possess two peaks, one in the region of unconjugated esters and the other in the relatively low and usual position (*i.e.*, similar to that of the tetrahedral species).

A further examination of models of the tetrahedrally arranged chelates shows that a fully conjugated structure with the carbonyl group facing the metal ion is possible. This interaction ($M\cdots O{=}C$) would be expected to lower the absorption frequency of the carbonyl to an increasing extent as the electropositive character of the metal ion increases. Calcium(II) is probably least shielded in this respect and a very low $C{=}O$ ester frequency is therefore observed for the calcium chelate at 1672 cm^{-1}. That this low frequency is in fact due to electrostatic metal ion carbonyl oxygen interaction is supported by the fact that the frequency of free ligand carbonyl is much higher (at 1730 cm^{-1}) than that of the calcium(II) chelate. The $C{=}O$ frequencies of the remaining metal chelates are lowered to corresponding extents as the electrostatic interaction with the metal ion varies. In the Ni(II) and Cu(II) chelates, where the ester group is twisted from conjugation, this interaction is not possible, as is seen from the relatively high frequency of the corresponding bands.

Reference to Table V shows that there are two $C{=}C$ stretching frequencies present in the ir spectra of halogenated dipyrromethenato chelates. The value of the first band in the spectra of halopyrroles[20] was fixed at 1558 ± 5 cm^{-1}. In dipyrromethenato chelates this value is some 43 cm^{-1} higher, at 1601 ± 9 cm^{-1}. The second band at about 1480 cm^{-1} is more variable and is in about the same position as that for pyrroles.[20] The first band is seen to be more sensitive to electropositive electron withdrawal by the M^{2+} ion. The second is more variant with the type of halogen than with the metal ion.

Conclusions

It is seen that the information discussed above leads to the conclusion that the dipyrromethene chelates of this study fall into two groups: the tetrahedral Ca(II), Mn(II), and Zn(II) and the distorted tetrahedral Ni(II) and Cu(II). Previous workers have indicated preference for Ni(II) being regular tetrahedral and Cu(II) somewhat distorted. The present compounds differ from those previously reported by the presence of 12 strongly electron-withdrawing groups per metal chelate molecule (eight halo plus four carbethoxy groups per metal ion). These electronegative groups would tend to weaken the ligand field considerably around the central ion, producing a metal complex having overall greater ionic character in the metal–ligand bonds. The strong steric effects of the carbethoxy groups would also favor tetrahedral arrangement of the pyrrole nitrogen donor atoms. The fact that spectral data lead to the conclusion that deviations from tetrahedral structure are considerable and more than had been concluded for other dipyrromethene chelates is considered significant. These results suggest that the deviations from tetrahedral structure (toward coplanarity of the ligand planes) of the less substituted dipyrromethene chelates are perhaps greater than had previously been believed.

Contribution from the Chemistry Department,
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The Preparation and Characterization of Fluorocarbon-Bridged Di(tertiary phosphine and arsine) Complexes Derived from Triruthenium Dodecacarbonyl

By W. R. Cullen and D. A. Harbourne

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The reactions of triruthenium dodecacarbonyl with the fluorocarbon-bridged ligands ffars, ffos, and $f_6$fos have been investigated under a variety of conditions. The complexes $L_2Ru_3(CO)_8$ (L = ffars and ffos), ffars$Ru_3(CO)_{10}$, $LRu_2(CO)_6$ (L = ffars, ffos, $f_6$fos), and $f_6$fos$Ru(CO)_3$ have been characterized. In addition, evidence for the existence of ffos$Ru_3(CO)_{10}$ and ffos$Ru(CO)_3$ is presented. The structures of these new compounds are discussed and compared with those of the corresponding iron derivatives.

Previous papers[1–4] have dealt with our investigation into the complex-forming properties of the unsaturated fluorocarbon-bridged ligands $\mathrm{E\overline{C{=}CE(CF_2)_nCF_2}}$: ffars, $E = As(CH_3)_2$, $n = 1$; ffos, $E = P(C_6H_5)_2$, $n = 1$; $f_6$fos, $E = P(C_6H_5)_2$, $n = 2$; $f_8$fos, $E = P(C_6H_5)_2$, $n = 3$. In particular, novel complexes have been obtained from their reaction with iron carbonyls.[2,4] The aim of this present investigation was to extend the study

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[1] W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).

