than on the second nitrogen atom removed. Also, in order to coordinate the Ca(II) ion at five or six positions, the alternate arrangement of ligand donor groups would require that the Ca(II) ion be coordinated to three nitrogen atoms and only two or three negative carboxyl groups. Since such complexes are usually considered to have relatively low stability, II is favored for the monoprotonated complexes.

The most probable coordinate bonding of all the binuclear complexes found in this investigation is III, since it involves the maximum coordination of both metal ions with negative carboxylate groups.

The formation constants for the ternuclear chelates of Ca(II) and Mg(II), illustrated by formula IV, are the first reported stability constants for a ternuclear metal chelate known to the authors. The relatively low stability of this chelate, as evidenced by $\log (K_{ML} \cdot K_{M_2L}K_{M_3L})/3 \ll \log K_{ML}$, is to be expected in view of the smaller number of coordinating groups, especially negative coordinating groups, available per metal ion. This type of effect is also clearly seen in the comparison of the stabilities of the mono- and binuclear chelates of La(III). Since a basic nitrogen atom would have very little affinity for the ions of Ca(II), Mg(II), La(III), and Th(IV), the coordination of a basic nitrogen atom in their complexes is conceivable only if there is contribution to the stability from an adjacent negative carboxylate group. Thus the alternatives for the 1:1 La(III) complexes are penta- and heptacoordination. In view of the stability of this complex, therefore, heptacoordination is favored. On this basis it is clear why the 1:1 complex has only a slight tendency to go over to a binuclear complex analogous to III. Since some of the coordinate bonds in a heptacoordinated mononuclear complex must be broken to form the binuclear complex, it is clear that the latter would not be much more stable than the mononuclear heptacoordinated complex.

Similar arguments may be used to indicate that the very stable Th(IV) TTHA chelate must be nona- or decadentate. This complex is considerably more stable than that of DTPA, which has been shown to hydrolyze at higher pH to give a monohydroxo species. This higher stability reflects higher coordination and hence must involve an additional nitrogen atom plus one or more of the carboxylate groups attached to that nitrogen atom. Also, it is known that the primary stability contributions of the polyaminopolycarboxylic acids come from the negative charges of the carboxylate groups. To achieve higher stability than that of the Th(IV)–DTPA chelate, the TTHA chelate must involve the coordination of one more carboxylate group than the number coordinated in the former.[9] Thus it seems that all six carboxylate groups, and by inference all four nitrogens, of TTHA must be coordinated to the Th(IV) ion, giving a decadentate complex.

CONTRIBUTION FROM THE INORGANIC CHEMISTRY RESEARCH LABORATORIES,
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Transition Metal Complexes Derived from Octafluorocyclohexa-1,3-diene[1]

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The interaction of octafluorocyclohexa-1,3-diene with octacarbonyldicobalt gives a complex of stoichiometry $Co_2(CO)_6C_6F_6$ which has been shown to have a cyclic fluorocarbon group bridging the metal atoms and bound to them by an acetylenic type bond. With di-π-cyclopentadienylnickel a π-cyclopentadienyl π-allyl complex is obtained, while the product with dicarbonylchlororhodium is an olefin complex.

Introduction

There are comparatively few π-complexes in which perfluoroolefins are bound to transition metal atoms: these are perfluorocyclohexadienetricarbonyliron[3] and its derivative,[4] the π-allylic ion $[C_6F_9Fe(CO)_3]^-$,[4] some recently reported perfluorocyclopentadiene complexes,[5] and a number of complexes derived from perfluorobut-2-yne.[6] We now describe further complexes obtained from octafluorocyclohexa-1,3-diene. This olefin is not particularly reactive toward metal carbonyls without bridging carbonyl groups, and at temperatures below 175° or under ultraviolet radiation no reaction occurs with $Fe(CO)_5$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, and $Mo(CO)_6$; further, there appears to be no reaction with $PdCl_2$, $PtCl_2$, or square complexes of the type L_2PdCl_2. However, interactions occurred with $Co_2(CO)_8$, $(\pi\text{-}C_5H_5)_2Ni$, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, $[\pi\text{-}C_5H_5Ni(CO)]_2$, and $[Rh(CO)_2Cl]_2$.

