Heterodimetallic Cycloheptatrienyl Complexes of the Transition Metals: Synthesis, Properties, and Structure[1]

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Abstract: The reaction of $(C_7H_7)Fe(CO)_3^-$ with metal carbonyl halides has resulted in the formation of heterodimetallic cycloheptatrienyl complexes of the form $(C_7H_7)Fe(CO)_3M(CO)_y$, where M = Mn or Re and $y = 3$, M = Rh and $y = 2$. The mass spectra of the molecules, besides exhibiting the characteristic stepwise losses of carbonyl groups, also show "bare" dinuclear FeM^+ fragments. The ^1H NMR spectra show a sharp singlet for the C_7H_7 group at room temperature which only broadens at the lowest accessible temperatures, 123 to 109 K, establishing very rapid ring "whizzing" for these molecules. It is argued that these observations are only consistent with a structure where the two metal carbonyl moieties are cis with respect to the seven-membered ring and are joined by a metal-metal bond. This structure was verified for the Fe-Rh complex by single-crystal x-ray crystallography. Crystal data as follows: monoclinic space group $C2/c$; $a = 12.756$ (6), $b = 15.044$ (9), $c = 13.446$ (5) Å; $\beta = 99.62$ (1)°; $Z = 8$; $d_{\text{obsd}} = 2.07$ (1), $d_{\text{calcd}} = 2.066$ g cm^{-3} (all measurements at 22 °C). Full-matrix least-squares refinement based on 1672 reflections having $I > 3\sigma(I)$ converged to a final conventional R factor (on F) of 0.027. The molecule contains a $Rh(CO)_2$ group bonded to the diene and a $Fe(CO)_3$ moiety attached to the allyl portion of a bridging cycloheptatrienyl ring. In addition, the two metal carbonyl fragments are joined by a metal-metal bond of length 2.764 (1) Å. A comparison between this structure and *trans*-$(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$, reveals a greater p$\pi$-p$\pi$ overlap between the diene and allyl portion of the ring in the cis compound (shorter C-C bond length, 1.449 (7) vs. 1.50 (1) Å, for the carbon atoms joining the allyl and diene units, and smaller ϕ angle between the pπ orbitals of these same atoms, 22.8 vs. 61.0°). This is in qualitative accord with the much increased fluxional character of the reported compounds. The variable temperature ^{13}C NMR spectra of the molecules show that while the local carbonyl scrambling within $M(CO)_3$ sets is indeed very facile, carbonyl group exchange between the two metal carbonyl moieties does not occur. The possible coupling between rearrangement of the ring and carbonyl scrambling is offered as a rationale for the rapidity of the former process. The absence of carbonyl group exchange between the two ends of the molecule is consistent with the presence of the bridging cycloheptatrienyl group and the associated long Fe-Rh bond length.

Although the reactivity of cycloheptatriene toward a variety of transition metal carbonyls has been extensively investigated,[2] only rarely did these reactions yield complexes containing two transition metals attached to the same cycloheptatrienyl moiety.[3a,b] Examples of cycloheptatrienyl complexes containing two different metal atoms are even rarer.[3c] The recent report of Stone et al.[4] on the utilization of $[Ru(CO)_4(SiMe_3)]_2$ for the synthesis of a series of dimetallic-ruthenium-cycloheptatrienyl complexes, $[Ru_2(CO)_5(SiMe_3)(C_7H_6R)]$, is therefore a significant contribution to this area of organometallic chemistry. In this paper, we describe the use of cycloheptatrienyliron tricarbonyl anion,[5] $(C_7H_7)Fe(CO)_3^-$, as a suitable starting material for the synthesis of heterodimetallic cycloheptatrienyl complexes, $(C_7H_7)Fe(CO)_3M(CO)_y$ (M = Mn, Re, $y = 3$; M = Rh, $y = 2$). In addition, we also present the x-ray structure determination of one of the complexes, $(C_7H_7)Fe(CO)_3Rh(CO)_2$.

Experimental Section

Syntheses. All operations were performed under an atmosphere of purified nitrogen using Schlenk type apparatus which were attached to a double manifold. The double manifold allows for quick and convenient access to either nitrogen or vacuum as required for a particular operation; furthermore, it ensures the rigorous and complete exclusion of air from the utilized Schlenk apparatus by permitting the carrying out of successive evacuation-inert gas refill cycles from the same three-way stopcock. The purification of the nitrogen was accomplished by first passing it through a heated (90-100 °C) column packed with activated BASF catalyst (R3-11) and then, to remove the residual moisture, through a column containing Aquasorb purchased from Mallinckrodt Chemical Works. Solvents were dried over Na/K alloy (THF (tetrahydrofuran) and benzene) or calcium hydride (pentane) and were deoxygenated prior to use.