[2] (a) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, **90**, 3293 (1968); (b) *Inorg. Chem.*, **8**, 95 (1969); (c) *ibid.*, **8**, 1464 (1969).

[3] W. R. Cullen, D. F. Dong, and J. A. J. Thompson, *Can. J. Chem.*, **47**, 4671 (1969).

[4] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **9**, 702 (1970).

TABLE I

ANALYTICAL RESULTS FOR NEW COMPLEXES

Complex	Color	Mp, °C	% calcd C	% calcd H	% calcd F	% found C	% found H	% found F
$(ffars)_2Ru_3(CO)_8$	Dark red	173–175	24.10	2.01	12.72	24.41	2.20	12.90
$ffarsRu_2(CO)_6$	Pale yellow	255[a]	23.86	1.71	10.80	24.13	1.70	10.91
$ffarsRu_3(CO)_{10}$	Dark red	191–192	23.56	1.31	8.29	24.02	1.36	. . .
$(ffos)_2Ru_3(CO)_8$	Dark red	200–202	50.70	2.64	10.03	51.31	2.90	9.61
$ffosRu_2(CO)_6$	White	238–241[b]	47.22	2.31	8.79	46.99	2.34	8.62
$f_6fosRu_2(CO)_6$	White	255[a]	47.05	2.19	12.47	47.43	2.47	12.11
$f_6fosRu(CO)_3$	Pale brown	. . .	52.7	2.74	15.64	54.09	3.55	. . .

[a] Does not melt. Decomposes above this temperature. [b] With decomposition.

of the behavior of these ligands using triruthenium dodecacarbonyl. The known properties of this ruthenium carbonyl[5] indicate that the triangular unbridged ruthenium cluster[6] is more stable than the carbonyl-bridged triiron dodecacarbonyl cluster.[7] Consequently, although only one Fe_3 compound, ffars-$Fe_3(CO)_{10}$ (Figure 1), was isolated from the reactions of the unsaturated fluorocarbon-bridged ligands with $Fe_3(CO)_{12}$[2a,4,8–10] it was expected that more Ru_3 compounds would be obtained in the present investigation. This expectation has now been found to be justified.

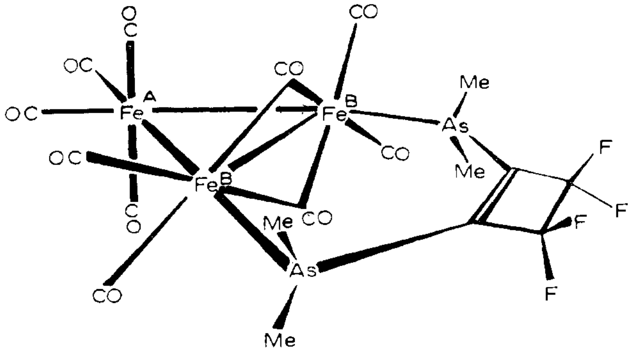

Figure 1.—The structure of $ffarsFe_3(CO)_{10}$.

Experimental Section

All reactions were done under a nitrogen atmosphere or in sealed Pyrex tubes (uv irradiations with a 100-W lamp 10 cm from the tube). All chromatographic procedures were carried out using Florisil and nitrogen-saturated solvents unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 457 instrument; nmr spectra, on Varian A-60 (^1H) and HA-100 (^{19}F) instruments. Chemical shifts are given in ppm *downfield* from internal TMS and upfield from internal CCl_3F. Mass spectra were recorded on an MS-9 instrument and analyses were carried out by Mr. P. Borda of this department. Melting points were determined in evacuated capillaries and are uncorrected. Triruthenium dodecacarbonyl was purchased from Alfa Inorganics, Inc.

Analytical data for new compounds are given in Table I. Spectroscopic data are listed in Tables II and III.