Experimental

Materials.—Analyses are by the Microanalytical Laboratory, Imperial College. Octafluorocyclohexa-1,3-diene was provided by Professor J. C. Tatlow, University of Birmingham, to whom we are indebted for generous gifts of this material. Octacarbon-

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[1] This research has been supported in part by the United States Air Force under Grant AF EOAR 64-75, European Office of Aerospace Research.

[2] National Science Foundation Postdoctoral Fellow.

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yldicobalt and other complexes were made by standard methods.

Infrared spectra were recorded on a Grubb-Parsons grating Spectromaster and nuclear magnetic resonance spectra on a Varian instrument at 56 Mc./sec. For ^{19}F, benzotrifluoride was used as reference; ^{1}H spectra are referred to tetramethylsilane. Melting points were taken on a Kofler hot-stage microscope and are uncorrected. Molecular weights were made using a Mechrolab osmometer.

Interaction of Octacarbonyldicobalt with C_6F_8.—Octacarbonyldicobalt (2.6 g.) and octafluorocyclohexa-1,3-diene (6.0 g.) were heated in a 25-ml. stainless steel bomb for 2 hr. at 80°. The excess diene was distilled off at reduced pressure and the residue transferred to a sublimation apparatus. After four sublimations at 35° under vacuum, red crystals were obtained (0.6 g., 15%), m.p. 47–48°.

Anal. Calcd. for $C_{12}Co_2F_6O_6$: C, 30.1; F, 24.2; Co, 25.1. Found: C, 30.5; F, 24.1; Co, 24.9. The compound is quite stable in air.

Infrared spectrum (CCl_4 and cyclohexane solutions): 2120 vs, 2086 vs, 2062 vs, 2024 w, 2014 vw, 1672 m, 1317 s, 1308 s, 1235 m, 1189 w, 1172 w, 1103 s, 1047 m, 970 m, 778 w, 738 m.

Interaction of Di-π-cyclopentadienylnickel with C_6F_8.—Di-π-cyclopentadienylnickel (2.2 g.) and octafluorocyclohexa-1,3-diene (4 g.) were heated together in a sealed Pyrex tube for 4 hr. at 85°. The excess diene was distilled from the reaction mixture at reduced pressure. The red residue was filtered through an alumina chromatographic column in petroleum ether (b.p. 60–80°) and the filtrate evaporated to dryness. The residue was crystallized twice from petroleum ether (b.p. 30–40°) at −35° to yield red crystals (0.4 g., 10%), m.p. 116–117°.

Anal. Calcd. for $C_{16}H_{10}F_8Ni$: C, 46.5; H, 2.42; Ni, 14.2; mol. wt., 413. Found: C, 46.9; H, 2.57; Ni, 14.3; mol. wt., 421 (hexane).

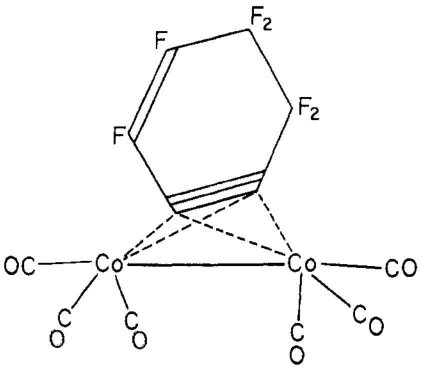
Infrared spectrum (CCl_4, CS_2, and cyclohexane solutions): 3101 vw, 3051 vw, 2955 w, 2920 w, 1757 m, 1373 m, 1360 m, 1281 s, 1258 w, 1183 s, 1165 s, 1110 m, 1073 m, 1038 w, 1008 w, 970 s, 933 s, 795 s.

Interaction of Dicarbonylchlororhodium with C_6F_8.—$[Rh(CO)_2Cl]_2$ (1 g.), octafluorocyclohexa-1,3-diene (2 g.), cesium fluoride (0.5 g.), and tetrahydrofuran (2 ml.) were heated overnight in a sealed tube at 100°. This was opened and the dark brown contents extracted in the air for 4 hr. with petroleum ether (200 ml., b.p. 40–60°). This mixture was filtered; the filtrate was concentrated to 25 ml. and cooled to −20°. An orange-brown solid was obtained which yielded a bright yellow solid after two sublimations at 170° under vacuum, m.p. 197.5–199°.

Infrared spectrum (CCl_4): 1512 m, 1453 s, 1280 vs, 1147 vs, 1078 w, 1058 s, 971 s, 940 s, 607 m.

