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Further Studies on the Reactions of Dicobalt Octacarbonyl with Fluorocarbon-Bridged Ligands

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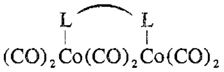
New evidence is presented to show that most fluorocarbon-bridged di(tertiary arsines and phosphines) (L-L) react with $Co_2(CO)_8$ to afford the carbonyl-bridged chelate complexes $(CO)_3Co(CO)_2Co(CO)(L\text{-}L)$. Some give the ligand- and carbonyl-bridged complex



$$(CO)_2\overset{\displaystyle L\frown L}{Co}(CO)_2Co(CO)_2$$

while one, f4fos, affords both isomers. Isomers of formula $(f_4fos)_2Co_2(CO)_4$ are described which seem to differ according to whether the ligands are chelating or bridging. Related unsymmetrical ligands L-L' yield complexes of structure $(L'\text{-}L)Co(CO)_3Co(CO)_3(L\text{-}L')$, where L' is the "hard" end of the ligand, although in one case, f4AsP, isomers are obtained.

In an earlier paper[1] we showed that fluorocarbon-bridged di(tertiary arsines and phosphines) react with dicobalt octacarbonyl affording complexes of formula $(L\text{-}L)Co_2(CO)_6$. These, apparently, retain their carbonyl-bridged structures in solution and do not exist as an equilibrium mixture containing both carbonyl-bridged and nonbridged forms such as is known for the parent carbonyl[2] and some tertiary phosphine and arsine derivatives.[3]

When the ligand L-L is f4fars,[4] the complex $f_4farsCo_2(CO)_6$ has the ligand bridging as indicated in Figure 1A.[1,5] The related complexes such as $f_6fosCo_2(CO)_6$ have a different structure which was believed to be as indicated in Figure 1B. The present investigation is concerned with an extension of this work in which we show that a more likely structure for these complexes is that shown in Figure 1C.

We also describe isomers of compounds such as $(f_4AsP)_2Co_2(CO)_6$ and $(f_4fos)_2Co_2(CO)_4$ and another isomer (bridged) of $f_4fosCo_2(CO)_6$.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 457 spectrometer. Nmr spectra were recorded on Varian T-60 and HA 100 spectrometers. Chemical shifts are reported in ppm downfield from internal TMS (^1H) and upfield from internal $CFCl_3$ (^{19}F). Mass spectra were run on an AEI MS9 spectrometer with direct introduction of solid samples. Molecular weights were determined in benzene solution using a Mechrolab vapor pressure osmometer. Elemental analyses were done by Mr. P. Borda of this department. All reactions were done in sealed tubes or under a nitrogen atmosphere.

Most ligands and starting materials were prepared as described in the literature. A description of the synthesis of some new ligands follows.

1. **Preparation of New Ligands.** The preparative details are listed in Table I. In general the reactants were sealed in a Carius tube and left for the time indicated at the stated temperature. The tube was opened and the less volatile contents were worked up by distillation under reduced pressure except for f4PS[4] which was chromatographed on Florisil using petroleum ether–diethyl ether (20:1) as an eluent and recrystallized from petroleum ether. Analytical data for these products are given in Table II.

2. **Reaction of $Co_2(CO)_8$ with Various Ligands. (a) With f6fars.** Dicobalt octacarbonyl (0.95 g, 2.78 mmol) and f6fars (1.05 g, 2.73 mmol) were stirred in petroleum ether (50 ml) at 20°. After 1.5 hr reaction was complete as indicated by the ir spectrum. The reaction mixture was filtered to remove a blue precipitate. The solvent was removed under reduced pressure and the red residue was dissolved in about 5 ml of dichloromethane and chromatographed on a Florisil column. A red band was eluted from the column with a mixture of petroleum ether–diethyl ether (20:1). The solution obtained was evaporated to dryness and the residual red solid was recrystallized from petroleum ether to give orange-red crystals of $f_6farsCo_2(CO)_6$ (1.0 g, 59%).

