that the perchlorate ion is trapped into coordination by a tailor-made structural environment.[16]

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(16) NOTE ADDED IN PROOF.—Examples of both monodentate and bidentate perchlorato groups in acetonitrile complexes of nickel(II) were reported recently: A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Ionic Perfluoroalkyl Complexes of Cobalt[1]

BY P. M. TREICHEL AND G. WERBER

Received March 8, 1965

Complexes of the general formula π-$C_5H_5CoLL'R_F{}^+ClO_4{}^-$ (where L and L' are electron-pair donors such as carbon monoxide, triphenylphosphine, acetonitrile, or pyridine and R_F is C_2F_5 or n-C_3F_7) have been prepared by reaction of $C_5H_5Co(CO)R_FI$, the respective donor molecule, and $AgClO_4$ in benzene solution. These ionic complexes are soluble in acetone and other polar solvents. Ligand exchange reactions have been studied which lead to an order of stability among the complexes roughly paralleling the basicity of the ligand L. The infrared and ^{19}F n.m.r. spectra of these complexes are discussed.

A number of cationic carbonyl complexes of transition metals have been described in the scientific literature. Among these, the compounds $M(CO)_6{}^+AlCl_4{}^-$ (M = Mn, Re),[2] $C_5H_5Fe(CO)_3{}^+X^-$,[3] and $C_5H_5Mo(CO)_4{}^+AlCl_4{}^-$,[4] and some derivatives of these ionic complexes,[5] represent isostructural analogs of known neutral or anionic complexes. These compounds have been prepared by rather straightforward reactions involving a metal carbonyl halide, a halogen acceptor such as $AlCl_3$, and carbon monoxide or another electron-pair donor. It might be noted, however, that other cationic derivatives predate these; for example the complexes $C_6H_6Mn(CO)_3{}^+$,[6] and $C_7H_7Mo(CO)_3{}^+$,[7] were prepared several years earlier. A variety of cationic complexes of other delocalized π-systems such as the pentadienyl,[8] cyclohexadienyl,[6,9] and other more complex groups[10] have also been investigated. In general, these latter derivatives are formed by protonation or hydride abstraction from neutral complexes; these reactions are sometimes accompanied by rearrangement of the hydrocarbon group.

It seems reasonable to consider both the neutral and ionic coordination complexes of metal carbonyls as related species, in that they are both complexes formed by coordination of ligands with a metal atom in a low oxidation state. In general such derivatives would be expected to obey the inert gas formalism; thus a rather simple means of predicting possible compounds is available. However it is evident from chemical behavior and physical properties of these complexes that pronounced differences result from the presence of positive or negative charges. It is such differences that led us to initiate this study of cationic complexes containing a perfluoroalkyl group bonded to a metal. In this paper complexes of the formula $C_5H_5Co(CO)_2R_F{}^+ClO_4{}^-$ (R_F = C_2F_5, n-C_3F_7), the parent carbonyl, and substitution derivatives of this complex are discussed.

Experimental

Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and the Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137B spectrophotometer, generally using Nujol mulls. The ^{19}F n.m.r. spectra in acetone or acetonitrile were obtained using a Varian HR-60 spectrometer at 56.4 Mc. with trichlorofluoromethane as an internal standard.

The preparation of the starting complexes π-$C_5H_5Co(CO)R_FI$ (R_F = C_2F_5, n-C_3F_7) has been described in the literature.[11] Commercial $AgClO_4$ was used; this material was always somewhat wet due to its deliquescent nature, but the small amounts of water present did not appear to affect these preparations greatly.

Infrared spectral absorptions of the compounds discussed below are tabulated in Table I, and ^{19}F n.m.r. results in Table II.

Preparation of π-$C_5H_5Co[(C_6H_5)_3P]C_2F_5I$.—This compound, which is used in a subsequent reaction, was prepared from triphenylphosphine (0.30 g., 1.14 mmoles) and π-$C_5H_5Co(CO)(C_2F_5)I$ (0.30 g., 0.67 mmole) in 50 ml. of benzene. The reactants were heated in benzene for 2 hr. at 50°. After the solvent was removed *in vacuo* the black crystalline product was purified by recrystallization from a benzene–petroleum ether mixture (0.25 g., 60% yield).

Anal. Calcd. for $C_{25}H_{20}F_5IPCo$: C, 47.5; H, 3.2; F, 15.0. Found: C, 47.3; H, 3.2; F, 14.9.

---

(1) Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p. 12L.