Reactions of ffars with $Ru_3(CO)_{12}$.—(a) The carbonyl (0.38 g, 0.60 mmol) and ffars (0.63 g, 1.89 mmol) were refluxed in cyclohexane (50 ml) for 3.5 hr (infrared monitoring indicated little change after 0.5 hr). The solution was concentrated and chromatographed. Trace products were eluted with petroleum ether–diethyl ether mixtures up to a 1:1 ratio. The product, $(ffars)_2Ru_3(CO)_8$ (63%), eluted as a red band using the same solvent mixture but with a greater proportion of diethyl ether.

TABLE II

INFRARED BANDS OF NEW COMPLEXES IN THE CARBONYL STRETCHING REGION[a]

$(ffars)_2Ru_3(CO)_8$	2045 m, 1991 m, sh, 1978 s, 1971 s, 1948 m, sh, 1894 w
$ffarsRu_3(CO)_{10}$	2087 m, 2024 m, sh, 2014 s, 2007 s, sh, 1980 w, sh, 1967 w, 1950 w, sh, 1938 w, sh
$ffarsRu_2(CO)_6$	2075 m, 2045 s, 2008 s, 2003 s, sh, 1983 w, 1970 w
$(ffos)_2Ru_3(CO)_8$[b]	2048 m, 1996 m, sh, 1978 s, sh, 1972 s, 1944 m, sh, 1898 w, sh
$ffosRu_3(CO)_{10}$	2087 m, 2027 m, sh, 2019 s, 2007 s, 1989 m, sh, 1974 w, 1960 w, 1950 w, sh
$ffosRu_2(CO)_6$	2077 s, 2047 s, 2018 s, 2002 m, 1988 m, 1983 m
$ffosRu(CO)_3$	2025 vs, 1959 s, 1937 vs
$f_6fosRu_2(CO)_6$	2079 s, 2048 s, 2021 s, 2005 m, 1991 m, 1985 m
$f_6fosRu(CO)_3$	2026 s, 1966 m, 1961 m, 1938 vs

[a] In cm^{-1}, C_6H_{12} solution. [b] CS_2 solution.

TABLE III

NMR DATA FOR NEW COMPLEXES

$(ffars)_2Ru_3(CO)_8$	^1H ((C_6F_6 solution): singlets at 2.00 and 2.05 ppm
	^{19}F (($CH_3)_2CO$ solution): complex symmetrical pattern of 14 peaks centered at 107.8 ppm. Most intense peaks are separated by 71.5 Hz
$ffarsRu_3(CO)_{10}$	^1H (C_6F_6 solution): singlet at 2.16 ppm
	^{19}F (($CH_3)_2CO$ solution): singlet at 108.4 ppm
$ffarsRu_2(CO)_6$	^1H ($C_6H_5NO_2$ solution): singlets at 2.25 and 1.80 ppm
	^{19}F (THF solution): complex symmetrical pattern centered at 101.4 ppm with four major areas of resonance at 110.0, 108.2, 94.8, 92.9 ppm
$(ffos)_2Ru_3(CO)_8$	^{19}F: no satisfactory solvent
$ffosRu_3(CO)_{10}$	^{19}F (C_6H_6 solution): singlet at 109.1 ppm
$ffosRu_2(CO)_6$	^{19}F (C_6H_6 solution): complex pattern of symmetrical groups of signals centered at 86.2 and 106.8 ppm. There are four major areas of resonance at 107.8, 105.8, 87.1, 85.2 ppm
$ffosRu(CO)_3$	^{19}F (C_6H_6 solution): singlet at 109.6 ppm
$f_6fosRu_2(CO)_6$	^{19}F (C_6H_6 solution): four sets of doublets of multiplets centered at 65.2, 103.3, 114.0, 122.2 ppm
$f_6fosRu(CO)_3$	^{19}F (C_6H_6 solution): a quintuplet ($J \approx 6.4$ Hz) with poorly resolved structure at 129.6 ppm and a triplet ($J \approx 6$ Hz) at 108.0 ppm

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(5) M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 427 (1968).

(6) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).

(7) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(8) P. J. Roberts, B. R. Penfold, and J. Trotter, unpublished results.

(9) The compound of formula $ffarsFe_3(CO)_9$ is also obtained but a structural investigation[10] shows that the ligand is no longer intact.

(10) F. W. B. Einstein and A.-M. Svensson, *J. Amer. Chem. Soc.*, **91**, 3663 (1969).