(b) With f4AsP. f4AsP (1.2 g, 3.0 mmol) and $Co_2(CO)_8$ (1.05 g, 3.0 mmol) were stirred in petroleum ether (100 ml) for 2.5 hr at 20°. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether. The combined extracts were filtered and evaporated to give a dark red oil. This was dissolved in 5 ml of dichloromethane and chromatographed on a Florisil column. A petroleum ether–diethyl ether solution (20:1) eluted a brown-orange band which yielded brown-red crystals of $f_4AsPCo_2(CO)_6$ (0.25 g, 12%). A second band, violet-red, was eluted with 5–50% diethyl ether—95–50% petroleum ether to yield violet crystals of $[f_4AsPCo(CO)_3]_2$ (0.90 g, 30%). Diethyl ether followed by dichloromethane eluted the third band which afforded an unstable orange powder $[f_4AsPCo(CO)_3]_2$ (0.25 g, 8%).

(c) With f4PS. Dicobalt octacarbonyl (0.75 g, 2.20 mmol) and f4PS (0.85 g, 2.39 mmol) were stirred in petroleum ether (120 ml) at 20° for 3 hr. The solvent was removed and the dark-brown residue was chromatographed on Florisil. Petroleum ether eluted a dark-brown band which gave black crystals of $f_4PSCo_2(CO)_7$ (0.2 g, 14%). Diethyl ether followed by methylene chloride eluted a second band which afforded brown crystals of $[f_4PSCo(CO)_3]_2$ (0.50 g, 23%).

(d) With f4AsS. Dicobalt octacarbonyl (0.90 g, 2.63 mmol) and f4AsS (1.0 g, 3.65 mmol) were stirred in petroleum ether (100 ml) for 1 hr at 20°. After removal of the solvent, the orange residue was chromatographed on Florisil. A petroleum ether–diethyl ether mixture (4:1) eluted an orange band which gave orange crystals. These were recrystallized from chloroform–petroleum ether to yield orange needles of $[f_4AsSCo(CO)_3]_2$ (0.70 g, 50%).

(e) With f4AsN. An identical procedure gave $[f_4AsNCo(CO)_3]_2$, as orange crystals; yield 42%.

(f) With dppm. Equimolar quantities of dppm and $Co_2(CO)_8$ (0.7 g) were stirred in benzene (50 ml) at room temperature for 3 hr. The solvent was removed, and the residue was dissolved in a minimum amount of dichloromethane and chromatographed on Florisil. The product was eluted with diethyl ether–petroleum ether (1:1). After removal of solvent, the orange powder was recrystallized from methylene chloride–petroleum ether to give orange crystals of $dppmCo_2(CO)_6$ (yield ~60%).

3. **Reaction of $f_4fosCo_2(CO)_6$ with f4fos.** The $f_4fosCo_2(CO)_6$ prepared as previously described[1] (0.5 g, 0.64 mmol), f4fos (0.5 g, 1.01 mmol), and acetone (25 ml) were sealed in a Pyrex Carius tube. The tube was irradiated with a 100-W uv lamp at *ca.* 10 cm from the source while shaking. After 2 days the tube was opened. The mixture was evaporated to dryness and then chromatographed on Florisil using methylene chloride as eluent to give a dark brown solution. After concentration and cooling, dark brown crystals of an isomer of $f_4fosCo_2(CO)_6$ (0.2 g, 40%), were obtained. The mother liquor was evaporated and recrystallized from a diethyl ether–petroleum ether mixture (1:4) to give black crystals of $(f_4fos)_2Co_2(CO)_4$ (0.2 g, 25%). This complex (0.2 mmol) was stirred in benzene (50 ml) at 50° for 2 hr while CO was slowly bubbled into the solution. The reaction mixture was evaporated to dryness and then chromatographed on Florisil. Petroleum ether followed by diethyl ether eluted a brown-red band. Concentration and cooling afforded dark brown crystals of the isomeric form of $f_4fosCo_2(CO)_6$ of known infrared spectrum.