(2) W. Hieber and T. Kruck, *Angew. Chem.*, **73**, 580 (1961); E. O. Fischer and K. Ofele, *ibid.*, **73**, 581 (1961).

(3) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961).

(4) E. O. Fischer, K. Fichtel, and K. Ofele, *ibid.*, **95**, 249 (1962).

(5) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963); T. Kruck and M. Hofler, *Chem. Ber.*, **96**, 3035 (1963); E. O. Fischer and K. Fichtel, *ibid.*, **95**, 2063 (1961); and references therein.

(6) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961).

(7) H. P. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

(8) J. E. Mahler and R. Pettit, *ibid.*, **85**, 3955 (1963).

(9) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).

(10) For example, see A. Davidson, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962); R. Burton, L. Pratt, and G. Wilkinson, *ibid.*, 594 (1961).

(11) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

TABLE I

INFRARED SPECTRA (CM.$^{-1}$) OF CATIONIC COBALT CARBONYLS

π-$C_5H_5Co(CO)(C_2F_5)I$[11]

2080 (s), 1280 (s), 1195 (sh), 1180 (s), 1060 (sh), 1040 (m), 1020 (m), 995 (w), 945 (w), 900 (s), 875 (w), 847 (m), 830 (w), 728 (s)

π-$C_5H_5Co(CO)_2C_2F_5^+ClO_4^-$

2140 (s), 2080 (s), 1420 (w), 1280 (s), 1220 (sh), 1180 (s), 1080 (s), 1050 (s), 1030 (sh), 992 (m), 974 (m), 915 (sh), 905 (m), 875 (m), 838 (w), 738 (s), 728 (sh)

π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5^+PF_6^-$

2080 (s), 1280 (s), 1200 (s), 1170 (m), 1160 (sh), 1080 (m), 1050 (m), 1020 (m), 975 (w), 930 (w), 893 (s), 855 (s), 842 (s), 830 (s), 750 (m), 730 (m), 705 (sh), 692 (m)

π-$C_5H_5Co[(C_6H_5)_3P]_2C_2F_5^+ClO_4^-$

1320 (m), 1270 (s), 1200 (m), 1170 (s), 1140 (s), 1100 (sh), 1080 (m), 1065 (m), 1030 (m), 1020 (m), 1005 (s), 970 (sh), 890 (s), 850 (s), 825 (m), 757 (m), 745 (m), 728 (s), 699 (m)

π-$C_5H_5Co(CH_3CN)[(C_6H_5)_3P]C_2F_5^+ClO_4^-$

1290 (s), 1200 (s), 1160 (s), 1100 (s), 1070 (sh), 1040 (s), 1010 (m), 920 (sh), 905 (s), 870 (m), 860 (m), 770 (m), 755 (m), 740 (m), 730 (m), 700 (m), 690 (m)

π-$C_5H_5Co(py)_2C_2F_5^+ClO_4^-$

1610 (m), 1480 (w), 1410 (w), 1280 (s), 1260 (w), 1220 (w), 1180 (s), 1090 (s), 1070 (m), 1040 (m), 1030 (s), 1000 (m), 950 (w), 900 (s), 850 (m), 760 (m), 725 (m), 700 (m)

π-$C_5H_5Co(CO)(C_3F_7)I$[11]

2100 (s), 1210 (s), 1420 (m), 1320 (s), 1280 (sh), 1245 (m), 1220 (s), 1205 (s), 1190 (s), 1170 (s), 1120 (w), 1080 (s), 1070 (m), 1045 (s), 1010 (s), 950 (w), 901 (s), 882 (m), 848 (s), 836 (m), 808 (s), 725 (s), 662 (s)

π-$C_5H_5Co(CO)_2C_3F_7^+ClO_4^-$

2150 (s), 2070 (s), 1410 (m), 1320 (s), 1220 (s), 1170 (m), 1100 (s), 1025 (s), 980 (m), 960 (m), 870 (w), 820 (w), 800 (m), 720 (s), 660 (m)

π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_3F_7^+ClO_4^-$

2080 (s), 1320 (s), 1230 (s), 1200 (s), 1080 (s), 1070 (sh), 1040 (sh), 1020 (m), 990 (s), 870 (w), 795 (m), 745 (m), 720 (s), 690 (m), 660 (m)

π-$C_5H_5Co(CH_3CN)_2C_3F_7^+ClO_4^-$

2370 (w), 1420 (m), 1320 (s), 1225 (s), 1190 (s), 1180 (sh), 1170 (sh), 1120 (sh), 1090 (s), 1060 (m), 1040 (s), 996 (m), 961 (m), 936 (w), 910 (w), 862 (s), 835 (m), 815 (s), 730 (s), 668 (m)