(b) ffars (0.32 g, 0.96 mmol) and the carbonyl (0.39 g, 0.61 mmol) were refluxed in toluene (50 ml) for 5.5 hr. The solvent was removed *in vacuo* and the residue was dissolved in acetone and filtered. Addition of heptane to this solution precipitated the bulk of the crude product. Chromatography of the mother liquor in air gave some unchanged $Ru_3(CO)_{12}$ and a yellow band; both were eluted with petroleum ether (bp 40–60°). The yellow band contained more crude product. The combined product was treated with charcoal, washed with diethyl ether, and recrystallized from hot hexane to which a small amount of acetone had been added. The yield of ffars$Ru_2(CO)_6$ was 61%.

(c) ffars (0.16 g, 0.48 mmol) and $Ru_3(CO)_{12}$ (0.31 g, 0.49 mmol) in acetone solution (40 ml) were irradiated for 89 hr. The reaction mixture was filtered and evaporated to dryness. The solid residue was recrystallized from diethyl ether to obtain a first crop of the product, ffars$Ru_3(CO)_{10}$. The mother liquor was evaporated to dryness, and the solid residue was dissolved in benzene. Chromatography gave some $Ru_3(CO)_{12}$ (eluted with petroleum ether), ffars$Ru_3(CO)_{10}$ (eluted with 1:9 diethyl ether–petroleum ether), and ffars$Ru_2(CO)_6$ (eluted with the same solvent mixture). The last compound contained an impurity which was removed by washing with diethyl ether. The yield of ffars$Ru_3(CO)_{10}$ was 63%, that of ffars$Ru_2(CO)_6$ was 2%.

Reactions of ffos with $Ru_3(CO)_{12}$.—(a) ffos (0.72 g, 1.46 mmol) and $Ru_3(CO)_{12}$ (0.35 g, 0.55 mmol) were refluxed in cyclohexane (50 ml) for 3.6 hr. The reaction solution was cooled and filtered to obtain the first crop of $(ffos)_2Ru_3(CO)_8$. The mother liquor was evaporated and the solid residue was dissolved in benzene. This solution was adsorbed onto Florisil and the solvent was then removed *in vacuo*. The dry powder was added to the top of a prepared chromatography column. Elution with petroleum ether–diethyl ether (4:1) gave a pale yellow band of ffos$Ru_2(CO)_6$ (21%). The same eluent also gave a blue band (unidentified) and a red band containing some ffos$Ru(CO)_3$ (~2%). Higher concentrations of diethyl ether (up to 1:1) eluted a red band of $(ffos)_2Ru_3(CO)_8$ and an unidentified yellow band. The combined $(ffos)_2Ru_3(CO)_8$ fractions were recrystallized from acetone to give an overall yield of 15%.

(b) ffos (0.50 g, 1.01 mmol) and $Ru_3(CO)_{12}$ (0.36 g, 0.56 mmol) were refluxed in toluene (50 ml) for 5.5 hr. The reaction solution was evaporated to dryness to give impure ffos$Ru_2(CO)_6$. This was washed with acetone. The washings were chromatographed to give many colored bands some of which contained more ffos$Ru_2(CO)_6$. The combined ffos$Ru_2(CO)_6$ fractions were recrystallized from hexane to give a total yield of 54%. The only other product which was identified was a trace of ffos$Ru(CO)_3$.

(c) ffos (0.60 g, 1.21 mmol) and the carbonyl (0.35 g, 0.55 mmol) in acetone solution (40 ml) were irradiated for 139 hr. Chromatography gave a trace of $Ru_3(CO)_{12}$ (petroleum ether), an orange-red band containing a mixture of ffos$Ru_3(CO)_{10}$ and ffos$Ru_2(CO)_6$ (diethyl ether–petroleum ether, 1:49), and a brown band of ffos$Ru(CO)_3$ (diethyl ether–petroleum ether, >1:1). The last compound was recrystallized from petroleum ether–diethyl ether and the yield was 10%. The mixture of $Ru_3(CO)_{10}$ and $Ru_2(CO)_6$ derivatives could not be separated on an alumina column. A few crystals of each compound were hand picked in order to measure their infrared spectra.