4. **Reaction of $[(\pi\text{-}C_7H_8)Co(CO)_2]_2$ with f4fos.** The reactants f4fos

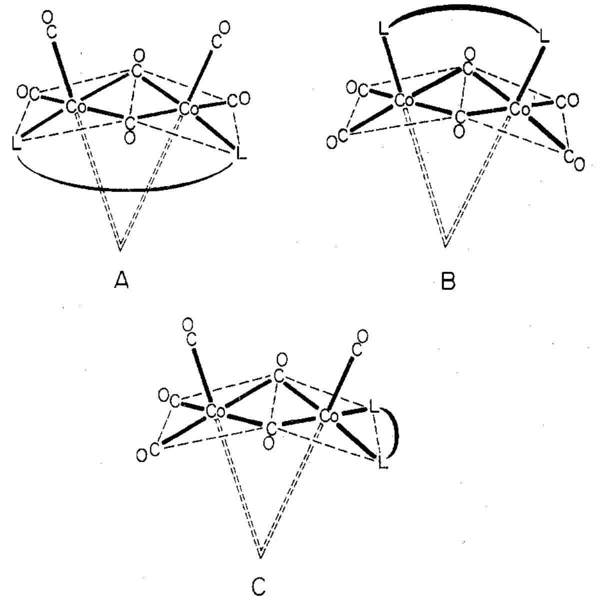
Table I. Preparative Data for New Ligands

Reactants (mmol)	Reaction temp, °C	Reaction time, hr	Product	Yield, %
$(CH_3)_2As\overline{C{=}CFCF_2CF_2}$ (38.3) KOH (53.6) CH_3OH (50 ml)	0	1	$(CH_3)_2As\overline{C{=}C(OCH_3)CF_2CF_2}$	65
$CH_3S\overline{C{=}CFCF_2CF_2}$ (52.6) $(CH_3)_2AsH$ (141)	120	100	$(CH_3)_2As\overline{C{=}C(SCH_3)CF_2CF_2}$	70
$(CH_3)_2As\overline{C{=}CFCF_2CF_2}$ (30.2) $(CH_3)_2NH$ (33.2)	25	2	$(CH_3)_2As\overline{C{=}CN(CH_3)_2CF_2CF_2}$	67
$CH_3S\overline{C{=}CFCF_2CF_2}$ (23.2) $(C_6H_5)_2PH$ (20.2)	25	24	$(C_6H_5)_2P\overline{C{=}C(SCH_3)CF_2CF_2}$	55

Table II. Analytical Data for New Ligands and Complexes[a]

		Calcd			Found		
	MP, °C	% C	% H	Mol wt	% C	% H	Mol wt
f_4AsO	34 (0.1 mm)[b]	32.3	3.50		32.4	3.55	
f_4AsS	57 (0.1 mm)[b]	30.4	3.30		30.3	3.50	
f_4AsN	67 (0.1 mm)[b]	35.2	4.44		35.1	4.43	
f_4PS	48	57.3	3.69		55.9	3.40	
$f_8farsCo_2(CO)_6$	90 dec	26.7	1.67		26.4	1.59	
$f_4AsPCo_2(CO)_6$	92	41.1	2.31	700	41.2	2.41	714
$[f_4AsPCo(CO)_3]_2$	117	45.3	2.90	1114	45.0	2.95	1070
$[f_4AsPCo(CO)_3]_2$	110	45.3	2.90		44.9	3.20	
$f_4PSCo_2(CO)_7$	105	43.0	1.96	670	42.8	2.20	597
$[f_4PSCo(CO)_3]_2$	152	48.1	2.63	998	48.2	3.00	950
$[f_4AsSCo(CO)_3]_2$[c]	70 dec	28.6	2.17	838	28.7	2.10	713
$[f_4AsNCo(CO)_3]_2$[d]	100	31.7	2.91	836	32.0	3.34	756
$dppmCo_2(CO)_6$	160	55.6	3.31	670	55.0	3.26	613
$(f_4fos)^bCo_2(CO)_6$	115	52.3	2.60	782	51.9	2.69	743
$(f_4fos)^c{}_2Co_2(CO)_4$	164	56.5	3.17	1218	55.1	4.03	1155
$(f_4fos)^b{}_2Co_2(CO)_4$	165	56.5	3.17	1218	55.8	4.00	1165