π-$C_5H_5Co(py)_2C_3F_7^+ClO_4^-$

1590 (m), 1320 (s), 1215 (s), 1185 (s), 1150 (m), 1085 (s), 1070 (sh), 1025 (s), 990 (m), 845 (m), 800 (m), 765 (m), 755 (m), 720 (s), 690 (s), 660 (s)

π-$C_5H_5Co(bipy)C_3F_7^+ClO_4^-$

1615 (m), 1420 (m), 1320 (s), 1240 (s), 1190 (s), 1155 (s), 1090 (s), 1025 (s), 1015 (m), 880 (w), 855 (m), 830 (w), 805 (m), 770 (s), 750 (m), 720 (s), 660 (m), 620 (s)

Preparation of π-$C_5H_5Co(CO)_2C_2F_5^+ClO_4^-$.—A solution of 0.10 g. of π-$C_5H_5Co(CO)(C_2F_5)I$ (0.25 mmole) in 3 ml. of benzene was placed in a glass-lined autoclave of 250-ml. capacity. A small test tube containing an excess of $AgClO_4$ dissolved in benzene[12] was also placed in the autoclave in an erect position. The autoclave was sealed and pressured to 1200 p.s.i.g. with carbon monoxide, and the reagents were then mixed by rocking the vessel. The reaction was maintained for 12 hr. at 25°. After venting the carbon monoxide and flushing the system with nitrogen the autoclave was opened. The clear benzene solution indicated reaction had reached completion. The autoclave contained only benzene and a grayish solid material. The latter was a mixture of π-$C_5H_5Co(CO)_2C_2F_5^+ClO_4^-$, which was identified by its infrared spectrum (Table I), and AgI. Unfortunately this mixture could not be separated and the carbonyl compound was not isolated in pure form, since all attempts to extract this product with the usual polar solvents led only to decomposition.

Preparation of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5^+ClO_4^-$.—A solution of 0.243 g. of $AgClO_4$ (1.17 mmoles) and 0.615 g. of triphenylphosphine (2.34 mmoles) in benzene was added to a benzene solution of 0.460 g. of π-$C_5H_5Co(CO)(C_2F_5)I$ (1.17 mmoles) at 25°. Precipitation of a yellow and white solid occurred immediately. This solid was filtered and then washed with acetone. The desired product π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5^+ClO_4^-$ was soluble in acetone, giving a yellow solution which was filtered to separate it from the insoluble AgI. The AgI was washed several times with small portions of acetone, and the acetone fractions were combined. The product π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5^+ClO_4^-$ precipitated as yellow crystals on addition of this acetone solution dropwise to a large volume of diethyl ether.

The yellow product was converted to the hexafluorophosphate salt for analysis by addition of a saturated aqueous solution of NH_4PF_6 to a solution of the compound in aqueous acetone.

Anal. Calcd. for $C_{26}H_{20}F_{11}OP_2Co$: C, 46.0; H, 2.95; F, 30.8. Found: C, 45.5; H, 2.8; F, 30.7.

The perchlorate salt of this complex cation was also prepared by two other methods. In the first, 0.1 g. of π-$C_5H_5Co[(C_6H_5)_3P](C_2F_5)I$ was allowed to react with excess $AgClO_4$ in benzene in the autoclave under 1200 p.s.i.g. carbon monoxide pressure at 25°. The product (0.033 g.) was obtained in 33% yield. In the second preparation this product was obtained by addition of an acetone solution containing 0.13 g. of triphenylphosphine (0.50 mmole) to the solid mixture of AgI and π-$C_5H_5Co(CO)_2C_2F_5^+ClO_4^-$, prepared from 0.10 g. of π-$C_5H_5Co(CO)(C_2F_5)I$ (0.25 mmole). A 0.068-g. sample of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5^+ClO_4^-$, representing 43% conversion, was obtained. The identity of the products prepared by these two routes was affirmed to be the same as that prepared above by comparisons of their infrared spectra.

Preparation of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_3F_7^+ClO_4^-$.—This compound was prepared (0.28 g., 41% yield) in a manner similar to that described above for the perfluoroethyl compound, from 0.45 g. of π-$C_5H_5Co(CO)(C_3F_7)I$ (1.0 mmole), 0.262 g. of triphenylphosphine (1.0 mmole), and excess $AgClO_4$ in 100 ml. of benzene. *Anal.* Calcd. for $C_{27}H_{20}ClF_7O_5PCo$: C, 47.5; H, 2.9; F, 19.5. Found: C, 47.6; H, 3.1; F, 19.4.