Reactions of $f_6$fos with $Ru_3(CO)_{12}$.—(a) The carbonyl (0.16 g, 0.25 mmol) and $f_6$fos (0.41 g, 0.75 mmol) were refluxed in cyclohexane (50 ml) for 3.5 hr. The reaction mixture was filtered and concentrated to obtain crystals of $f_6$fos$Ru(CO)_3$ (46%). The mother liquor was chromatographed and only a trace of $f_6$fos$Ru_2(CO)_6$ was obtained.

(b) $Ru_3(CO)_{12}$ (0.39 g, 0.61 mmol) and $f_6$fos (0.67 g, 1.23 mmol) were refluxed in toluene (50 ml) for 5.5 hr. Chromatography gave a yellow band of $f_6$fos$Ru_2(CO)_6$ which eluted with mixtures of petroleum ether–diethyl ether in the range 19:1 to 9:1. The compound was recrystallized from hexane–acetone (44% yield). Higher concentrations of diethyl ether eluted traces of at least three other compounds.

(c) $Ru_3(CO)_{12}$ (0.29 g, 0.45 mmol) and $f_6$fos (0.57 g, 1.05 mmol) in acetone (40 ml) were irradiated for 139 hr. Chromatography gave a little $Ru_3(CO)_{12}$ (26 mg) which eluted with petroleum ether. Petroleum ether–diethyl ether mixtures in the range 49:1 to 19:1 eluted a red-orange band which contained mainly $f_6$fos$Ru_2(CO)_6$. Higher concentrations of diethyl ether (up to 100%) eluted a diffuse brown band which contained both $f_6$fos$Ru_2(CO)_6$ and $f_6$fos$Ru(CO)_3$. Diethyl ether (100%) eluted a further diffuse band of $f_6$fos$Ru(CO)_3$ which was taken off the column using acetone. The $f_6$fos$Ru_2(CO)_6$ was recrystallized from hexane–acetone (22% yield), the $f_6$fos$Ru(CO)_3$ from cyclohexane (25% yield).

Results and Discussion

In general the reactions of the ligands ffars, ffos, and $f_6$fos with $Ru_3(CO)_{12}$ are a little less clean than the corresponding ones with $Fe_3(CO)_{12}$ and involve a slightly higher percentage of intractable or unseparable side products. The reaction of each ligand with triruthenium dodecacarbonyl was investigated under at least three sets of conditions since our experience with the iron carbonyls indicated that the products would be very dependent upon the prevailing reaction conditions.[2,4,11] This expectation has been found to be correct since, for example, different major products are obtained from the reactions of ffars with the carbonyl at 81° ($(ffars)_2Ru_3(CO)_8$ in 63% yield), at 111° (ffars$Ru_2(CO)_6$, 61%), and under uv irradiation (ffars$Ru_3(CO)_{10}$, 63%). A number of experiments other than those described in the Experimental Section were done to investigate the effect of altering the ratios of the reactants. For example if the ratio of ffars to $Ru_3(CO)_{12}$ is slightly increased to 1.5:1 in the uv irradiation induced reaction, then the yield of ffars$Ru_3(CO)_{10}$ drops to 35% (the yield is 63% when the ratio is 1:1); moreover, more trace products are formed. At higher ratios the yields of known compounds are lower even when shorter irradiation times are used and under these conditions some $(ffars)_2Ru_3(CO)_8$ is produced. When ffos and the carbonyl react in cyclohexane, the yields of $(ffos)_2Ru_3(CO)_8$ and ffos$Ru_2(CO)_6$ are 15 and 21%, respectively, from a 3:1 ratio of ffos to $Ru_3(CO)_{12}$. However, under the same conditions, if the ratio is kept at 3:1 but the total concentration is doubled, the yields of both compounds are ~30%.

Although chromatography was used extensively as a method of separation and purification of products, the ruthenium complexes are less amenable to good separation by this technique than the iron complexes.