[a] Reference 4. [b] Boiling point. [c] *Anal.* Calcd: As, 17.9; Co, 14.1; S, 7.64; Cl, 0.0. Found: As, 18.1; Co, 14.1; S, 7.74; Cl, 0.0. [d] *Anal.* Calcd: N, 3.37. Found: N, 3.54.



A B

C

Figure 1. Possible structures for the complexes $(L\text{-}L)Co_2(CO)_6$.

(1.0 mmol) and $[(\pi\text{-}C_7H_8)Co(CO)_2]_2$ (0.5 mmol) were stirred in benzene (50 ml) at 60°. After 0.5 hr the red solution had changed to dark brown. After 1 hr the solution was evaporated to dryness to give a dark brown oil. This was dissolved in dichloromethane (*ca.* 5 ml) and chromatographed on Florisil. Petroleum ether eluted a trace of $[(\pi\text{-}C_7H_8)Co(CO)_2]_2$. Diethyl ether eluted a dark brown band which gave dark brown crystals. These were recrystallized from a dichloromethane–petroleum ether mixture (1:20) to give an isomer of $(f_4fos)_2Co_2(CO)_4$ (50%). This complex (0.2 mmol) was stirred in benzene (50 ml) at 50° for 2 hr while CO was slowly bubbled into the solution. The deep red solution was evaporated to dryness and then chromatographed on Florisil. Petroleum ether followed by diethyl ether eluted a dark red band which yielded dark red crystals whose ir spectrum is identical with that of the first reported[1] form of $f_4fosCo_2(CO)_6$.

5. Reaction of $(\pi\text{-}C_7H_8)Co_2(CO)_6$ with f6fos, f8fos, and *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$. Equimolar quantities (10 mmol) of $(\pi\text{-}C_7H_8)Co_2(CO)_6$ and the ligand (f6fos, f8fos, or *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$) were stirred in petroleum ether (50 ml) at room temperature. After a few hours (~3) most of the $(\pi\text{-}C_7H_8)Co_2(CO)_6$ had reacted as indicated by the infrared spectrum of the solution. The resulting mixture was filtered, evaporated, and chromatographed on Florisil. Petroleum ether–diethyl ether (2:1) eluted a brown band which afforded brown crystals whose infrared spectra were identical with those reported for the appropriate $(L\text{-}L)Co_2(CO)_6$ complexes.[1]

Results and Discussion

Analytical and spectroscopic data for new compounds are given in Tables II and III.

$(L\text{-}L)Co_2(CO)_6$ Complexes. Like f4fars[1] and f8fars,[6] f6fars also reacts with $Co_2(CO)_8$ to give a brown-red solid of formula $(L\text{-}L)Co_2(CO)_6$ (Table II). However, unlike $f_4farsCo_2(CO)_6$ which shows two bridging CO bands at 1842 and 1786 cm^{-1}, a difference of 56 cm^{-1}, the other di(tertiary arsine) complexes give two bridging CO bands at ~1815 and ~1801 cm^{-1}, a difference of only *ca.* 14 cm^{-1} (Table III) indicating a more symmetrical structure. Since the frequencies and pattern of the CO bands in these compounds are very similar to those previously reported[1] for some other $(L\text{-}L)Co_2(CO)_6$ complexes (L-L = f6fos, f8fos, and *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$, it is reasonable to assume that they have the same type of more symmetrical structure. X-Ray studies[5] have confirmed that $f_4farsCo_2(CO)_6$ has the structure indicated in Figure 1A which is similar to that of $Co_2(CO)_8$,[7] the ligand

