

(m), 1342 (s), 1170 (w), 1015 (w), 872 (w), 850 (m), 660 (w), and 281 cm^{-1} (w).

Anal. Calcd for $\text{C}_{49}\text{H}_{43}\text{P}_3\text{RhN}_2\text{O}_4\text{Cl}$: C, 61.61; H, 4.54; N, 2.93; Cl, 3.71; mol wt 955. Found: C, 60.90; H, 4.52; N, 2.89; Cl, 3.71; mol wt (CHCl_2) 996.

Reaction of $\text{RhCl}(\text{CO})(\text{TDPME})$ with HCl .—A sample of 0.1 mmol of $\text{RhCl}(\text{CO})(\text{TDPME})$ was placed in a 6-ml serum bottle and flushed and evacuated with N_2 ; to this was added 3 ml of CH_2Cl_2 . Dry HCl gas, 2.5 ml (0.103 mmol at 760 mm (25°)), was added and the red-brown color of the solution immediately faded to a bright yellow. After stirring for 1 hr at room temperature, *n*-hexane was added to the cloud point. After cooling for 12 hr at 0°, yellow microcrystals formed. These were filtered, washed with *n*-hexane, and dried (65° (0.1 mm)) to yield 47 mg (59%); ir spectrum (CsI): 2030 (w), 800 (w), 298 (w), and 286 cm^{-1} (w).

Anal. Calcd for $\text{C}_{41}\text{H}_{40}\text{P}_3\text{RhCl}_2$: C, 61.59; H, 5.04; Cl, 8.87; mol wt 799. Found: C, 61.13; H, 5.30; Cl, 8.95; mol wt (CH_2Cl_2) 815.

Reaction of $\text{RhCl}(\text{CO})(\text{TDPME})$ with Cl_2 .—Chlorine gas was bubbled into the red-brown suspension of 110 mg of $\text{RhCl}(\text{CO})(\text{TDPME})$ in 6 ml of dry benzene. After a few minutes the solution turned yellow. After sitting at room temperature for 10 min, the suspension was filtered and the residue was washed with ether and with benzene and then dried at 65° (0.1 mm). A yellow powder was obtained; ir spectrum (CsI): no carbonyl bands, 300 (w), 288 (w), and 275 cm^{-1} (w).

Anal. Calcd for $\text{C}_{41}\text{H}_{39}\text{P}_3\text{RhCl}_3$: C, 59.05; H, 4.71; Cl 12.75. Found: C, 56.47; H, 4.55; Cl, 13.47.

Preparation of $\text{IrN}_3(\text{CO})(\text{TDPME})$.—To 0.19 mmol of $\text{IrN}_3(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ in a Schlenk tube was added 14 ml of dry benzene. To this bright yellow solution was added 0.19 mmol of TDPME. The solution, which immediately became orange, was stirred at room temperature for *ca.* 12 hr by which time an orange solid had precipitated. A total of 20 ml of *n*-hexane was added in small aliquots and the mixture was filtered under argon. The precipitate was washed with *n*-hexane and dried (0.1 mm) to yield 147 mg (88%) of an air-sensitive orange powder; ir spectrum (KBr): 2040 (vs), 1900 (s), and 1275 cm^{-1} (w).

Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{P}_3\text{N}_3\text{O}$: C, 56.88; H, 4.43; N, 4.74. Found: C, 56.45; H, 4.43; N, 4.36.

Reaction of $\text{IrN}_3(\text{CO})(\text{TDPME})$ with CO .—To 40 mg of $\text{IrN}_3(\text{CO})(\text{TDPME})$ in a Schlenk tube under argon was added 1.5 ml of dry CH_2Cl_2 . The argon atmosphere above the solution was exchanged for CO (by repeatedly evacuating and filling); after stirring under CO for *ca.* 5 min, the solution changed from orange to pale yellow. Solution samples were withdrawn at intervals and their ir spectra were recorded in 0.1-mm KBr cells. After 0.5 hr, the 2040 (vs) and 1905 cm^{-1} (s) bands had been replaced with new peaks at 2140 (m), 2045 (s), and 1970 cm^{-1} (s); after 4 hr the spectrum remained the same but after 17 hr a weak absorption at 2230 cm^{-1} had appeared. The CO atmosphere above the solution was exchanged for argon and the solution was heated to 70°, but no changes were observed in the ir spectrum. After stirring under CO for 17 hr, a small amount of white solid precipitated from solution. Attempts to isolate homogeneous products from this run or larger scale runs were unsuccessful. The powders obtained often contained strong isocyanate and/or carbonate bands in addition to a band at *ca.* 2040 cm^{-1} (probably azide).

Reaction of $\text{IrN}_3(\text{CO})(\text{TDPME})$ with O_2 .—A sample of $\text{IrN}_3(\text{CO})(\text{TDPME})$ was exposed to air for several days. A pale yellow powder was obtained which was only sparingly soluble in CH_2Cl_2 ; ir spectrum (KBr): 2040 (vs), 1665 (s, br), 1620 (m), and 1280 cm^{-1} (w).

Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{P}_3\text{IrN}_3\text{O}_2$: C, 54.90; H, 4.28; N, 4.57. Found: C, 55.70; H, 4.44; N, 4.20.