In general the types of products obtained in the reactions of $Ru_3(CO)_{12}$ are similar to those obtained with $Fe_3(CO)_{12}$ although differences do occur. As with iron $LM_3(CO)_{10}$ (L = ligand, M = transition metal), $LM_2(CO)_6$, and $LM(CO)_3$ complexes may be obtained with specific ligands. Ruthenium complexes with no iron analogs are the $L_2Ru_3(CO)_8$ (L = ffars, ffos) complexes, while no ruthenium analogs of $LFe(CO)_4$ (L = ffos, ffars), ffars$(Fe(CO)_4)_2$, ffars$Fe_3(CO)_9$, and $f_6$fos$Fe_2(CO)_7$, have been isolated in the present study.

As in the case of iron an $LM_2(CO)_6$ complex is formed by each ligand. The analytical data confirm the empirical formulas (Table I). The mass spectra all

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[11] W. R. Cullen and D. A. Harbourne, unpublished results.

show a parent ion $\text{LRu}_2(\text{CO})_6^+$ and loss of six carbonyl groups. The ions LRu^+ and L^+ are either weak or not seen. The arsenic compound shows a series $(\text{ffars-CH}_{3\text{ or }4})\text{Ru}_2(\text{CO})_n^+$, $n = 6 \rightarrow 0$. The compounds are white or pale yellow and do not have the dark red color of $\text{Ru}_3(\text{CO})_{12}$ indicating that the Ru_3 fragment is no longer present. The carbonyl infrared spectra of the ruthenium complexes (Table II) are very similar to those of the corresponding iron complexes and hence we assume the the compounds have similar structures. Figure 2 shows the expected structure of $\text{ffarsRu}_2(\text{CO})_6$ based on the known structure of $\text{ffarsFe}_2(\text{CO})_6$.[12] The ^{1}H nmr spectrum of $\text{ffarsRu}_2(\text{CO})_6$ shows the expected doublet. The infrared carbonyl spectra of the two ffars derivatives are slightly different from those of the ffos and f$_6$fos derivatives (which are very similar) but we believe that since the Mössbauer spectra of the three iron compounds can be interpreted in terms of structures related to that of Figure 2,[2b] there is no reason to suppose a different structure for the ruthenium analogs.

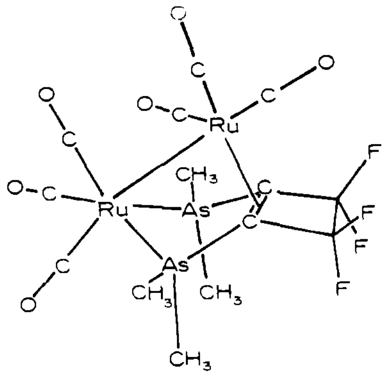

Figure 2.—Probable structure of $\text{ffarsRu}_2(\text{CO})_6$.

The compounds $\text{LRu}(\text{CO})_3$ (L = ffos, f$_6$fos) have also been obtained, the former in sufficient quantity for spectroscopic identification only. The analytical figures for the f$_6$fos compound (Table I) are not very good but great difficulty was encountered in recrystallizing this substance as it is unstable in solution. The mass spectrum of the f$_6$fos compound was poor and difficult to calibrate. The parent ion seems to correspond to $\text{f}_6\text{fosRu}(\text{CO})_3^+$ and shows successive loss of three carbonyl groups followed by loss of a phenyl group. The mass spectrum of the ffos complex was not obtainable. The infrared and nmr spectra of both these ruthenium compounds are very similar to the corresponding, well-characterized iron compounds whose structures have been discussed recently.[2c] These were believed to be based on a rigid distorted equatorial–equatorial-substituted trigonal bipyramid. The nmr evidence such as the singlet fluorine resonance of $\text{ffosRu}(\text{CO})_3$ indicates a symmetrical structure for this compound as would be present in an equatorial–equatorial-substituted trigonal bipyramid. The ^{1}H nmr spectrum of the compound $\text{diarsFe}(\text{CO})_3$ (diars = $o\text{-C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2$)[13] in the As–CH$_3$ region is a singlet down to −80° suggesting that compounds of this type have a *rigid* structure.[2c] At the time of proposing this the authors were not aware of an X-ray investigation of solid $\text{diarsFe}(\text{CO})_3$[14] which shows that the di(tertiary arsine) occupies axial and equatorial positions of a trigonal bipyramid. It must be concluded that this molecule is not rigid in solution or that the structure in solution is different, so caution is needed in interpreting the data for related compounds.