Florisil (100-200 mesh) was used as received from Fisher Scientific Co.; alumina of activity I was purchased from Waters Associates Inc. and converted to activity II by the addition of 3% (w/w) water. Hexane solutions of *n*-BuLi (15%) were obtained from Matheson Coleman and Bell. Carbon monoxide, 90% enriched in ^{13}CO, was purchased from Monsanto Research Corporation. All other chemicals were readily available and were used as received.

Lithium cycloheptatrienyltricarbonyl ferrate(−1) ($Li[(C_7H_7)Fe(CO)_3]$) was prepared according to the method of Maltz[5] from $(C_7H_8)Fe(CO)_3$[6] and used immediately. The compounds $[Mn(CO)_4Br]_2$,[7] $[Rh(CO)_2Cl]_2$,[8] and $[Re(CO)_3BrTHF]_2$[9] were also synthesized according to published procedures.

μ-[1-3-η:4-7-η-Cycloheptatrienyl]-tricarbonylirondicarbonylrhodium(*Fe-Rh*). A cold (ca. −10 °C), dark red solution of $Li[(C_7H_7)Fe(CO)_3]$ (2.57×10^{-2} mol) in 50 ml of dry and deoxygenated THF was added dropwise from a vacuum-jacketed pressure-equalized addition funnel over a period of 5 h to a cooled (−20 °C) and magnetically stirred solution of 5.07 g of $[Rh(CO)_2Cl]_2$ (1.29×10^{-2} mol) in 50 ml of THF. After the addition was completed, the reaction mixture was allowed to warm up to room temperature during 2 h. Solvent was removed from the resulting reddish brown solution under vacuum and the residue was extracted with 50 ml of benzene. The filtered extract was concentrated to about 5 ml and was then placed on a chromatography column packed with alumina of activity II. Elution with hexane caused the separation of a yellow band which was identified as $[(C_7H_7)Fe(CO)_3]_2$. Further elution with a 50/50 mixture of hexane/benzene produced a dark wine-red band. Removal of the solvent followed by crystallization from pentane at dry ice-acetone temperature gave 1.5 g (15% yield) of reddish brown crystals of $(C_7H_7)Fe(CO)_3Rh(CO)_2$, m.p. 96-98 °C. An analytical sample was obtained by recrystallization from pentane.

Anal. Calcd. for $C_{12}H_7O_5FeRh$: C, 36.96; H, 1.81. Found: C, 36.68, 36.43; H, 2.11, 2.09.

The infrared spectrum of a cyclohexane solution had CO stretching maxima at 2057.5 (s), 2008 (s), 2006 (sh), 1961 (sh), and 1958 (m) (all ±1 cm^{-1}).

μ-[1-3-η:4-7-η-Cycloheptatrienyl]-tricarbonylirontricarbonylmanganese(*Fe-Mn*). The reaction was carried out as described above by utilizing 6.5 g (1.32×10^{-2} mol) of $[Mn(CO)_4Br]_2$. The separation was effected on a florisil column. Elution with hexane gave an orange band from which a very small amount of crystals, identified (ir and mass spectrum) as $(CO)_4Fe[Mn(CO)_5]_2$, was isolated. Further elution with a 50/50 mixture of hexane/benzene produced a dark wine-red band. The product from this last band, which proved to be a mixture, was rechromatographed on alumina, activity II. This time elution with hexane gave a yellow band containing $Mn_2(CO)_{10}$ and $[(C_7H_7)Fe(CO)_3]_2$, further elution with benzene gave a reddish orange band from which 0.242 g (2.3% yield) of orange crystals of $(C_7H_7)Fe(CO)_3Mn(CO)_3$ was isolated. Recrystallization from pentane at −78 °C yielded an analytically pure sample melting at 141–142 °C.

Anal. Calcd for $C_{13}H_7O_6FeMn$: C, 42.20; H, 1.91; O, 25.95. Found: C, 41.76, 42.32; H, 2.14, 2.47; O, 26.69, 26.58.