Preparation of π-$C_5H_5Co(CH_3CN)_2C_3F_7^+ClO_4^-$.—A solution of 0.45 g. of π-$C_5H_5Co(CO)(C_3F_7)I$ (1.0 mmole) and 0.41 g. of CH_3CN (10 mmoles) in 10 ml. of benzene was treated with 0.414 g. of $AgClO_4$ (2 mmoles) at 25°. Precipitation of AgI and the product was accompanied by evolution of CO. After filtration the product was dissolved in acetone; this solution was filtered and the product reprecipitated upon addition to ether, yielding 0.25 g. of a red crystalline material (43% yield). *Anal.* Calcd. for $C_{12}H_{11}F_7O_4N_2ClCo$: C, 30.4; H, 2.3; F, 28.0. Found: C, 30.4; H, 2.6; F, 27.8.

Preparation of π-$C_5H_5Co(py)_2C_3F_7^+ClO_4^-$.—Excess pyridine was added to a solution of 0.308 g. of π-$C_5H_5Co(CO)(C_3F_7)I$ (0.685 mmole) and excess $AgClO_4$ in benzene at 25°. The product appeared reasonably soluble in benzene, giving a red solution. This was filtered to remove AgI and evaporated to dryness *in vacuo*, and the red residue was recrystallized from acetone and ether (0.31 g., 82% yield). It was converted to the hexafluorophosphate salt for analysis. *Anal.* Calcd. for $C_{18}H_{15}F_{13}N_2PCo$: C, 36.2; H, 2.5; F, 41.5. Found: C, 36.8; H, 2.8; F, 40.5.

The perchlorate salt of this cation was also obtained in 36% yield by reaction of excess pyridine with π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_3F_7^+ClO_4^-$.

Preparation of π-$C_5H_5Co(bipy)C_3F_7^+ClO_4^-$.—A solution of 0.15 g. (0.33 mmole) of π-$C_5H_5Co(CO)(C_3F_7)I$ in 2 ml. of benzene was treated with 5 ml. of 4% $AgClO_4$ solution in benzene (0.33 mmole),

---

[12] Caution is recommended for handling of perchlorates in organic solvents. Though we experienced no difficulties in this work serious explosions from such mixtures have been reported.

TABLE II

^{19}F N.M.R. DATA

Compound	(α-CF$_2$)	(β-CF$_2$)	(CF$_3$)	$J_{\alpha-\gamma}$, c.p.s.	Other spin coupling and chemical shift data
π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5{}^{-}PF_6{}^{-}$ [a]	AB pattern, 4 doublets, +60.8 p.p.m.	. . .	Singlet, +78.0 p.p.m.		$\delta(F_{\alpha1}-F_{\alpha2}) = 8.26$ p.p.m. $J(F_{\alpha1}-F_{\alpha2}) = 245$ c.p.s. $J(F_{\alpha1}-P) = 12.3$ c.p.s. $J(F_{\alpha2}-P) = 32.9$ c.p.s.
π-$C_5H_5Co(CH_3CN)[(C_6H_5)_3P]C_2F_5{}^{+}ClO_4{}^{-}$	AB pattern, 4 doublets, +71.2 p.p.m.	. . .	Singlet, +79.5 p.p.m.		$\delta(F_{\alpha1}-F_{\alpha2}) = 4.72$ p.p.m. $J(F_{\alpha1}-F_{\alpha2}) = 238$ c.p.s. $J(F_{\alpha1}-P) = 10.1$ c.p.s. $J(F_{\alpha2}-P) = 30.8$ c.p.s.
π-$C_5H_5Co(py)_2C_2F_5{}^{+}ClO_4{}^{-}$	Singlet, +88.2 p.p.m.	. . .	Singlet, +77.8 p.p.m.		
π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_3F_7{}^{+}ClO_4{}^{-}$	AB pattern, 4 broad resonances, +56.8 p.p.m.	Asymmetric doublet, +115 p.p.m.	Sharp triplet, +74.8 p.p.m.	11.4	$J(F_{\alpha1}-F_{\alpha2}) = 246$ c.p.s. $\delta(F_{\alpha1}-F_{\alpha2}) = 6.40$ p.p.m.
π-$C_5H_5Co(CH_3CN)_2C_3F_7{}^{+}ClO_4{}^{-}$	Broad, 5 peaks, +77.7 p.p.m.	Broad resonance, +116.4 p.p.m., 1:2:1 triplet $J = 2.5$ c.p.s.	Triplet, +74.0 p.p.m.	10.2	
π-$C_5H_5Co(bipy)C_3F_7{}^{+}ClO_4{}^{-}$	Broad quartet, +89.1 p.p.m.	Singlet, +119 p.p.m.	Triplet, +78.8 p.p.m.	11.9	
π-$C_5H_5Co(py)_2C_3F_7{}^{+}ClO_4{}^{-}$	Broad quartet, +89.8 p.p.m.	Broad resonance, +116.4 p.p.m., 1:2:1 triplet $J = 3.8$ c.p.s.	Triplet, +76.9 p.p.m.	15.9	