Results and Discussion

Octacarbonyldicobalt reacts quite readily with octafluorocyclohexa-1,3-diene to give a compound of stoichiometry $C_6F_6Co_2(CO)_6$ which is quite stable with respect to oxidation by air or to substitution, *e.g.*, by molten triphenylphosphine. The infrared and ^{19}F nuclear magnetic resonance spectra are consistent with the structure I, which involves coordination to two metal atoms of a six-membered carbocyclic ring containing a triple bond. The binding of the organic moiety appears to be similar to that in other well-known acetylene complexes such as $(CO)_3Co(C_6H_5C{\equiv}CC_6H_5)Co(CO)_3$. X-Ray diffraction results have confirmed the structure proposed.[7] The spectroscopic evidence for the structure is as follows. The infrared spectrum has peaks due to carbon monoxide stretching modes at 2120, 2086, and 2062 cm.$^{-1}$ with very weak bands at 2024 and 2016 cm.$^{-1}$. A band at 1672 cm.$^{-1}$ can be assigned to a carbon–carbon stretch of some kind; this value is considerably higher than the coordinated C=C stretch in $C_6F_8Fe(CO)_3$ (1550 cm.$^{-1}$)[3] and is only 32 cm.$^{-1}$ lower than the lower of the C=C frequencies in perfluorocyclohexa-1,3-diene itself. The band is best assigned to that of the uncoordinated olefinic bond in I. The ^{19}F n.m.r. spectrum (Figure 1) has four bands with area ratios of 2:2:1:1. This total of six fluorine atoms per molecule is in agreement with the stoichiometry found by analyses. Each of the bands is a fairly complex multiplet, symmetrical about its center. The n.m.r. spectrum does not show the characteristic AB pattern for the aliphatic fluorine atoms which is observed in cases where the fluorines on the same atom have different orientations relative to the metal atom in the complex.[3] From this it is seen that the effects of the variation of the Co—C (acetylenic) distances and the deviation of the dihedral angle between the C≡C bond and the Co—Co axis from 90° found in the X-ray structure data are not observable in solution. The length of the Co—Co bond and the conformation of the CO groups is not unexpected but the geometry of the coordinated ligand is. Thus the bridging triple bond is extremely short (1.29 Å.) as compared to that in the corresponding diphenylacetylene complex[8] of 1.45 Å.; the bond length is similar to that of an uncoordinated acetylene. The remainder of the ring, which is close to planar, shows similar unusual bond lengths, varying from 1.54 Å. for the bond directed from the acetylenic carbon atoms toward their neighbors to 1.41 Å. for the bond between two aliphatic carbon atoms. On the other hand, preliminary approximate



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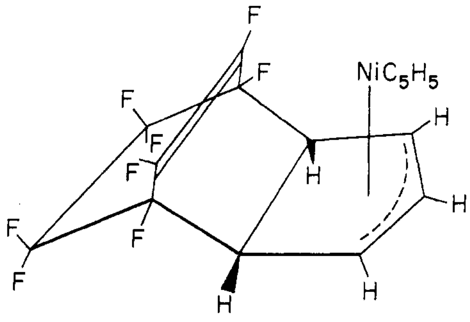

II

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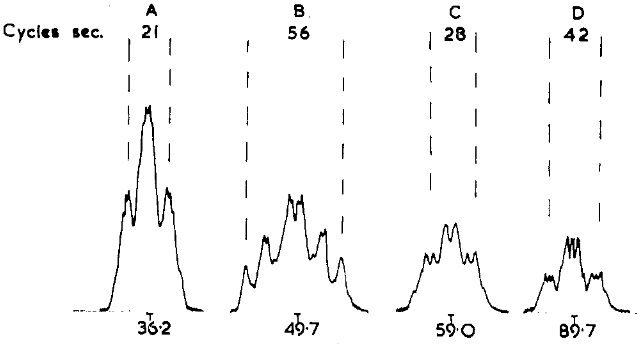

Figure 1.—^{19}F Nuclear magnetic resonance spectrum of $C_6F_6Co_2(CO)_6$ at 56 Mc./sec. Chemical shifts are given (δ) in parts per million above benzotrifluoride. The areas of bands A, B, C, and D are 2, 2, 1, and 1, respectively.

calculations for benzyne itself[9] have indicated that the acetylenic bond will be quite short (1.22 Å.), also that the longest bonds in the ring skeleton will be those from the acetylenic carbons to their neighbors; this expectation agrees with what is observed in the present case.