The infrared spectrum in cyclohexane had the following CO stretching maxima: 2052.5 (s), 1997 (s), 1995 (sh), 1992.5 (sh), 1944.5 (w), and 1939 (m) (all ±1 cm^{-1}).

μ-[1–3-η:4–7-η-Cycloheptatrienyl]-tricarbonylirontricarbonylrhenium(*Fe-Re*). The reaction was carried out as described for the Fe–Rh complex by utilizing 1.70 g (2.01×10^{-3} mol) of $[Re(CO)_3BrTHF]_2$ and performing the addition at ambient temperature. The separation was effected on a column packed with alumina of activity II. Elution with hexane caused the appearance of an orange band which contained a mixture of $Re_2(CO)_{10}$ and $[(C_7H_7)Fe(CO)_3]_2$. Changing to benzene developed a second, yellow-orange band from which 0.29 g (14% yield) of yellow-orange crystals of $(C_7H_7)Fe(CO)_3Re(CO)_3$ was isolated. Recrystallization from pentane gave an analytically pure sample melting at 162–163 °C.

Anal. Calcd for $C_{13}H_7O_6FeRe$: C, 31.15; H, 1.41. Found: C, 31.48, 30.98; H, 1.64, 1.92.

The infrared spectrum of a cyclohexane solution contained CO stretching maxima at 2052 (s), 2006 (s), 1988 (s), 1973 (w), 1945 (w), and 1937 (m) (all ±1 cm^{-1}).

Instrumental Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using 0.5-mm NaCl cells and were calibrated with gaseous CO.

Proton NMR spectra were recorded on a Varian HA-100 spectrometer. Samples for room-temperature or low-temperature (in diethyl-d_{10} ether) studies were prepared with degassed solvents in serum-capped NMR tubes (Wilmad Glass Co., Inc.). For the low-temperature work requiring CHF_2Cl/CD_2Cl_2 (80/20) mixture as solvent, the sample was prepared on the vacuum line and the NMR tube sealed under high vacuum. Temperature calibration was achieved with a copper/Constantan thermocouple with one junction immersed in ice water and the other in the NMR probe below the sample tube.

Carbon-13 NMR spectra were recorded on a deuterium-lock Bruker HFX-90/Nicolet 1085 FT spectrometer operating at 22.628 MHz. For variable temperature work, depending on the solvent and temperature, serum-capped or sealed 10-mm o.d. tubes were employed. Temperature measurements and calibration were made with a Bruker temperature control unit, Model B-ST 100/700 and are believed to be accurate to ±1°. For the low temperature study, ^{13}CO enriched samples of $(C_7H_7)Fe(CO)_3Rh(CO)_2$ and $(C_7H_7)Fe(CO)_3Mn(CO)_3$ were prepared by dissolving 50 mg of the compounds in 20 ml of cyclohexane and stirring the solution under 1 atm of 90% ^{13}CO for 1.5 h (FeRh) or irradiating for 0.5 h (FeMn). The progress of the enrichment was followed by ir and its extent (ca. 65% for FeRh and 25% for FeMn) was determined by mass spectrometry.

Mass spectra were taken with an A.E.I. MS12 spectrometer (operating conditions: energy 70 eV, resolution 2000, accelerating voltage 8 kV. The samples were introduced into the ion source using the direct inlet technique at a temperature just sufficient to observe the spectrum.

The melting points are uncorrected and were determined on a Thomas-Hoover apparatus on samples which were sealed in a capillary.

Microanalyses were performed by the Microanalytical Laboratory of this department.

X-Ray Study of the Fe-Rh Complex. Weissenberg and precession photographs revealed that the crystals belong to the monoclinic space group $C2/c$. Least-squares refinement of the cell parameters on the 2θ values observed for 12 high-order ($24° < 2\theta < 38°$) reflections accurately centered on a Picker four-circle automatic diffractometer gave the following values: $a = 12.756$ (6) Å, $b = 15.044$ (9) Å, $c = 13.446$ (5) Å, and $\beta = 99.62$ (1)°, using monochromatized Mo Kα radiation (λ 0.7093 Å). The density measured by flotation in an aqueous mixture of Clericis solution, 2.07 (1) g cm^{-3}, agrees well with 2.066 g cm^{-3} calculated for eight molecules in the unit cell. All measurements were made at 22 °C.