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The Preparation of Some Cobalt Carbonyl Complexes Containing Ligand-Bridged Metal Atoms

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The complexes $\text{LCO}_2(\text{CO})_6$, $\text{LCO}_2(\text{CO})_4\text{HCCCC}_6\text{H}_5$, $\text{ffarsCO}_2(\text{CO})_5$, $\text{CH}_3\text{CCO}_3(\text{CO})_7\text{ffars}$, and $\text{Co}_4(\text{CO})_8(\text{ffars})_2$ are described, and ligand-bridged structures are assigned to them on the basis of their infrared spectra. The ligands L and ffars are fluoro-carbon-bridged ditertiary arsines and phosphines.

Introduction

Tertiary phosphine and arsine derivatives of dicobalt octacarbonyl often exist in solution as an equilibrium mixture containing both carbonyl-bridged and non-bridged forms. As a result these species tend to have complicated infrared spectra in the carbonyl stretching region.¹ This behavior is the same as that of the parent dicobalt octacarbonyl which has been shown, from a study of the carbonyl infrared spectrum, to exist in pentane solution at room temperature as $\sim 45\%$ bridged

form and $\sim 55\%$ nonbridged form.^{2,3} Other tertiary phosphine derivatives of dicobalt octacarbonyl such as $[(\text{C}_6\text{H}_5)_3\text{PCo}(\text{CO})_3]_2$ and $[(\text{C}_4\text{H}_9)_3\text{PCo}(\text{CO})_3]_2$ exist in solution⁴ and in the solid state⁵ in the nonbridged form only. This may be a result of steric interaction between the very bulky organophosphine groups. Other ligands, such as 1,2-bis(diphenylphosphino)ethane, which might be expected to fix the dicobalt carbonyl moiety in a

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bridged or nonbridged form, react with dicobalt octacarbonyl to give ionic species containing no metal-metal bonds.⁶

In a preliminary communication we showed that $\text{ffarsCo}_2(\text{CO})_6$,⁷ **1** [ffars = 1,2-bis(dimethylarsino)tetrafluorocyclobutene], has a crystal structure closely related to that of dicobalt octacarbonyl,⁸ in which the ligand ffars bridges two carbonyl-bridged cobalt atoms. Infrared studies show that this structure is retained in solution. This present paper enlarges upon these results and also describes preparation of other derivatives of dicobalt octacarbonyl, methynyltricobalt enneacarbonyl, and tetracobalt dodecacarbonyl in which two cobalt atoms are bridged by ffars and related ligands. Structures are assigned to these compounds on the basis of infrared and mass spectroscopy. This behavior where ffars and similar ligands bridge two metal atoms in a metal carbonyl cluster now appears fairly general; thus this work can be regarded as an extension of our earlier work, where we showed that $\text{ffarsFe}_3(\text{CO})_{10}$ ⁹ and $\text{ffarsRu}_3(\text{CO})_{10}$ and $\text{ffarsRu}_3(\text{CO})_8$ ¹⁰ retained the parent carbonyl skeleton, and the ligand bridged two metal atoms.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 457 spectrometer. The solvent was cyclohexane. ¹H nmr spectra were recorded on Varian T-60 and HA 100 spectrometers. TMS was used as internal standard. All elemental analyses were done by Mr. P. Borda of this department, and the data for new compounds are listed in Table I. Mass spectra were run on an AEI MS 9 spectrometer with direct introduction of solid samples. All reactions were done under nitrogen.

The preparation of most of the ligands has been described previously;¹¹ however, we have not reported the preparation of the mixed ligand used in this investigation.

Preparation of 1-Diphenylphosphino-2-dimethylarsinohexafluorocyclopentene.—1-Dimethylarsinoheptafluorocyclopentene (14 g, 47 mmol), made by the reaction of equimolar quantities of dimethylarsine and perfluorocyclopentene at 20°, and diphenylphosphine (8.7 g, 47 mmol) were heated at 45° for 2 days. The solid products were separated by dissolving in acetone and filtering the solution. The acetone was removed at reduced pressure and the residue was dissolved in dichloromethane and chromatographed on a Florisil column. The product was eluted using a 1:1 mixture of benzene and petroleum ether (bp 30–60°) and crystallized from hexane (yield 4 g, 18%). *Anal.* Calcd for

$(\text{CH}_3)_2\text{AsC}=\text{CP}(\text{C}_6\text{H}_5)_2\text{CF}_2\text{CF}_2\text{CF}_2$: C, 49.1; H, 3.4; F, 24.5. Found: C, 49.0; H, 3.3; F, 24.6.

1. Preparation of $\text{LCO}_2(\text{CO})_6$.—Equimolar quantities of ligand and dicobalt octacarbonyl (~0.4 g) were stirred in hexane or ether solution (35 ml) for 2 hr at about 20°. The solvent was removed under reduced pressure and the residue was dissolved in about 1 ml of dichloromethane and chromatographed on a Florisil column using petroleum ether (bp 30–60°) as the eluent. The major band was eluted from the column, the volume of the solvent was reduced at low pressure, and the solution was then cooled (0 to –80°) to yield small red-brown crystals of the product $\text{LCO}_2(\text{CO})_6$ which was washed with a small amount of cold hexane and dried (yields 0.4–0.2 g, 60–30%). The other

brown bands on the column which could also be eluted with petroleum ether yielded sticky solids thought to consist of decomposed or polymerized ligand. The ¹H nmr spectrum of $\text{ffarsCo}_2(\text{CO})_6$ (**1**) showed one peak at τ 8.29 in the temperature range +30 to –60°. The ¹H nmr of $\text{CF}_3\text{As}(\text{CH}_3)_2\text{C}=\text{CAs}(\text{CH}_3)_2\text{CF}_3\text{Co}_2(\text{CO})_6$ (**2**) showed one peak at τ 8.21 at 30°.