Attempts have been made, so far without success, to obtain a similar complex containing "perfluorobenzyne," C_6F_4. The thermal or ultraviolet radiation induced reactions of 1,2-dibromotetrafluorobenzene, hexafluorobenzene, and 1,2,3,4-tetrafluorobenzene with $Co_2(CO)_8$ lead only to decomposition. Attempts to treat cobalt carbonyl in tetrahydrofuran with the above organic compounds, bromopentafluorobenzene, or 1,2-dihalobenzenes in the presence of sodium, magnesium, or zinc produced large amounts of black material, insoluble in tetrahydrofuran.

The product from the interaction of di-π-cyclopentadienyl nickel with C_6F_8 can be fairly certainly established by spectroscopic data as II. This structure, involving conversion of a π-C_5H_5 ring to a π-allyl system, is similar to those proposed in other cases, *e.g.*, for the adduct of tetrafluoroethylene with (π-C_5H_5)$_2$Ni.[10] Thus the infrared spectrum has peaks in the C—H stretching region at 3101 (π-C_5H_5), 3053, 2955, and 2920 cm.$^{-1}$; there is only one peak in the C═C stretching region at 1757 cm.$^{-1}$ which is at slightly higher frequency than the corresponding peak in C_6F_8 at 1741 cm.$^{-1}$. This small variation could be attributed to some additional rigidity in the tricyclic system. The ^{1}H n.m.r. spectrum (Table I) for the allylic and π-C_5H_5 protons is very similar to those observed for π-cyclopentadienyl-π-cyclopentenylnickel[11] and the nickelocene–tetrafluoroethylene adduct,[10] and the relative areas are in satisfactory agreement with II. Thus band A may be assigned to the central allylic proton, band B to the π-C_5H_5 protons, band C to the terminal allylic protons, and band D to the bridgehead aliphatic protons. The ^{19}F n.m.r. spectrum is somewhat less informative. The characteristic AB pair spectrum indicates the position of the two aliphatic fluorine pairs. The other two structureless pairs give little information about the nature of the fluorine atoms involved, but the higher field band might be assigned to the olefinic fluorines on the basis of the chemical shift as compared to those in 1,3-C_6F_8. Four isomers for the compound can be drawn. However, from the ^{19}F spectrum only one seems to be present. From the relatively small chemical shift in the "AB" system, the large chemical shift upfield of the two broad bands, and simple geometrical considerations, isomer II seems most likely.

Table I

Nuclear Magnetic Resonance Spectra of π-Cyclopentadienylnickel Allyls

π-$C_5H_5Ni(C_{11}H_5F_8)$				π-C_5H_5Ni-($C_7H_5F_4$)[10]	
^{19}F		^{1}H[i]		^{1}H[i]	
Area	Position[h]	Area	Position	Area	Position
4	57.8[a]	1	4.57[d]	1	4.48[d]
	61.9[a]	5	4.73[g]	5	4.75[g]
	64.3[a]	2	6.12[e]	2	6.07[e]
	68.3[a]	2	8.56[f]	2	7.33[f]
2	91.3[b]				
2	141.7[c]				

[a] Doublet with splitting 10 c.p.s. at half-widths of 30 c.p.s. [b] Structureless band, half-width 12 c.p.s. [c] Structureless band, half-width 30 c.p.s. [d] Triplet with splitting of ~5 c.p.s. [e] Broad, half-width ~10 c.p.s. [f] Structureless band, half-width ~20 c.p.s. [g] Sharp, half-width ≤ 2 c.p.s. [h] P.p.m. upfield from benzotrifluoride. [i] ^{1}H positions are measured in p.p.m. downfield from tetramethylsilane.

The interaction of dicarbonylchlororhodium with octafluorocyclohexa-1,3-diene occasionally yielded small amounts of yellow crystals as the only product. The infrared and ^{19}F nuclear resonance spectra are consistent with the formulation $[(C_6F_8)_2RhCl]_2$. The ^{19}F spectrum consisted of an AB pair with one doublet at 30 p.p.m. and a doublet at 52 p.p.m., each with splittings of about 230 c.p.s. Two bands were also observed, at 106 and 125 p.p.m. These suggest that the complex has a coordinated 1,3-diene similar to that found in $C_6F_8Fe(CO)_3$.[3]

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