The infrared spectrum of $\text{f}_6\text{fosRu}(\text{CO})_3$ shows a similar splitting of one of the carbonyl stretching bands to that observed previously for $\text{f}_6\text{fosFe}(\text{CO})_3$.[2c] This same ligand gives anomalous spectra (one extra carbonyl band) in the chelated compounds $\text{f}_6\text{fosM}(\text{CO})_4$ (M = Cr, Mo, W).[3] It has been suggested that different conformations of the two five-membered rings present in the f$_6$fos complexes may give rise to species in solution with different energies thus accounting for "extra" bands in the carbonyl spectra.[3] Structural and low-temperature nmr studies are being undertaken to investigate this possibility.

It is interesting to note that as with iron no ruthenium $\text{ffarsM}(\text{CO})_3$ complex is isolable. At lower temperatures or under ultraviolet irradiation, when delicate products are not so easily destroyed, we notice a definite increase in the chelating ability of the ligands in the order ffars < ffos < f$_6$fos if we accept that the comparative yields of $\text{LRu}(\text{CO})_3$ obtained are indicative of this fact. Probably as a consequence of its poor chelating ability, ffars shows a distinct mildness as a ligand in iron and ruthenium carbonyl reactions and allows a greater proportion of trinuclear complexes and complexes containing monosubstituted metal atoms such as $\text{ffarsFe}(\text{CO})_4$ and $\text{ffarsFe}_2(\text{CO})_8$.[2,4,11]

Under the mild conditions of ultraviolet irradiation the complex $\text{ffarsRu}_3(\text{CO})_{10}$ is obtained from ffars and $\text{Ru}_3(\text{CO})_{12}$. Although the analytical figures (Table I) are not as good as for some of the other compounds, the spectroscopic evidence confirms this formulation. Thus the mass spectrum shows a parent ion corresponding to $\text{ffarsRu}_3(\text{CO})_{10}^+$ and shows successive loss of 10 carbonyl groups. Both the ^{19}F and ^{1}H nmr spectra consist of a singlet indicating a very symmetrical structure. The complex $\text{ffarsFe}_3(\text{CO})_{10}$ has the structure indicated in Figure 1.[4,8] Here also singlets are obtained in both the ^{1}H and ^{19}F spectra of the compound. In Figure 1 the ligand occupies two equatorial positions and equatorial substitution has been found in the few known Fe$_3$ complexes of monodentate ligands as in the compounds $(\text{C}_6\text{H}_5)_3\text{PFe}_3(\text{CO})_{11}$[15] and $[(\text{CH}_3)_2\text{P}(\text{C}_6\text{H}_5)]_3\text{Fe}_3(\text{CO})_9$.[16] In the case of $\text{Ru}_3(\text{CO})_{12}$ monodentate phosphines react to give compounds of the sort $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Ru}_3(\text{CO})_9$[17] and the phosphines ap-

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

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[17] J. P. Candlin and A. C. Shortland, *J. Organometal. Chem.*, **16**, 289 (1969).

pear to be attached to different ruthenium atoms.[17,18] Isomeric mixtures seem to be formed because the phosphine can substitute carbonyl groups from axial or equatorial positions in the $Ru_3(CO)_{12}$ skeleton. On the other hand, triphenylarsine gives the compound $((C_6H_5)_3As)_2Ru_3(CO)_{10}$ where the ligands are believed to occupy the two axial positions of one of the ruthenium atoms in the $Ru_3(CO)_{12}$ skeleton.[18] Tetradentate ligands such as $[o\text{-}(C_6H_5)_2PC_6H_4]_3P$ (QP) are reported to break up the Ru_3 cluster to give complexes of the sort (QP)RuCO.[19] The possible symmetrical structures for ffars$Ru_3(CO)_{10}$ are indicated in Figure 3.