2. Preparation of $\text{ffarsCo}_2(\text{CO})_6$, **9.**— $\text{ffarsCo}_2(\text{CO})_6$ (~0.8 g) was dissolved in cyclohexane (20 ml) and refluxed until the carbonyl infrared spectrum of the starting material had disappeared. The product was chromatographed and crystallized as in experiment 1 to yield $\text{ffarsCo}_2(\text{CO})_6$ as crumbly red-brown crystals (0.4 g, 50%) highly sensitive to air.

3. Preparation of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{ffars}$, **10.**— $\text{ffarsCo}_2(\text{CO})_6$ (3.0 g, 5 mmol) was stirred in acetone (50 ml) with phenylacetylene (0.5 g, 5 mmol) for 6 hr. The acetone was removed at reduced pressure and the residue was washed with hexane (5 ml) leaving behind unreacted $\text{ffarsCo}_2(\text{CO})_6$ (1.5 g). The hexane washings were concentrated and the residue was chromatographed on a Florisil column. A red band was eluted with petroleum ether, and a brown band was eluted with a mixture of petroleum ether-ether (10:1). The red band yielded a red oil which gave a few crystals at –80° (0.1 g, 10%). The red oil was characterized as $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5$ by its mass spectrum (strong molecular ion and progressive loss of six carbonyl groups) and carbonyl infrared spectrum. An authentic sample of this was made for comparison, by reaction of phenylacetylene and dicobalt octacarbonyl.¹² The brown band yielded $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{ffars}$ (0.6 g, 50%) as an amorphous brown solid. The ¹H nmr spectrum showed peaks at τ 8.68, 6.17, and 2.9–2.4 in the ratio 12:1:5, at 30° and at –50° the peak at high field split into three peaks at τ 8.81, 8.73, and 8.69 in the ratio 1:1:2.

4. Preparation of $\text{ffarsCo}_2(\text{CO})_4\text{C}_6\text{H}_5\text{CCH}$ and $\text{f}_4\text{fosCo}_2(\text{CO})_4\text{C}_6\text{H}_5\text{CCH}$ (11** and **12**).**—Dicobalt octacarbonyl (1.0 g, 3 mmol) was stirred in hexane solution (30 ml) with phenylacetylene¹² (0.3 g, 3 mmol) for 2 hr or until the color of the solution had turned deep red. ffars (1.0 g, 3 mmol) was added and the mixture refluxed for 6 hr. The solution was concentrated, chromatographed, and crystallized to yield $\text{ffarsCo}_2(\text{CO})_4\text{C}_6\text{H}_5\text{CCH}$ (1.5 g, 75%) as long black crystals. The same product could also be made by refluxing $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{ffars}$ in hexane for 3 hr. Chromatography and recrystallization yielded $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{ffars}$. The ¹H nmr spectrum showed peaks at τ 8.55, 8.44, 4.50, and 2.9–2.7 in the ratio 6:6:1:5 at 30°. $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ was made by the direct route described for the analogous ffars complex.

5. Methynyltricobalt Enneacarbonyl Reactions.¹³—(a) $\text{CF}_3\text{C}(\text{CO})_3(\text{CO})_6$ (0.7 g, 1.5 mmol) and ffars (0.5 g, 1.5 mmol) were refluxed in hexane (20 ml) for 7 hr. The solution was filtered and left at 0° for 36 hr. Small black crystals separated from the brown solution (infrared examination of the solution showed it to contain mainly monosubstituted $\text{CF}_3\text{CCO}_3(\text{CO})_9$ ¹⁴). These were collected and recrystallized from dichloromethane-hexane to yield $\text{Co}_3(\text{CO})_9(\text{ffars})_2$, **13** (0.1 g, 8%), as black needle-shaped crystals.

(b) $\text{CH}_3\text{CCO}_3(\text{CO})_9$ and ffars were treated as above, but the infrared spectrum showed that only one carbonyl group was being displaced from the metal carbonyl. $\text{CH}_3\text{CCO}_3(\text{CO})_9$ (0.65 g, 1.4 mmol) and ffars (0.48, 1.4 mmol) were sealed in a Carius tube with hexane (3 ml) and heated to 105° for 14 hr. The tube was opened, the hexane was removed at reduced pressure, and the residue was chromatographed and crystallized as described earlier. A red band which eluted with petroleum ether-ether (98:2) yielded $\text{CH}_3\text{CCO}_3(\text{CO})_9\text{ffars}$, **14** (0.4 g, 30%), as bright red crystals. All other ligands when treated in an analogous manner with $\text{CF}_3\text{CCO}_3(\text{CO})_9$ or $\text{CH}_3\text{CCO}_3(\text{CO})_9$ yielded brown oils or solids with infrared spectra characteristic of the monosubstituted tricobalt complexes.¹⁴