For intensity measurements, a crystal of approximate dimensions $0.25 \times 0.14 \times 0.08$ mm along a^*, b^*, and c^* was mounted approximately with its b^* axis coincident with the ϕ axis of a Picker automatic four-circle diffractometer. For absorption correction purposes, nine distinct crystal faces, (001), (00$\bar{1}$), (100), ($\bar{1}$00), (0$\bar{1}$0), (110), ($\bar{1}$10), (021), and (02$\bar{1}$) were identified and measured. Intensities were measured by the coupled ω–2θ scan method using Mo Kα radiation with a graphite monochromater. The x-ray tube was set to a 4° takeoff angle. Symmetric 2° scan ranges and a scan rate of 1° min^{-1} were used. Twenty-second stationary background counts were taken at the upper and lower limits of each scan. Intensities were measured with a scintillation counter with the pulse height analyzer set to accept approximately a 95% window when centered on the Mo Kα peak. Crystal and instrumental stability were monitored by a set of three standards measured after every 50 reflections. The variations in these standards were about 2% with no apparent systematic trend, indicating that there was no decomposition of the crystal during data collection. Data were collected for $2\theta \leq 50°$ for the octants $hk\bar{l}$, hkl, $\bar{h}k\bar{l}$, and $h\bar{k}\bar{l}$, which were later merged to the two nonequivalent octants $\bar{h}kl$ and hkl to yield 2457 unique relections. Net intensities were calculated assuming a linear background profile between the scan limits of each relection. The reflections (1672) for which $I > 3.0\sigma(I)$ were used in the solution and refinement of this structure. Standard derivations on I were calculated using an ignorance factor, $P = 0.03$. Intensities were reduced to values of F^2 after correction for Lorentz and polarization effects. The linear absorption coefficient of this compound for Mo Kα radiation is 24.55 cm^{-1}, and the transmission factors ranged from 0.870 to 0.921 for this crystal.

The rhodium and iron atoms were located from a three-dimensional Patterson map.[10] A subsequent difference Fourier map phased on these two atoms revealed the positions of the ring carbons and the iron carbonyls. Full-matrix least-squares refinement with isotropic temperature factors for these atoms converged at $R_1 = 0.161$ and $R_2 = 0.220$. The residuals are defined by $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ where the weights $w = 1/\sigma^2(F_o)$. All least-squares refinements were made on F where the function minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors used were those of Cromer and Mann[11] for non-hydrogen atoms and those of Stewart et al.[12] for hydrogen atoms. Rhodium and iron atom scattering factors include the real and imaginary components of anomalous dispersion for Mo Kα radiation.[13] The rhodium carbonyls were subsequently located and the residuals converged at $R_1 = 0.068$ and $R_2 = 0.085$. All the atoms were given anisotropic temperature factors and absorption corrections were made bringing $R_1 = 0.036$ and $R_2 = 0.043$. At this point, absorption-corrected data from the second octant were merged with the first octant data which had been used in the refinement up to this stage. The merged data gave $R_1 = 0.041$ and $R_2 = 0.068$ and a difference map, in which the contributing data were restricted to reflections with $2\theta < 35°$, was done to locate the hydrogen atoms.

With the hydrogen atoms in the refinement (their temperature factors set at one unit greater than the respective carbon atom), the residuals converged at $R_1 = 0.027$ and $R_2 = 0.026$. In the final refinement cycle the maximum change in a non-hydrogen parameter was 0.07σ. The final goodness of fit, $[\sum w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$, was 1.08.

The final positional parameters and temperature factors are given in Table III, together with their associated standard deviations as derived from the inverse matrix. The root-mean-square amplitudes of thermal vibration and direction cosines for the atoms refined anisotropically are given in Table IV. Selected bond distances and angles, consistent with the numbering scheme of Figure 3, are to be found in Table V, while Table VI lists the planes and their equations that make up the given molecular ring. Table IV and the final values of the observed and calculated structure factors have been deposited.[14]

Results and Discussion

Scheme I shows the generalized reaction sequence for the preparation of the complexes described in this report.

