mmole of the gas.

Tetrafluoroethylenetris(triphenylphosphine)nickel(0) (**6**). A solution of 1.0 g. of ethylenebis(triphenylphos-phine)nickel(0)[8] in 10 ml. of *m*-xylene was treated with tetrafluoroethylene at atmospheric pressure. The red solution immediately became brown, and yellow crystals separated. The crystals were filtered under nitrogen, washed three times with benzene, and dried under reduced pressure; the yield was about 0.4 g. The product decomposed when heated above 150° and was very sensitive to air. The P^{31} n.m.r. spectrum determined at 19.2 Mc/sec. on a saturated solution in benzene contained a single peak at −20.3 p.p.m. relative to 85% H$_3$PO$_4$ as an external standard.

Kinetics of the Reactions of Pentacyanocobaltate(II) with Organic Halides

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Pentacyanocobaltate(II) reacts with organic halides in aqueous solution to form pentacyanoorganocobaltate(III) compounds according to the reaction, $2Co(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5R^{3-} + Co(CN)_5X^{3-}$. The kinetics of this reaction were examined for a number of organic halides and found in each case to be first order in pentacyanocobaltate(II) and in the halide. Second-order rate constants at 25° ranged from 2.5×10^{-4} M^{-1} sec.$^{-1}$ for Cl–$CH_2CO_2{}^-$ to 9×10^4 M^{-1} sec.$^{-1}$ for I–CH_2COOCH_3, the general trend reflecting an inverse dependence of the rate constant on the carbon-halogen bond strength. Activation parameters were determined for a number of the reactions. The results are interpreted in terms of the stepwise mechanism, Co-

$(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R \cdot$ *(rate determining)*, followed by $Co(CN)_5{}^{3-} + R \cdot \rightarrow Co(CN)_5R^{3-}$.

Introduction

We have previously reported[1] that pentacyanoco-baltate(II) reacts with organic halides to form stable organocobalt compounds according to eq. 1. The

$$2Co^{II}(CN)_5{}^{3-} + RX \longrightarrow Co^{III}(CN)_5R^{3-} + Co^{III}(CN)_5X^{3-} \quad (1)$$

formation of pentacyanoorganocobaltate(III) compounds, both by this method and by an alternative route involving the addition of Co(CN)$_5$H^{3-} to acti-

(1) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964).