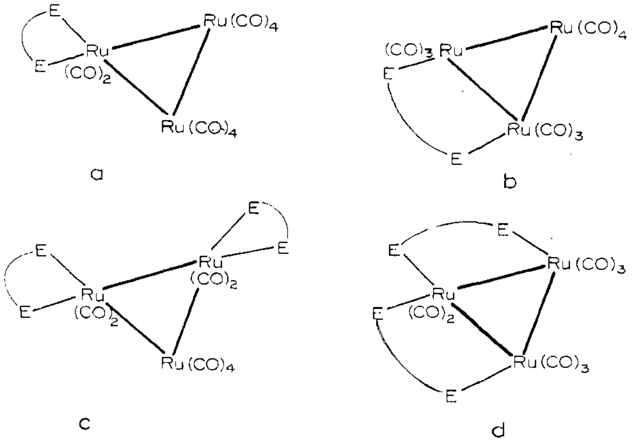

Figure 3.—Possible structures for $LRu_3(CO)_{10}$ and $L_2Ru_3(CO)_8$ (L = ffars or ffos).

These are the equatorially substituted chelate complex involving one ruthenium atom (Figure 3a) and the equatorially substituted bridged complex involving two ruthenium atoms (Figure 3b). It is impossible to differentiate between them with the available data; however, we favor the structure of Figure 3b because of the reluctance of ffars to form chelate complexes with iron carbonyls (without also involving the double bond of the cyclobutene ring as in ffars$Fe_2(CO)_6$) and because of the structure of ffars$Fe_3(CO)_{10}$. Added support comes from the similarity of the infrared spectra of ffars$Fe_3(CO)_{10}$ and ffars$Ru_3(CO)_{10}$ in the terminal carbonyl stretching region.

The ultraviolet initiated reaction of ffos with $Ru_3(CO)_{12}$ gives an inseparable mixture of ffos$Ru_2(CO)_6$ and a compound whose infrared spectrum in the carbonyl region (run as a solution of hand-picked crystals) is almost identical with that of ffars$Ru_3(CO)_{10}$. Moreover the ^{19}F nmr spectrum of this compound consists of a singlet. Although no mass spectrum was obtainable, it is reasonable that the compound be formulated as ffos$Ru_3(CO)_{10}$ with the same structure as ffars$Ru_3(CO)_{10}$.

If a cyclohexane solution of ffars$Fe_3(CO)_{10}$ is refluxed, the major product is the new complex ffars$Fe_3(CO)_9$.[4,10] Under similar conditions ffars$Ru_3(CO)_{10}$ converts to ffars$Ru_2(CO)_6$.

Both ffars and ffos react with $Ru_3(CO)_{12}$ in refluxing cyclohexane to give compounds of formula $L_2Ru_3(CO)_8$. The mass spectrum of only the ffars compound could be obtained. It gives a parent ion corresponding to $(ffars)_2Ru_3(CO)_8{}^+$ and shows loss of eight carbonyl groups. The red color of the parent carbonyl is retained so the Ru_3 cluster is presumably still intact in both $Ru_3(CO)_8$ compounds. The similarity of their infrared spectra in the carbonyl stretching region indicates that they are isostructural. Two of the many possible structures are shown in Figure 3. The ^1H nmr spectrum of the ffars complex consists of two singlets which indicates a fairly symmetrical structure. The ^{19}F spectrum of the same compound is complex and the pattern shows some similarity to that of ffars$Fe(CO)_4$ where only one arsenic is complexed. Thus the complexed ligand does not have a mirror plane perpendicular to the cyclobutene ring and the evidence seems to favor the structure indicated in Figure 3d for these compounds where the ligands occupy equatorial positions.[20]

The yellow complex obtained from the reaction of ffos with $Ru_3(CO)_{12}$ in cyclohexane has not yet been identified. However it is significant that its carbonyl infrared spectrum is unlike any previously prepared derivatives of iron or ruthenium.

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(18) M. I. Bruce, C. W. Gibbs, and F. G. A. Stone, *Z. Naturforsch. B*, **23**, 1543 (1968).

(19) M. T. Halfpenny and L. M. Venanzi, unpublished results quoted in ref 5.

(20) This structure has now been confirmed for solid $(ffars)_2Ru_3(CO)_8$ (P. J. Roberts and J. Trotter, personal communication), which makes the structure of Figure 3b even more likely for ffars$Fe_3(CO)_{10}$.