As can be seen in the scheme, the interaction of the anion, $(C_7H_7)Fe(CO)_3^-$, with metal carbonyl halides could conceivably yield two, structurally quite different, products. In one case, the two metal carbonyl moieties are trans to one

Scheme I

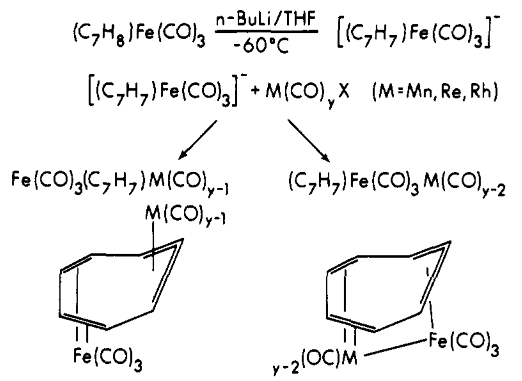


Table II. ^1H and ^{13}C NMR Data

Compound	$\delta(C_7H_7)^a$	$\delta(C_7)^b$	$\delta(FeCO)^b$	$\delta(MCO)^b$
Mn-Fe	4.05	70.7	213.0^d	224.3^d
Re-Fe	4.22	64.2	211.4	192.4 (broad)
Rh-Fe	4.16	64.9	217.8^d	194.3^c

[a] Diethyl-d_{10} ether solution, chemical shift with respect to internal Me_4Si. [b] Toluene-d_8 solution, chemical shift converted to Me_4Si scale using as reference the quarternary carbon of toluene, δ 137.5 ppm. [c] Doublet due to $J_{^{103}Rh-^{13}C} = 72.4$ Hz. [d] Singlets down to the lowest temperature. See text for discussion.

another; in the other we have the production of a cisoid structure with concurrent formation of a heterodimetallic metal-metal bond. A priori it is difficult to choose between the two paths. Maltz[5] has shown that deuteration of the anion proceeds in an exo fashion (trans to the $Fe(CO)_3$ group), clearly indicating that, at least with certain electrophiles, the transoid arrangement of the final substituent on the ring is indeed possible. However, the known dependence of the direction of the attack, in this type of reaction, on the nature of the electrophile and/or nucleophile[15] also implies that to take the above observation as a sufficient reason to rule out the cisoid structure would almost certainly be met with failure. In fact, there are several lines of reasoning which allow us to deduce that all the complexes of this work possess the cis arrangement of the carbonyl moieties with respect to the seven-membered ring.[17,18]

Mass Spectral Results. Besides the presence or absence of a metal-metal bond, an additional difference between the cis and trans structures, which has not as yet been mentioned, is the number of carbonyl groups the molecules contain. The question is irrelevant when one considers the reaction between the anion and $[Rh(CO)_2Cl]_2$. However, with $[Mn(CO)_4Br]_2$ Scheme I, in harmony with the 18-electron rule,[20] will give the following two compounds: *cis*-$(C_7H_7)Fe(CO)_3Mn(CO)_3$ with six carbonyl groups and *trans*-$(CO)_3Fe(C_7H_7)Mn(CO)_4$ with seven carbonyl groups. In principle then, the mass spectrum of the complex could be utilized as a tool to distinguish between the two possibilities. Unfortunately, although the principle that "the peak of largest *m/e* in the mass spectrum of a metal carbonyl derivative normally gives the *minimum* number of carbonyl groups present" has been given good experimental support,[21] the observation that the highest peak in the product isolated from the above reaction corresponds to $(C_7H_7)FeMn(CO)_6^+$ only shows that the compound contains a *minimum* of six carbonyl groups. Since there are well known cases where the mass spectrum shows *fewer* than the actually present number of carbonyls in the molecule,[22] the above observation, by itself, is not sufficient to rule out the trans structure. However, the identification of peaks corresponding to FeM^+, with the appropriate isotopic multiplets, in all three compounds can be taken as a strong supportive evidence for the cis structure. Indeed, the observation of "bare" metal cluster ions in the mass spectra of organometallic species is rare and many a times remains unobserved even in cases where other observations have conclusively proven the presence of metal-metal bonds.[23,24] Therefore, to observe such fragments from the trans arrangement of the carbonyl moieties is outside the realm of possibility.