Table III. Spectroscopic Data for New Complexes

	ν(CO),[a] cm^{-1}	^1H nmr
$(f_6fars)^cCo_2(CO)_6$	2067 (10), 2004 (9), 1995 (10), 1813 (5), 1800 (8)	1.80 (s)
$(f_4AsP)^cCo_2(CO)_6$	2068 (9), 2019 (9), 2000 (10), 1996 (10), 1823 (7), 1797 (8)	1.40 (s) area 6, 7.35 (m) area 10
$[f_4As\mathit{P}Co(CO)_3]_2$	1991 (3, sh), 1969 (10)	1.10 (s) area 12, 7.50 (m) area 20
$[f_4\mathit{As}PCo(CO)_3]_2$	2040 (1), 2000 (10, br)	2.05 (s) area 12, 7.40 (m) area 20
$f_4\mathit{P}SCo_2(CO)_7$	2070 (9), 2025 (9), 2000 (10), 1968 (8)	2.25 (s) area 3, 7.55 (m) area 10
$[f_4\mathit{P}SCo(CO)_3]_2$	1990 (4, sh), 1968 (10)	2.40 (s) area 6, 7.50 (m) area 20
$[f_4AsSCo(CO)_3]_2$	2066 (1), 2045 (2), 1990 (10, br)	2.10 (s, br) area 12, 2.50 (s) area 6, 2.70 (s) area 6
$[f_4\mathit{As}NCo(CO)_3]_2$[b]	2040 (2), 1993 (10, br)	2.00 (s, br) area 12, 3.10 (s, br) area 12
$dppm^cCo_2(CO)_6$	2050 (5), 2016 (9), 1990 (10), 1840 (4), 1794 (3)	3.05 (t), J = 10 Hz
$(f_4fos)^cCo_2(CO)_6$	2070 (9), 2018 (9.5), 1994 (10), 1815 (6), 1770 (7)	
$(f_4fos)^c{}_2Co_2(CO)_4$[c]	1972 (8), 1952 (10), 1765 (6), 1732 (9)	
$(f_4fos)^b{}_2Co_2(CO)_4$[d]	1950 (10, br), 1735 (6, br)	7.40 (m)

[a] All infrared spectra were run on dichloromethane solution except for the $f_6$fars and dppm complexes which were run in cyclohexane. Symbols and abbreviations are explained in ref 4. [b] ^{19}F nmr: 108.0 (s) area 2, 108.4 (s) area 2. [c] ^{19}F nmr: 107.8 (s). [d] ^{19}F nmr: 108.0 (s).

$f_4$fars acting as a bridging bidentate ligand replacing one equatorial CO group from each Co atom. Crow, *et al.*,[1] favored the bridged structure of Figure 1B for the other $(L-L)Co_2(CO)_6$ complexes and discounted a chelate structure (Figure 1C) because this "contains a unique CO group on the substituted Co 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 spectrum." (The chelate structure would of course also fit the observed infrared spectrum in the bridging carbonyl region.[8])