Results and Discussion

(1) $\text{LCO}_2(\text{CO})_6$ Complexes.—The complexes formed by the facile reaction of dicobalt octacarbonyl and ligand (L) were found by means of their elemental

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TABLE I
 ANALYTICAL DATA FOR NEW COMPOUNDS^a

Complex	No.	Calcd			Found		
		C	H	F	C	H	F
ffarsCo ₂ (CO) ₆	1	27.1	1.9	12.3	27.3	2.0	12.0
(CH ₃) ₂ AsCCF ₃ =CCF ₃ As(CH ₃) ₂ Co ₂ (CO) ₆	2	25.6	1.8	17.3	25.7	1.9	17.0
(CH ₃) ₂ AsCF(CF ₃)CF ₂ As(CH ₃) ₂ Co ₂ (CO) ₆	3	24.2	1.9	17.7	24.2	1.8	18.0
(CH ₃) ₂ AsCHF ₂ CF ₂ As(CH ₃) ₂ Co ₂ (CO) ₆	4	24.9	2.2	...	24.0	1.8	...
(CH ₃) ₂ AsC=CP(C ₆ H ₅) ₂ CF ₂ CF ₂ CF ₂ Co ₂ (CO) ₆	5	40.0	2.1	15.2	40.2	2.2	14.9
f ₄ fosCo ₂ (CO) ₆	6	52.3	2.6	9.7	52.0	2.5	9.8
f ₃ fosCo ₂ (CO) ₆	7	50.6	2.4	13.9	50.5	2.3	13.7
f ₂ fosCo ₂ (CO) ₆	8	49.1	2.3	17.2	49.8	2.4	17.0
ffarsCo ₂ (CO) ₆	9	26.4	2.0	...	26.7	2.0	...
C ₆ H ₅ CCHCo ₂ (CO) ₅ ffars	10	36.4	2.6	10.9	36.1	2.3	11.0
C ₆ H ₅ CCHCo ₂ (CO) ₄ ffars	11	36.1	2.7	11.4	35.8	2.8	11.3
C ₆ H ₅ CCHCo ₂ (CO) ₄ f ₄ fos	12	58.1	3.2	9.2	58.1	3.0	9.5
(ffars) ₂ Co ₄ (CO) ₈	13	25.7	2.1	...	25.6	1.7	...
CH ₃ CCo ₂ (CO) ₇ ffars	14	27.8	2.0	10.3	28.0	2.2	10.1

^a ffars ≡ (CH₃)₂AsC=CAAs(CH₃)₂CF₂CF₂; f_nfos ≡ (C₆H₅)₂PC=CP(C₆H₅)₂(CF₂)_{n/2} (n = 4, 6, 8).

analysis (Table I) and mass spectra to have the stoichiometry LC₂(CO)₆. The mass spectra of most LC₂(CO)₆ complexes showed a molecular ion followed by successive loss of six carbonyl groups and also peaks attributable to LC₂⁺ and L⁺, the latter often being the most intense peak in the spectrum. Complexes of the ditertiary phosphine ligands 6–8 showed peaks at highest mass attributable to [molecular ion – CO]⁺.

The infrared spectra of these complexes in the carbonyl region are tabulated in Table II. The spectra are simple

 TABLE II
 CARBONYL INFRARED STRETCHING
 FREQUENCIES OF LC₂(CO)₆^a

Complex	Terminal	Bridging CO
1	2052 (6), 2020 (8), 1996 (10)	1842 (3), 1786 (3)
2	2068 (5), 2006 (6), 1996 (10)	1812 (1), 1800 (3)
3	2072 (6), 2007 (8), 2000 (10)	1816 (2), 1802 (4)
4	2061 (5), 2052 (6), 2017 (8), 2002 (6) sh, 1996 (10)	1844 (5), 1818 (1), 1802 (4), 1774 (4)
5	2068 (9), 2013 (9) sh, 2010 (9), 1995 (10) br	1826 (3), 1792 (6)
6	2066 (1), 2052 (5), 2022 (8), 1998 (10)	1842 (2), 1798 (2)
7	2072 (7), 2006 (10), 1998 (8)	1818 (2), 1800 (5)
8	2072 (7), 2004 (10), 1998 (9)	1818 (2), 1802 (5)

^a Spectra were run in C₆H₁₂ solution. Values are listed in cm⁻¹ and relative intensities are given in parentheses.

and indicate that unlike Co₂(CO)₈ the complexes maintain their bridged structure in solution and do not appear to exist as an equilibrium mixture of both bridged and unbridged forms.