The fragmentation pattern of the complexes, besides containing peaks corresponding to the parent molecular ion of the cisoid geometry, is characterized by successive losses of carbon monoxide[25] followed by characteristic breakdown of the $C_7H_7Fe^+$ group[25,26] (i.e., production of $C_6H_6Fe^+$ and $C_5H_5Fe^+$). We may note that whereas in the case of the Mn-Fe compound, the base peak corresponds to $C_7H_7Fe^+$, in the Re and Rh complexes, the peak of highest intensity is $C_7H_7FeM^+$ again in accord with the strength of the metal-metal bond in these compounds.[24] Further details on the mass spectra of the compounds can be obtained from Table I.[14]

^{1}H NMR Results. Additional evidence to support the cisoid structure comes from the variable temperature NMR behavior of the reported complexes. From the known fluxional nature of both *cis*-$Ru_2(CO)_5(SiMe_3)(C_7H_6R)$[4] and *trans*-$(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$[3b,27] complexes, it was anticipated that our compounds will also be fluxional irrespective of the produced geometry. The observation of a single sharp line, Table II and Figure 1, due to the C_7H_7 group in the proton NMR spectra of all three compounds is clearly irreconcilable with any static arrangement of the molecule, but can be explained in terms of a rapidly rotating cycloheptatrienyl moiety about the two attached metal carbonyl groups thereby resulting in a single, time averaged environment for all seven protons of the ring system. However, our inability to reach the limiting spectrum or to even collapse the singlet at the lowest available temperature in this study,[29] Figure 1, also implies a cis structure with an Fe-M bond for the complexes. This conclusion is based on the empirical observation that cis dimetallic organometallic derivatives of conjugated cyclic polyenes have activation barriers for rearrangement which are much smaller than the related trans complexes. Indeed in the study of Cotton and Reich[3c] the limiting spectrum for *trans*-$(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$ was reached at 202 K, whereas in the related *cis*-$Ru_2(CO)_5(SiMe_3)(C_7H_7)$[4] the singlet persisted down to 163 K. We may note that similar spectacular changes in fluxional behavior have been observed in organometallic derivatives of cyclooctatetraene also, *trans*-$(C_8H_8)[Fe(CO)_3]_2$ shows no fluxional behavior;[30] however, the spectrum of *cis*-$(C_8H_8)Fe_2(CO)_5$ remains a single peak even at 173 K.[31]

^{13}C NMR Results. A further intriguing possibility with metal carbonyl compounds is a rearrangement that involves the carbonyl groups themselves. In fact, during the last few years the power of ^{13}C NMR spectroscopy has been very successfully applied to this problem. Two main processes have been identified. In one process, observed in polynuclear carbonyls,[32] the averaging of the carbonyl groups environment is achieved by movement of the carbonyls from one metal to the next. The other process, which is mainly limited to mononuclear species having nonequivalent carbonyl groups in an $M(CO)_3$ moiety, averages the carbonyl groups environment within the same $M(CO)_3$ set.[33,34] By virtue of their cis geometry our compounds, in principle, are capable of manifesting both processes and for this reason a study of their ^{13}C NMR spectra was carried out. The results are to be found in Table II, while Figure 2 shows the actual spectra for the Fe-Mn and Fe-Rh complexes. We should add that the spectrum of the Fe-Rh complex remained unchanged from 137 to 343 K and that the two-line spectrum of the Fe-Mn complex persisted down to 143 K.

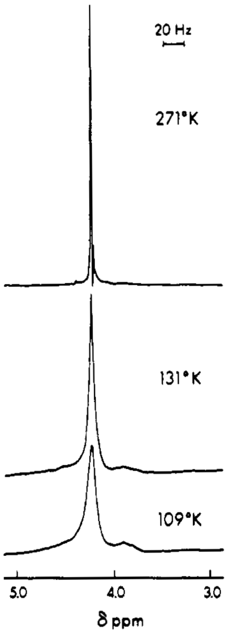
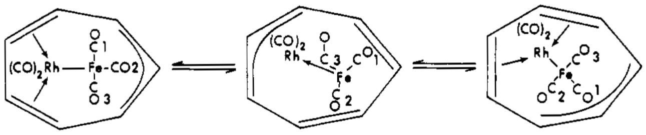


Figure 1. Variable temperature ^{1}H NMR spectra of $(C_7H_7)Fe(CO)_3Rh(CO)_2$ in a mixture of CHF_2Cl/CD_2Cl_2 (4:1 v/v).