[a] The $PF_6{}^{-}$ resonance was observed as a doublet centered at 74.2 p.p.m., with $J_{P-F} = 699$ c.p.s., rather close to literature values for this ion.[13]

immediately followed by the addition of a solution of 0.052 g. (0.33 mmole) of 2,2′-bipyridine in 2 ml. of benzene. The reactants were allowed to stand for 24 hr. at room temperature, during which time silver iodide and the red crystalline product precipitated. The AgI was removed by filtration from an acetone solution of the product. An orange impurity was precipitated from the acetone solution by careful addition of ether and removed by filtration. The product was precipitated by the further addition of ether followed by filtration. This procedure was repeated for additional purification. The product was converted to the hexafluorophosphate salt for analysis (0.100 g., 50.5% yield). *Anal.* Calcd. for $C_{18}H_{13}F_{13}N_2PCo$: C, 36.38; H, 2.21; F, 41.57. Found: C, 36.43; H, 2.31; F, 41.49.

This compound was also prepared from a yellow insoluble silver perchlorate bipyridine complex, formed by adding 5 ml. of the 4% $AgClO_4$ solution in benzene (0.33 mmole) to 0.052 g. (0.33 mmole) of 2,2′-bipyridine. Upon the addition of 0.15 g. (0.33 mmole) of π-$C_5H_5Co(CO)(C_3F_7)I$, the yellow complex slowly disappeared and was replaced by the red crystalline product. The product was isolated and purified by the previously outlined procedure (0.06 g., 30% yield).

Preparation of π-$C_5H_5Co(py)_2C_2F_5{}^{+}ClO_4{}^{-}$.—Direct reaction of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5{}^{-}ClO_4{}^{-}$ with pyridine was accompanied by evolution of carbon monoxide and formation of a red solution. The product was precipitated on addition of this solution to ether and was recrystallized from acetone and ether. *Anal.* Calcd. for $C_{17}H_{15}ClF_5N_2O_4$: C, 40.8; H, 3.0; F, 19.0. Found: C, 40.9; H, 3.2; F, 18.8. This compound was also prepared (0.065 g., 87% yield) from an excess of pyridine and 0.13 g. of π-$C_5H_5Co[(C_6H_5)_3P]_2C_2F_5{}^{+}ClO_4{}^{-}$ (0.15 mmole) at 60°.

Preparation of π-$C_5H_5Co[(C_6H_5)_3P]_2C_2F_5{}^{+}ClO_4{}^{-}\cdot HI$.—A benzene solution of 0.20 g. of triphenylphosphine (0.73 mmole) and 0.10 g. of $AgClO_4$ (0.48 mmole) was added to 0.25 g. of π-$C_5H_5Co[(C_6H_5)_3P](C_2F_5)I$ (0.40 mmole) in 50 ml. of benzene at 25°. Solid AgI precipitated and was filtered off; the filtrate was evaporated to dryness. After the excess triphenylphosphine was removed by sublimation the black solid product was purified by recrystallizing from benzene and petroleum ether. Analyses corresponded best to a formulation π-$C_5H_5Co[(C_6H_5)_3P]_2C_2F_5{}^{-}$-$ClO_4{}^{-}\cdot HI$. *Anal.* Calcd. for $C_{43}H_{36}Cl_2F_5O_8P_2Co$: C, 52.0; H, 3.62; F, 9.6; P, 6.2. Found: C, 52.2; H, 3.86; F, 9.98; P, 6.03.