Using the well-known solid-state structure of dicobalt octacarbonyl as a model,⁸ it is apparent that there are three possible structures—A, B, and C of Figure 1—for all the complexes 1–8. Structure C contains a unique carbonyl group on the substituted cobalt atom which would be expected to have its stretching frequency at lower energy and would manifest itself as a single isolated peak in the infrared spectra. As this is not seen in any of the complexes 1–8, structure C can be discounted. By inspection of the bridging carbonyl frequencies of the complexes we have assigned complexes 1 and 6 structure A and complexes 2, 3, 7, and 8 structure B of Figure 1. It can be seen that the bridging carbonyl groups in structure A are not placed symmetrically with respect to the ligand whereas in structure B they are both located in positions

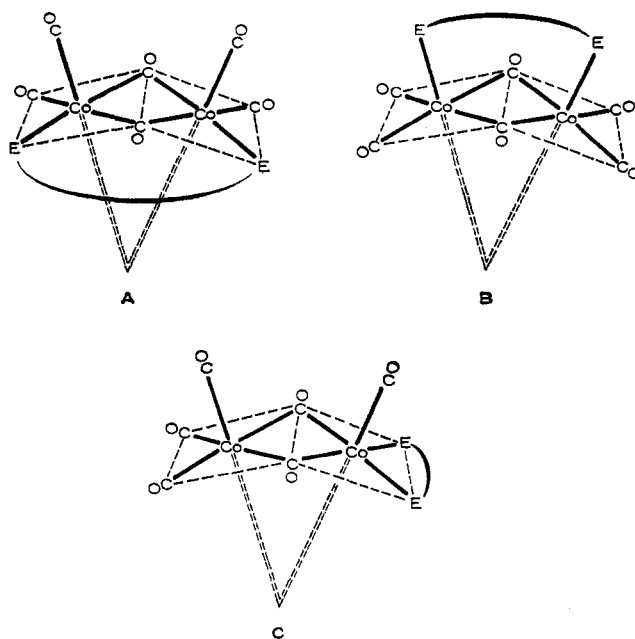


Figure 1.—Possible structures of LC₂(CO)₆. The bidentate ligand L is represented by EE.

cis to the ligand. Thus it is likely that the asymmetric and symmetric stretches of the bridging carbonyl groups will be of a much larger energy difference in complexes with structure A than in those with structure B. It is on this basis that we have assigned structure A to complex 1, where the bridging carbonyl stretching frequencies are 1842 and 1786 cm⁻¹, a difference of 56 cm⁻¹, and structure B to complex 2, where the bridging carbonyl stretching frequencies are 1812 and 1800 cm⁻¹, a difference of only 12 cm⁻¹. These two typical spectra are shown in Figure 2. As we mentioned in the Introduction, X-ray studies have shown that complex 1, ffarsCo₂(CO)₆, has essentially the structure predicted (Figure 1A).⁷ These structural assignments are also given weight by the remarkable similarity of the terminal carbonyl stretching frequency patterns of the complexes assigned the same structure.

Complex 4 has a more complicated carbonyl infrared stretching spectrum which is also shown in Figure 2. In this case the bridging carbonyl stretching frequencies give a clear indication that *this* complex exists in solution

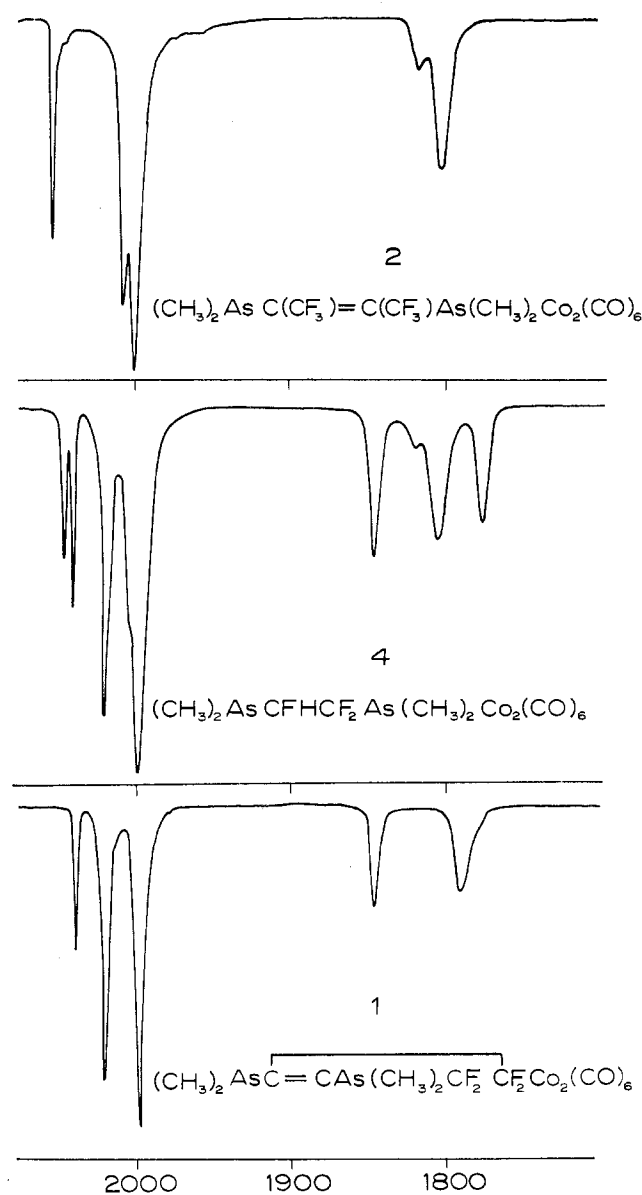


Figure 2.—Infrared spectra in the region 2100–1600-cm⁻¹ of complexes 1, 2, and 4.