Based on the structure of these molecules one would expect two resonances in the ratio 2:1 for the $M(CO)_3$ moieties, one resonance for the two carbonyl groups trans to the organic ligand and one for the unique carbonyl group trans to the metal-metal bond. The observation of sharp singlets for these moieties therefore indicates carbonyl scrambling within the respective metal tricarbonyl fragments.[36] Furthermore, it is also apparent that the process is very facile since it still operates at the lowest accessible temperatures. As shown in Scheme II, it is possible to postulate a transition state in the 1,2-shifts which, by the intermediacy of a semibridging carbonyl group,[37] could activate the carbonyl groups scrambling and thereby "explain" its rapidity; however, in the absence of experimental support, the above explanation remains highly speculative, and we must conclude that the reason for the rapidity of carbonyl groups exchange in these molecules remains unclear.[38]

Scheme II



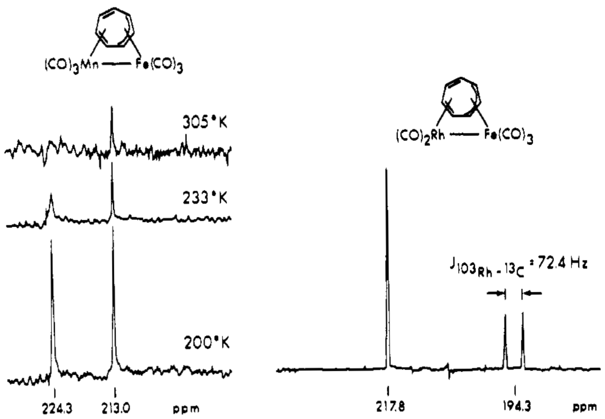
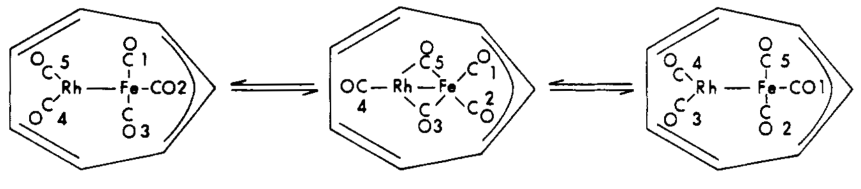


Figure 2. ^{13}C NMR spectra of $(C_7H_7)Fe(CO)_3Mn(CO)_3$ and $(C_7H_7)Fe(CO)_3Rh(CO)_2$ in the carbonyl region. Chemical shift in parts per million downfield from Me_4Si, solvent toluene-d_8.

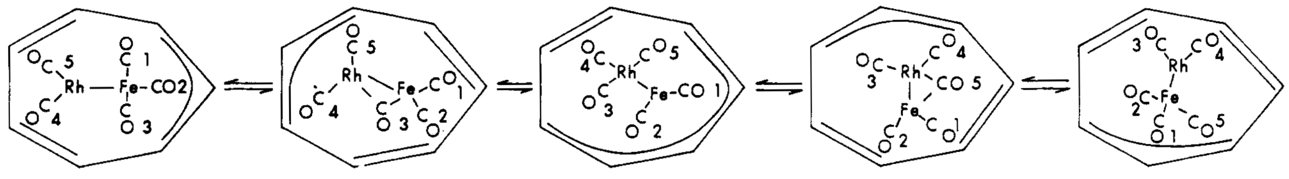
The observation of two signals for the Fe-Rh complex up to 343 K indicates that no carbonyl exchange is occurring between the two metals in this molecule. Thus for these complexes a double bridge or single bridged intermediate with proper bonding pattern, Scheme III, which would result in such carbonyl groups scrambling is a high energy state and is not achieved at this temperature. This could be attributed to the presence of the bridging cycloheptatrienyl ring which by its relatively rigid nature could inhibit the changes necessary to achieve the geometrical requirements of the above intermediates.[35e]

One final point of interest is the ^{13}C NMR spectrum of the Mn-Fe compound. As can be seen in Figure 2, at room temperature the resonance due to the $Mn(CO)_3$ is not seen, whereas at 200 K the peak shows up as a sharp singlet, which is only slightly broader than the signal due to the $Fe(CO)_3$ group. Similar temperature effects on the ^{13}C NMR spectra of transition metal carbonyl derivatives having quadrupolar nuclei (^{55}Mn, $I = \frac{5}{2}$) have been noted recently[39] and have been attributed to the effective decoupling of the quadrupolar manganese from the ^{13}C of the carbonyl group at low temperature.[40] Increased solvent viscosity at low temperature is also apparently quite important in certain cases in this regard. In an effort to obtain spectra of the Fe-Mn complex at lower temperature, the study was repeated in CHF_2Cl/CD_2Cl_2 solvent mixture. At 203 K the $Mn(CO)_3$ signal could not be seen (the $Fe(CO)_3$ group showed up as a sharp peak as observed before) and even at 143 K the resonance was significantly broader than in toluene-d_8 at 203 K (width at half-