Reaction of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5{}^{+}ClO_4{}^{-}$ and Acetonitrile.—On addition of π-$C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5{}^{-}ClO_4{}^{-}$ to acetonitrile at 25° carbon monoxide was evolved and a deep red solution was obtained. The solution was diluted with toluene and evaporated to dryness under vacuum. Recrystallization from acetone–ether gave the red crystalline complex π-$C_5H_5Co(CH_3CN)[(C_6H_5)_3P]C_2F_5{}^{-}ClO_4{}^{-}$. *Anal.* Calcd. for $C_{27}H_{23}ClF_5NPO_4Co$: C, 50.2; H, 3.6; F, 14.7. Found: C, 50.1; H, 3.8; F, 13.7.

Discussion

All of the compounds prepared here except π-C_5H_5-$Co(CO)_2R_F{}^{+}ClO_4{}^{-}$ are rather stable to moisture. In some cases slight solubility without decomposition in water was observed, but the presence of water in aqueous acetone did not degrade these compounds rapidly in any event. The compounds π-C_5H_5Co-$(CO)_2R_F{}^{+}ClO_4{}^{-}$ were hydrolyzed to nonisolable products, however. None of the compounds was sensitive to atmospheric oxygen and no precautions to work under nitrogen were necessary.

Synthesis of the cationic complexes described here was accomplished through the reaction of the compounds π-$C_5H_5Co(CO)R_FI$ ($R_F = C_2F_5$, n-C_3F_7) and a benzene solution of the respective donor molecule and $AgClO_4$, the latter substance serving as a halide ion acceptor. In its general features therefore this reaction is similar to others used in the preparation of cationic complexes. Several features of this reaction should be considered more carefully, however.

Donor molecules such as triphenylphosphine or pyridine are known to displace carbon monoxide from metal carbonyl derivatives. We observed in this study that displacement of carbon monoxide in π-C_5H_5-$Co(CO)R_FI$ compounds by these donors occurs rather rapidly. Pyridine and acetonitrile but not triphenylphosphine will rapidly displace carbon monoxide from the complexes π-$C_5H_5Co(CO)[(C_6H_5)_3P]R_F{}^{+}ClO_4{}^{-}$ also. Since in the reaction of triphenylphosphine, $AgClO_4$, and π-$C_5H_5Co(CO)R_FI$ no carbon monoxide was observed to be evolved, we have concluded that the rate of reaction of $AgClO_4$ and triphenylphosphine with the π-$C_5H_5Co(CO)R_FI$ compounds is much faster than the

---

(13) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

rate of displacement of carbon monoxide with the phosphine in these compounds. Moreover, it was observed qualitatively that the AgI precipitate was formed more rapidly when $AgClO_4$ and triphenylphosphine were added together to π-$C_5H_5Co(CO)R_FI$ compounds than when $AgClO_4$ alone was added, suggesting some type of mechanism involving all three species.

A benzene-insoluble complex of 2,2′-bipyridine and $AgClO_4$ was formed when these two reagents were mixed. This was shown to react with π-$C_5H_5Co(CO)(C_3F_7)I$, but the reaction was markedly slower. It seems probable that $AgClO_4$ coordinates with other donor molecules in solution as well and that these adducts might be the reactive intermediates in these reactions.

Silver perchlorate on direct addition to π-$C_5H_5Co(CO)R_FI$ compounds precipitated AgI and gave a solution whose sensitivity to moisture suggested the presence of a σ-bonded perchlorate. Addition of a donor molecule such as bipyridine displaced the perchlorate ion forming the ionic compound.

Ligand exchange reactions of the type

$$\pi\text{-}C_5H_5CoL[(C_6H_5)_3P]C_2F_5{}^+ClO_4{}^- + L' \longrightarrow \pi\text{-}C_5H_5CoL'[(C_6H_5)_3P]C_2F_5{}^+ClO_4{}^- + L$$

using approximately equimolar quantities allowed us to define a qualitative order of stability for these complexes, with respect to the electron-pair donor ligands involved. This order, py = bipy > CH_3CN > $(C_6H_5)_3P$ > CO, is similar to the electron-pair donor power of these bases toward Lewis acids, if one disregards the position of triphenylphosphine in this series. The position of triphenylphosphine in this series might be explained in terms of steric considerations which in these compounds might be expected to have considerable influence. It should be noted that the loss of carbon monoxide when this is a component of an equilibrium system would be a factor as well, so an accurate placement of carbon monoxide in this series is not possible. However, in cases where carbon monoxide is involved the infrared spectra of these complexes (discussed below) suggest that its position at the end of this series is not without some merit.