as a mixture of isomers of structures A and B. The peaks at 2052, 2017, 1996, 1844, and 1744 cm⁻¹ are those from structure A, and peaks at 2061, 2002, 1996, 1818, and 1802 cm⁻¹ are those from structure B. Unsuccessful attempts were made by means of chromatography and crystallization to separate these two isomers of complex 4, so it is likely that they are interconvertible in solution. This conversion could probably proceed *via* a nonbridged structure similar to that observed in the solution infrared spectrum of dicobalt octacarbonyl.² It is probable that the presence of substituents with a low steric bulk on the fluorocarbon bridge of the ligand (CH₃)₂AsCHFCF₂As(CH₃)₂ allows this ligand to adopt a variety of conformations about the carbon-carbon bond; hence both structures A and B can be accommodated, whereas all other complexes are held in or prefer a single structure because of the bulkiness or rigidity of these ligands. The lability of complex 4 may also result in its low stability to air and light compared with some of the other complexes.

The ¹H nmr spectrum of ffarsCo₂(CO)₆, 1, is a single sharp peak at temperatures down to -60°, which indi-

cates that the stereochemically nonequivalent methyl groups in this molecule⁷ are rendered magnetically equivalent in solution by an averaging process that could involve formation of a noncarbonyl bridged form of ffarsCo₂(CO)₆ followed by rearrangement of the carbonyl groups and subsequent re-formation of the carbonyl bridges. The net result of this process would be to change the angle between the planes containing the cobalt atoms from 90 to 270° and thus average the environment of the arsenic methyl groups.

The "bite" of the ligand, *i.e.*, the arsenic-arsenic distance, may be the controlling factor as to which structure is preferred by the complex. Our previous work^{7,10,15} indicates that the ligands containing butene rings form chelate complexes less readily than the other ligands. From this one might deduce that there is a considerably different distance between the group V atoms in the cyclobutene-derived ligands than there is in the other ligands and that this may also be why their LCo₂(CO)₆ complexes assume structure A in preference to structure B which is assumed by the complexes of most other ligands. This topic, however, has not been simplified by the recent finding¹⁶ that the group V atom separation in these ligands may change drastically on complex formation.

(2) **Reactions of ffarsCo₂(CO)₆ (Scheme I).**—While ffarsCo₂(CO)₆ is stable in the solid form to light and air for an almost indefinite period, it shows a marked instability to heat both in the solid state and in solution. During attempts to sublime ffarsCo₂(CO)₆ it was found that discoloration and decomposition of the solid occurred around 80–90°. Attempts to prepare (ffars)₂Co₂(CO)₄ by heating ffars and ffarsCo₂(CO)₆ in hexane solution failed to yield the desired product; decomposition of the ffarsCo₂(CO)₆ occurred. However by careful control of the experimental conditions during the decomposition of ffarsCo₂(CO)₆ a complex of stoichiometry ffarsCo₂(CO)₅ (9) could be isolated. The mass spectrum of this complex shows a molecular ion followed by five peaks due to progressive loss of carbon monoxide, whereas the mass spectrum of ffarsCo₂(CO)₆ shows an additional peak due to ffarsCo₂(CO)₆⁺. The infrared spectrum of 9 in the carbonyl region shows five sharp peaks in the region characteristic of terminal carbonyl groups (Table III). The probable structure of this com-

TABLE III
INFRARED SPECTRA IN RANGE 1600–2100
CM⁻¹ OF SOME NEW COMPLEXES

Complex	CO str freq, cm ⁻¹
9	2074 (5), 2056 (10), 2012 (6), 1994 (9), 1981 (8)
10	2076 (9), 2019 (10), 2010 (10), 2002 (2) sh, 1973 (2) br
11	2036 (9), 2001 (10), 1978 (10), 1955 (3)
12	2036 (9), 2011 (9) sh, 2007 (10), 1986 (10), 1964 (3)
13	2012 (10), 1976 (8), 1967 (7), 1950 (6), 1790 (6), ^a 1766 (4) ^a
14	2059 (6), 2010 (10) br, 1999 (10), 1885 (1), ^a 1864 (5), ^a 1831 (4) ^a

^a Bridging carbonyl stretching frequencies.

pound is shown in Figure 3. This has five terminal carbonyl groups and both cobalt atoms have a krypton electronic configuration. The carbon-carbon double bond is supplying two electrons to a cobalt atom in place of the carbon monoxide group which has been lost from the

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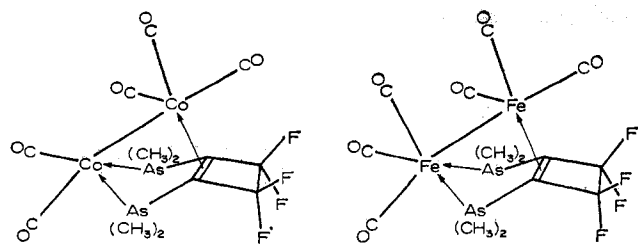
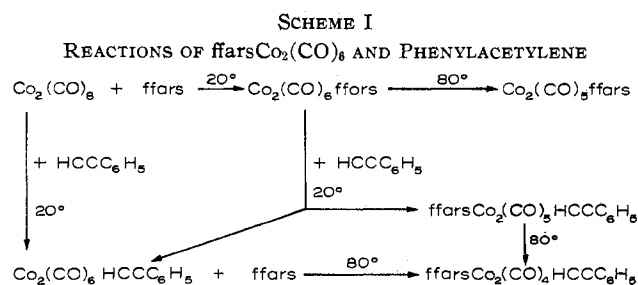