Recent studies[9] have shown that (π-diene)$Co_2(CO)_6$ (π-diene = norbornadiene, C_7H_8) has the chelated structure 1C in which the diene (L-L) acts as a bidentate ligand replacing two equatorial terminal CO groups from one Co atom. The infrared spectrum of this compound shows four terminal CO bands at 2076, 2024, 2012, and 2009 (sh) cm^{-1}. Since there is no evidence that this compound is tautomeric in solution,[10] the four observed bands are probably all fundamentals. This suggests that the infrared band due to the unique terminal CO group on the substituted cobalt atom in (π-C_7H_8)$Co_2(CO)_6$ has a stretching frequency of at least 2009 cm^{-1}, a frequency not much different from those of the terminal CO groups on the other cobalt atom. The present investigation also found that the new derivative $f_4AsPCo_2(CO)_6$, (Table II) which has an infrared spectrum similar to the other (not of structure 1A) $(L-L)Co_2(CO)_6$ complexes (Table III) and is not tautomeric in solution, shows *four* presumably fundamental terminal CO bands at 2068, 2019, 2000, and 1996 cm^{-1}. Thus it seems that the CO band due to the unique terminal CO group in $(L-L)Co_2(CO)_6$ if it had the structure 1C *could* have a frequency comparable to those of the other terminal CO groups. Hence structure 1C cannot be excluded for the other $(L-L)Co_2(CO)_6$ complexes. Furthermore, the patterns of the CO stretching bands in these $(L-L)Co_2(CO)_6$ complexes and (π-C_7H_8)-$Co_2(CO)_6$ are very similar and therefore they probably have the same structure. This conclusion is supported by our finding that the reaction of (π-C_7H_8)$Co_2(CO)_6$ with L-L gives $(L-L)Co_2(CO)_6$ (L-L = $f_6$fos, $f_8$fos, or *cis*-$(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$) under mild conditions. Since under the same conditions, excess ligand does not react with (ligand)$Co_2(CO)_6$ (ligand = L-L or C_7H_8), the formation of $(L-L)Co_2(CO)_6$ from (π-C_7H_8)$Co_2(CO)_6$ is evidently simply due to the replacement of C_7H_8 by L-L. (Figure 1C (L-L) = π-C_7H_8 → Figure 1C (L-L) = $f_6$fos, etc). Thus it seems that the $(L-L)Co_2(CO)_6$ complexes of fluorocarbon-bridged ligands can be of two types, bridged (1A) or chelated.

Previously it was reported that $f_4$fos reacts with $Co_2(CO)_8$ to give $f_4fosCo_2(CO)_6$ whose infrared spectrum is similar to that of $f_4farsCo_2(CO)_6$ and hence the complex has the same type of bridged structure, 1A. It has now been found that under ultraviolet irradiation $(f_4fos)^bCo_2(CO)_6$ can be isomerized to $(f_4fos)^cCo_2(CO)_6$, whose infrared spectrum is now similar to those of the $(L-L)Co_2(CO)_6$ complexes with structure 1C except that the bridging CO bands are separated enough to suggest they are in different environments. Thus axial–equatorial chelation is likely. This provides yet another example of isomerism caused by a ligand being ether bridging or chelating in a metal carbonyl cluster.[11]

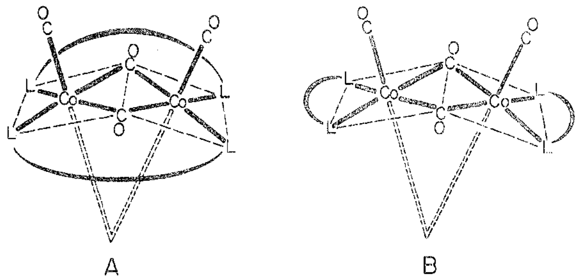


Figure 2. Possible structures for the complexes $(L-L)_2Co_2(CO)_4$.

Recently Thornhill and Manning[12] prepared $diarsCo_2(CO)_6$, $Me_2As(CH_2)_3AsMe_2Co_2(CO)_6$, and $Me_2As(CH_2)_nAsMe_2Co_2(CO)_6$ (n = 6, 8). The former two complexes have infrared spectra very similar to those of our structure 1C complexes and consequently probably have this chelated structure. The terminal CO bands of the latter two complexes are similar to those of $[(MeO)_3P]_2(PhC\equiv CPh)Co_2(CO)_4$ where the two $(MeO)_3P$ ligands are believed to occupy axial–axial positions.[13] The spectra are also unlike those of the 1A and 1C types of $(L-L)Co_2(CO)_6$ complexes. It is possible that the large bite of these di(tertiary arsines) would allow bridging in the manner illustrated in 1B.