The infrared spectra of these complexes proved to be most helpful in their characterization. The spectra of pentafluoroethyl and heptafluoro-*n*-propyl groups give a very characteristic series of absorptions. In the pentafluoroethyl compounds strong or medium bands at 1275 ± 15, 1190 ± 10, 1040 ± 10, 1010 ± 15, 895 ± 5, and 725 ± 5 cm.$^{-1}$ were observed. In compounds containing the heptafluoro-*n*-propyl group absorptions occurred at 1320 ± 5, 1220 ± 10, 1190 ± 10, 1160 ± 10, 1085 ± 5, 1035 ± 10, 1005 ± 15, 805 ± 10, 725 ± 5, and 665 ± 5 cm.$^{-1}$. Assignments for these bands have been discussed in the literature.[14]

The carbonyl stretching frequencies in cationic metal carbonyl derivatives are shifted to higher frequency above these absorptions in neutral metal carbonyls. In the isoelectronic complexes π-$C_5H_5Co(CO)_2C_2F_5{}^+ClO_4{}^-$ and π-$C_5H_5Fe(CO)_2C_2F_5$ carbonyl bands are observed at 2140 and 2080 cm.$^{-1}$ (Nujol mull) and at 2040 and 1998 cm.$^{-1}$ ($CHCl_3$ solution), respectively. While quantitative arguments are not meaningful in view of differences between the metals involved, nevertheless the results suggest qualitatively that in cationic derivatives less delocalization of electron density from the metal to antibonding π^* orbitals on carbon monoxide occurs. Such observations have also been made for other systems.[3,4]

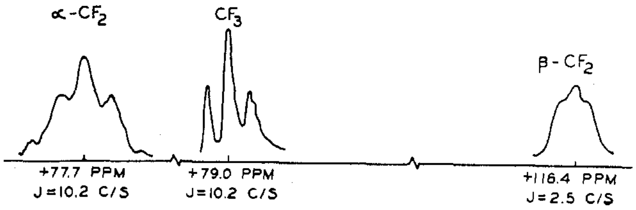


Figure 1.—^{19}F n.m.r. spectrum of π-$C_5H_5Co(CH_3CN)_2C_3F_7{}^+ClO_4{}^-$; 56.4-Mc. acetonitrile solution, CCl_3F internal standard.

The results of ^{19}F n.m.r. investigations are tabulated in Table II. For each of the heptafluoro-*n*-propyl compounds studied three groups of peaks were observed, assigned to the α- and β-CF_2 groups and the CF_3 group. A $J_{\alpha-\gamma}$ coupling constant of approximately 10–16 c.p.s. was characteristic of these spectra also. In these details the spectra for these compounds resemble known spectra of other perfluoropropyl transition metal compounds.[15] The two resonances of pentafluoroethyl groups were also anticipated. However, the over-all spectra of both pentafluoroethyl and heptafluoropropyl compounds show significant variations from those of the perfluoroalkyl groups in neutral molecules reported earlier.

When L and L′ in π-$C_5H_5CoLL'R_F{}^+X^-$ were different groups the fluorine resonances of the α-CF_2 group were seen as an AB pattern. The dissimilarity of these fluorines is a consequence of asymmetric substitution of the metal and a slow rate of rotation of the perfluoroalkyl group about the cobalt–carbon bond. Though asymmetry at the cobalt atom in the compounds π-$C_5H_5Co(CO)R_FI$ also exists, presumably equivalence of the α-fluorines results from rapid rotation about the carbon–metal bond.[16]

In addition to the α–γ coupling, further splittings were sometimes observed for the fluorine atoms of the α-CF_2 group. The resonances were broad and often difficult to evaluate completely. The observed splitting of each resonance in the AB pattern for $C_5H_5Co(CO)[(C_6H_5)_3P]C_2F_5{}^+PF_6{}^-$ and $C_5H_5Co(CH_3CN)[(C_6H_5)_3P]C_2F_5{}^+ClO_4{}^-$ into a doublet suggests coupling of each fluorine with the phosphorus atom in the triphenylphosphine ligand. Further support to this hypothesis came from the α-CF_2 pattern observed for the compound $C_5H_5Co(CH_3CN)_2C_3F_7{}^+ClO_4{}^-$. This spectrum is reproduced in Figure 1. Here the observed broad

---

[14] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

[15] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1962).