Figure 3.—Likely structure of $\text{ffarsCo}_2(\text{CO})_5$ and known structure of $\text{ffarsFe}_2(\text{CO})_6$.



molecule. This postulated structure for $\text{ffarsCo}_2(\text{CO})_5$ is similar to that of $\text{ffarsFe}_2(\text{CO})_6$ whose structure has been determined by X-ray diffraction,¹⁷ and the only significant difference, apart from the number of carbonyl groups present, is that in the case of the iron complex the metal-metal bond is of a dative covalent type, whereas in the cobalt complex there is a normal covalent metal-metal bond. The solution infrared spectra in the carbonyl region of $\text{ffarsCo}_2(\text{CO})_5$ and $\text{ffarsFe}_2(\text{CO})_6$ ^{11b} are surprisingly similar, which can be taken as some evidence for the postulated structure shown in Figure 3. $\text{ffarsCo}_2(\text{CO})_5$ is highly unstable and can be regarded as a very stable reaction intermediate in the total decomposition of $\text{ffarsCo}_2(\text{CO})_6$. Also shown in Scheme I is one of the other reactions of the otherwise somewhat unreactive $\text{ffarsCo}_2(\text{CO})_6$. This is the reaction with phenylacetylene. Infrared data for these new products are shown in Table III. From the scheme it can be seen that phenylacetylene will displace carbon monoxide or ffars from $\text{ffarsCo}_2(\text{CO})_6$ to yield $\text{ffarsCo}_2(\text{CO})_5\text{C}_6\text{H}_5\text{CCH}$ (10) or $\text{Co}_2(\text{CO})_6\text{C}_6\text{H}_5\text{CCH}$; however, it seems probable for steric reasons that phenylacetylene first displaces a carbonyl group which then displaces the arsenic ligand. At higher temperatures the ligands ffars and f_4fos will displace two carbonyl groups from $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_6$ to give the black, air-stable solids $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ (11) and $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ (12). Other ligands reacted with $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_6$ to yield only oily liquids or tarry solids which could not be purified.

The ¹H nmr spectrum of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ shows, as expected, two peaks at τ 8.55 and 8.44 which can be ascribed to the inequivalent methyl groups on the same arsenic atom. The ¹H nmr spectrum of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{f}_4\text{fos}$ at 30° shows one asymmetric peak at τ 8.68 which must be due to all the arsenic methyl protons; however, at lower temperatures this peak splits into a doublet and a singlet. Presumably the doublet is due to the methyl groups on the coordinated arsenic atom, and the single peak (to lower field) is due to the methyl groups on the uncoordinated arsenic atom. The two methyl groups on the coordinated arsenic atom are ren-

(17) F. W. B. Einstein and J. Trotter, *J. Chem. Soc. A*, 824 (1967).

dered inequivalent by the asymmetry of the adjacent cobalt atom. The mass spectra of both $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ and $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{f}_4\text{fos}$ show parent ions and successive loss of four carbonyl groups. The mass spectrum of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{f}_4\text{fos}$ shows a peak at highest mass attributable to $[\text{P} - \text{CO}]^+$; this is probably because rearrangement to $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ occurs on the probe at the inlet temperature ($\sim 160^\circ$). The structures of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ and $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_5\text{f}_4\text{fos}$ are likely to be similar to that of $\text{ffarsCo}_2(\text{CO})_6$, with the phenylacetylene molecule replacing the bridging carbonyl groups, as illustrated in Figure 4.

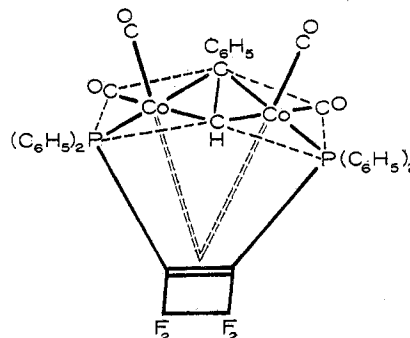


Figure 4.—Likely structure of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ (12).

The presence of only one acetylenic proton resonance in the ¹H nmr of $\text{C}_6\text{H}_5\text{CCHCo}_2(\text{CO})_4\text{f}_4\text{fos}$ means that only one isomer is present and for steric reasons it is thought that this one would have the phenyl group located away from the ligand.

(3) **Other Complexes.**—The reaction between $\text{CH}_3\text{CCO}_2(\text{CO})_5$ and ffars at 100° in hexane yields, after purification, a red air-stable solid whose elemental analysis indicates the stoichiometry $\text{CH}_3\text{CCO}_2(\text{CO})_7\text{ffars}$. A mass spectrum was obtained which showed the presence of a parent ion followed by successive loss of seven carbonyl groups confirming the formulation. The infrared spectrum of $\text{CH}_3\text{CCO}_2(\text{CO})_7\text{ffars}$ has three or possibly four terminal carbonyl bands and three bridging carbonyl bands (Table III). With these infrared data in mind the structure shown in Figure 5 has been postu-