In the present study we have prepared $(dppm)Co_2(CO)_6$ where the ligand has a very small bite. Not unexpectedly, this complex has an infrared spectrum consistent with that of a chelated derivative, but as for $(f_4fos)^cCo_2(CO)_6$, the bridging carbonyl bands indicate axial–equatorial substitution.

It should be pointed out that the nmr spectra of these $(L-L)Co_2(CO)_6$ complexes, although useful in checking purity, are not much help in establishing structure since both the bridged and chelated complexes exemplified by $f_4farsCo_2(CO)_6$ and $f_6farsCo_2(CO)_6$, respectively, show only one arsenic methyl resonance instead of the expected two.

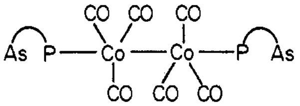
$(L-L)_2Co_2(CO)_4$ Complexes. In addition to the isomerization to the chelated form of $f_4fosCo_2(CO)_6$, ultraviolet irradiation of the bridged complex $f_4fosCo_2(CO)_6$ in the presence of $f_4$fos gives a black solid for which analytical data and molecular weight measurement suggest the formula $(f_4fos)_2Co_2(CO)_4$. The pattern and frequencies of the infrared spectrum in the carbonyl region are quite similar to those of the spectra of $(dppe)_2Co_2(CO)_4$ and related molecules. These are obtained by allowing $[\pi$-$C_7H_8Co(CO)]_2$ to react with bidentate ligands[14] and for this reason the same type of structure shown in Figure 2B can be proposed. The successful conversion of $(f_4fos)_2Co_2(CO)_4$ into the chelated form of

$f_4fosCo_2(CO)_6$ by reaction with CO lends some support to this suggestion, although the possibility of chelation involving axial–equatorial substitution cannot be eliminated.

In an attempt to synthesize $(f_4fos)_2Co_2(CO)_4$ by treating $[(\pi\text{-}C_7H_8)Co(CO)_2]_2$ with f4fos, a new isomeric compound, $(f_4fos)^b{}_2Co_2(CO)_4$, was obtained. Again the ^{19}F nmr spectrum of this compound indicates that the two f4fos ligands are equivalent. However its infrared spectrum is quite different from its isomer described in the previous paragraph. Since this new isomer reacts with CO to give the bridged isomer of $f_4fosCo_2(CO)_6$ (of structure 1A), its most likely structure is shown in Figure 2A. This is the first example of isomerism of this type involving two identical ligands. Although the isomeric pair $(f_4AsP)^cf_4AsPFe_2(CO)_4$ and $(f_4AsP)^bf_4AsPFe_2(CO)_4$ is known, only one ligand changes its mode of coordination[13] and hence is an example of the type of isomerization already discussed.

(L-L)$Co_2(CO)_7$ Complex. The new ligand f4PS reacts with $Co_2(CO)_8$ to give a compound $f_4PSCo_2(CO)_7$, in low yield. The ^1H nmr spectrum of this compound shows a singlet at 2.25 ppm and a multiplet centered at 7.55 ppm in the ratio of 3:10. The singlet at 2.25 ppm is little changed from its position in the free ligand f4PS (2.40 ppm) indicating that the sulfur atom is uncoordinated (coordination would shift the resonance downfield considerably[15]). It is therefore concluded that the ligand is coordinated to one of the Co atoms *via* a phosphorus atom. The infrared spectrum of this complex shows four terminal CO bands whose position and intensity are very similar to those reported for $(C_6H_5)_3PCo_2(CO)_7$,[16] and, therefore, the same C_{3v} structure is proposed for this compound.