[16] However, an AB pattern for the corresponding rhodium compounds was recently observed: J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

five-line multiplet appeared most probably to arise from overlap of three quartets in a 1:1:1 intensity ratio with the further restriction that the triplet splitting be approximately one-half of the value of the quartet splitting. Again it must be stressed that the α-CF_2 resonances were always broad and thus it was difficult to obtain accurate data on coupling constants from such resonances. In one compound (π-$C_5H_5Co(CO)$-$[(C_6H_5)_3P]C_3F_7{}^+ClO_4{}^-$) the expected quartet pattern could not be resolved. Broadening of these α-CF_2 resonances might be a result of relaxation caused by the nuclear quadrupole moment of the cobalt atom or the chlorine atom of the perchlorate group.

The β-CF_2 group in some of the perfluoropropyl compounds showed evidence of further splitting. This splitting was generally quite small.

The variation of the chemical shift of the α-CF_2 in both the pentafluoroethyl and heptafluoropropyl compounds as a function of the ligand groups was striking. The chemical shift differences of almost 30 p.p.m. seem to parallel basicity of the ligands. In view of previous discussion of the α-CF_2 chemical shifts in perfluoroalkyl transition metal complexes[15] such a shift is not surprising. Certainly a variation of the electronic structure in these compounds would be in a regular pattern and the resulting paramagnetic contribution to the chemical shift would also be expected to vary accordingly.

Acknowledgment.—We are pleased to acknowledge the partial support of this work by the Wisconsin Alumni Research Foundation. Summer support to G. W. was provided by the Chemistry Department through a grant from E. I. du Pont de Nemours and Co.

Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, London W.C.1., England

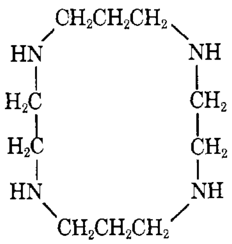
Complexes of Cobalt(III) with a Cyclic Tetradentate Secondary Amine

By B. BOSNICH, C. K. POON, and M. L. TOBE

Received February 18, 1965

1,4,8,11-Tetraazacyclotetradecane (cyclam) has been prepared by the action of 1,3-dibromopropane on 1,3-bis(2'-aminoethylamino)propane. The following complex cations have been characterized: $[Co(cyclam)Cl_2]^+$, $[Co(cyclam)Br_2]^+$, $[Co(cyclam)(NCS)_2]^+$, $[Co(cyclam)(NO_2)_2]^+$, $[Co(cyclam)(N_3)_2]^+$, $[Co(cyclam)(NH_3)_2]^{3+}$, $[Co(cyclam)N_3Cl]^+$, and $[Co(cyclam)NCSCl]^+$. Apart from the dichloro complex, only one isomeric form has been obtained, and a comparison of the visible absorption spectra with those of the corresponding bis(ethylenediamine)cobalt(III) complexes suggests that all have a *trans* configuration of the monodentate ligands. The solvolytic equilibrium of the dichloro complex has been studied in aqueous solution and the aquo complexes have been shown to be less stable than those of the corresponding bis(ethylenediamine)cobalt(III) complexes. The possible configurational isomers of these complexes are discussed and a structure is suggested.

Studies of the stereochemical consequences of substitution in octahedral complexes have led to the concept of a trigonal bipyramidal intermediate in the dissociative substitution reactions of the cobalt(III) amine complexes.[1] Most of the data refer to systems containing two ethylenediamine molecules which do not significantly resist any change in the shape of the complex, and it is now desirable to extend the investigations to molecules with greater rigidity due to the presence of macrocyclic quadridentate ligands. Although such cyclic ligands have been known for a long time, most have been of natural origin, *e.g.*, porphyrins, etc., and are highly conjugated. More recently, considerable interest has been aroused by the synthesis of such macrocyclic ligands using a metal ion as a "template,"[2,3] but, in the search for a ligand which would not differ greatly in its electronic effects from those amines used in previous studies and which did not contain superfluous organic side chains, we were fortunate to find 1,4,8,11-tetraazacyclotetradecane (cyclam)



Cyclam

which could be readily synthesized by conventional methods. This compound was first claimed by Van Alphen[4] as a product of the reaction between 1,3-dibromopropane and 1,3-bis(2'-aminoethylamino)-propane in the presence of alkali. More recently,

---

[1] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 215; R. S. Nyholm and M. L. Tobe, "Essays in Coordination Chemistry," Birkhäuser Verlag, Basel, 1964, p. 112, and references therein.

[2] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

[3] D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962); G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

[4] J. Van Alphen, *Rec. trav. chim.*, **56**, 343 (1937).