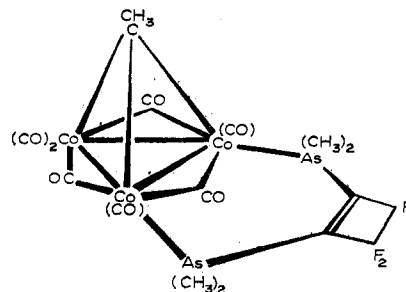


Figure 5.—Likely structure of $\text{CH}_3\text{CCO}_2(\text{CO})_7\text{ffars}$ (14).

lated for this ffars complex in solution. A recent structural determination^{18a} of $\text{CH}_3\text{CCO}_2(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ has shown that substitution of carbonyl groups occurs in the plane of the cobalt atoms, so by analogy the ligand ffars would be expected to be in an equatorial position bridging two cobalt atoms.^{18b,19} Bridging by the ligand is

(18) (a) M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, **9**, 302 (1970). (b) This gross structure has now been confirmed by an X-ray investigation. However, the ligand lies below the plane of the three cobalt atoms.¹⁹

likely to occur because as mentioned above ffars is reluctant to form chelate type complexes.

In contrast the reaction of $\text{CF}_3\text{CCO}_3(\text{CO})_9$ and ffars in refluxing hexane produces a small amount of some air-stable black crystals which have an elemental analysis corresponding to the formula $\text{Co}_4(\text{CO})_8(\text{ffars})_2$. The fate of the CF_3C group is unknown. The mass spectrum of the solid is consistent with the formula. The structure of the solid as determined by X-ray studies¹⁹ is shown in Figure 6. It consists of a tetrahedron of cobalt atoms

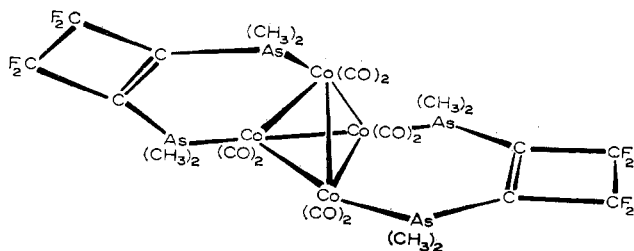


Figure 6.—X-Ray diffraction structure of $(\text{ffars})_2\text{Co}_4(\text{CO})_8$ (13).

bridged by two ligands. Because of the absence of bridging carbonyl groups, the structure is related to that of $\text{Ir}_4(\text{CO})_{12}$, (T_d symmetry)²⁰ rather than the carbonyl-bridged (C_{3v}) structures of $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$.^{21–23} The infrared spectrum of $\text{Co}_4(\text{CO})_8(\text{ffars})_2$ has five sharp

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bands in the terminal carbonyl region and two in the bridging carbonyl region. Thus the structure in solution is probably different. Although there has been some debate^{24–26} about the possibility that in solution $\text{Co}_4(\text{CO})_{12}$ has a structure (or structures) different from that of the solid state, including a nonbridged structure of T_d symmetry, the ^{59}Co nmr results^{27,28} indicate that this is not so.

Very few other tertiary phosphine, arsine, or stibine derivatives of $\text{Co}_4(\text{CO})_{12}$ have been isolated²⁹ and only a little more is known about the derivatives of $\text{Ir}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$.^{30,31} It is worth noting that both $\text{Ir}_4(\text{CO})_{10}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and $\text{Ir}_4(\text{CO})_9(\text{P}(\text{C}_6\text{H}_5)_3)_3$ have bridging carbonyl groups.

In view of the ease with which $\text{Co}_2(\text{CO})_8$ is converted into $\text{Co}_4(\text{CO})_{12}$ on warming, we thought that strong heating of $\text{ffarsCo}_2(\text{CO})_8$ might yield $(\text{ffars})_2\text{Co}_4(\text{CO})_8$ (as mentioned above, Scheme I, mild heating gives $\text{ffarsCo}_2(\text{CO})_8$). This does not happen.

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Mixed-Ligand Complexes of Cobalt(III). Chelated (Amino acid)(tetramine)cobalt(III) Complexes

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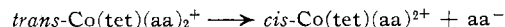
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The syntheses, resolution, and properties of some cobalt(III) complexes with 1,3-diaminopropane (tn) and with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine, alanine, valine, and sarcosine are reported. The tetramine ligands exhibit marked topological specificity; $\alpha\text{-Co}(3,2,3\text{-tet})\text{aa}^{2+}$ and $\beta\text{-Co}(2,3,2\text{-tet})\text{aa}^{2+}$ appear to be formed exclusively under the conditions of these syntheses.

Introduction

We have described the synthesis and properties of some *trans*-bis(amino acid)(tetramine)cobalt(III) complexes.¹ The *trans*-bis(amino acid)(tetramine) complexes react in warm alkaline solution to produce chelated amino acid complexes as the ultimate product. We have prepared and characterized some mixed-ligand complexes with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine,

alanine, valine, and sarcosine. These chelated amino acid complexes clearly define the products of the rearrangement



The details of the steric course of these reactions are now under study.

Experimental Section

Syntheses.—The preparations of the tetramine ligands 3,7-diaza-1,9-nonanediamine and 4,7-diaza-1,10-decanediamine and of the complexes *trans*-dichloro(3,7-diaza-1,9-nonanediamine)-

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