[L-LCo(CO)$_3$]$_2$ Complexes. Three products are obtained from the reaction of f4AsP with $Co_2(CO)_8$. One of these is $f_4AsPCo_2(CO)_6$ already described. The other two, a violet solid and an orange powder, are isomers of formula $(f_4AsP)_2Co_2(CO)_6$. The ^1H nmr spectrum of the violet isomer has a single methyl proton peak for the $As(CH_3)_2$ group at 1.10 ppm which is close to that of the free ligand (1.30 ppm) indicating that only the phosphorus atoms are coordinated.[15] The infrared spectrum is similar to other compounds of the type $[(C_6H_5)_3PCo(CO)_3]_2$[17] of known structure,[18] and hence the structure I is suggested for the f4AsP complex. This has been confirmed by a recent X-ray determination.[19] The ^1H nmr spectrum of the orange isomer shows a singlet at 2.05 ppm due to coordinated $-As(CH_3)_2$ groups. Hence the structure is probably the same as I except that the phosphorus- and arsenic-containing moieties are interchanged. $(f_4PS)_2Co_2(CO)_6$, obtained in addition to $f_4PSCo_2(CO)_7$ from the reaction of the ligand with $Co_2(CO)_8$, probably has this nonbridged Co–Co bonded structure with the $-SCH_3$ groups dangling since the $-SCH_3$ peak is at 2.40 ppm in the ^1H nmr spectrum. Similar arguments can be used to assign the same structure to $[f_4AsNCo(CO)_3]_2$ where both arsenic atoms are bonded. f4AsO gives a very unstable complex of the same type as do $(CH_3)_2AsC{=}CXCF_2CF_2$ (X = F or Cl).[13]



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The ^1H nmr spectrum of the last complex of this type $[f_4AsSCo(CO)_3]_2$ is difficult to interpret. The broad singlet at 2.10 ppm suggests that both $-As(CH_3)_2$ groups are bonded. This would leave equivalent dangling $-SCH_3$ groups which could produce a singlet at 2.50 or 2.70 ppm but not both. This compound is very unstable in solution but seems to be indefinitely stable at 0° in the solid state. It does not give a parent ion in the mass spectrometer and fragments to give a large number of ions of small (<443) nominal mass.

Thus we see that in general unsymmetrical potentially bidentate ligands afford $[(L\text{-}L')Co(CO)_3]_2$ complexes in which only the "soft" donor or atom is coordinated to the cobalt. This is not unexpected since "hard" donors tend to react with cobalt carbonyls to afford ionic compounds and the presence of the electronegative "hard" donor on the unsymmetrical ligand would tend to enhance the "softness" of the other donor.

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Registry No. $f_8farsCo_2(CO)_6$, 53385-26-5; $f_4AsPCo_2(CO)_6$, 53385-27-6; $f_4PSCo_2(CO)_7$, 53385-29-8; $[f_4PSCo(CO)_3]_2$, 53385-30-1; $[f_4AsSCo(CO)_3]_2$, 53432-91-0; $[f_4AsNCo(CO)_3]_2$, 53385-31-2; $dppmCo_2(CO)_6$, 53385-32-3; $(f_4fos)^bCo_2(CO)_6$, 30171-46-1; $(f_4fos)^c{}_2Co_2(CO)_4$, 53385-36-7; $(f_4fos)^b{}_2Co_2(CO)_4$, 53432-92-1; $(f_6fars)^cCo_2(CO)_6$, 53385-28-7; $[f_4As\mathit{P}Co(CO)_3]_2$, 53385-34-5; $[f_4\mathit{As}PCo(CO)_3]_2$, 53385-35-6; f4AsO, 53385-15-2; f4AsS, 53385-16-3; f4AsN, 53385-17-4; f4PS, 53385-18-5; $(f_4fos)^cCo_2(CO)_6$, 53385-33-4; $(CH_3)_2AsC{=}CFCF_2CF_2$, 650-77-1; CH_3OH, 67-56-1; $CH_3SC{=}CFCF_2CF_2$, 13888-98-7; $(CH_3)_2AsH$, 593-57-7; $(CH_3)_2NH$, 124-40-3; $(C_6H_5)_2PH$, 676-59-5; $Co_2(CO)_8$, 10210-68-1; $[(\pi\text{-}C_7H_8)Co(CO)_2]_2$, 50404-93-8.

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