Scheme III



A. DOUBLE-BRIDGED INTERMEDIATE



B. SINGLE-BRIDGED INTERMEDIATE WITH APPROPRIATELY REORGANIZED BONDING PATTERN

Table III. Final Positional and Thermal Parameters for $(C_7H_7)Fe(CO)_3Rh(CO)_2$[a]

	x	y	z	β_{11}[e]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2
Rh	0.23824 (3)	−0.05443 (2)	0.12700 (2)	70.0 (3)	31.4 (2)	44.1 (2)	1.7 (2)	2.0 (2)	5.5 (2)	3.51[b]
Fe	0.29225 (5)	−0.17318 (4)	0.28403 (4)	56.4 (5)	38.1 (3)	36.5 (4)	−3.0 (3)	0.0 (3)	3.4 (3)	3.25
C(1)	0.3913 (4)	−0.0939 (3)	0.3305 (4)	67 (4)	50 (3)	65 (3)	−9 (3)	6 (3)	2 (3)	4.47
O(1)	0.4531 (3)	−0.0436 (3)	0.3658 (3)	84 (3)	73 (3)	127 (4)	21 (2)	−3 (3)	23 (2)	7.10
C(2)	0.3301 (3)	−0.2487 (3)	0.3835 (3)	63 (4)	45 (2)	46 (3)	−6 (2)	3 (2)	1 (2)	3.78
O(2)	0.3611 (3)	−0.2975 (2)	0.4471 (2)	116 (3)	68 (2)	61 (2)	−25 (2)	1 (2)	26 (2)	6.02
C(3)	0.3562 (4)	−0.2320 (3)	0.1964 (3)	66 (4)	56 (3)	49 (3)	−6 (3)	−1 (3)	4 (2)	4.30
O(3)	0.3987 (3)	−0.2735 (3)	0.1438 (3)	101 (3)	85 (3)	65 (3)	−25 (2)	19 (2)	16 (2)	6.17
C(4)	0.3295 (4)	0.0448 (3)	0.1413 (4)	74 (4)	37 (3)	84 (4)	−7 (3)	21 (3)	3 (3)	4.59
O(4)	0.3842 (3)	0.1049 (2)	0.1469 (3)	106 (4)	39 (2)	181 (5)	16 (2)	41 (3)	17 (3)	7.53
C(5)	0.2984 (4)	−0.0971 (3)	0.0183 (4)	110 (5)	43 (3)	57 (3)	11 (3)	21 (3)	3 (2)	4.86
O(5)	0.3355 (4)	−0.1228 (3)	−0.0467 (3)	178 (5)	69 (3)	76 (3)	14 (3)	58 (3)	11 (2)	7.33
C(11)	0.0659 (4)	−0.0789 (3)	0.0989 (4)	66 (4)	52 (3)	56 (3)	14 (3)	−16 (3)	16 (2)	4.44
C(12)	0.1191 (4)	−0.1626 (3)	0.1181 (3)	68 (4)	42 (2)	42 (3)	12 (2)	−9 (3)	0 (2)	3.83
C(13)	0.1369 (3)	−0.2132 (3)	0.2111 (3)	60 (3)	37 (2)	46 (3)	10 (2)	−6 (2)	5 (2)	3.55
C(14)	0.1388 (3)	−0.1774 (3)	0.3071 (3)	53 (3)	45 (3)	45 (3)	−1 (2)	4 (2)	10 (2)	3.56
C(15)	0.1720 (3)	−0.0899 (3)	0.3285 (3)	56 (3)	48 (3)	45 (3)	−8 (2)	2 (3)	6 (2)	3.72
C(16)	0.1601 (4)	−0.0167 (3)	0.2575 (4)	64 (3)	37 (2)	63 (3)	−4 (2)	11 (3)	4 (2)	3.94
C(17)	0.0864 (4)	−0.0092 (4)	0.1660 (4)	64 (4)	39 (3)	81 (4)	−14 (3)	5 (3)	−15 (3)	4.49
H(11)[c]	0.026 (3)	−0.076 (3)	0.032 (3)							[d]
H(12)	0.119 (3)	−0.198 (3)	0.062 (3)							
H(13)	0.125 (3)	−0.274 (3)	0.201 (3)							
H(14)	0.129 (3)	−0.212 (3)	0.360 (3)							
H(15)	0.183 (3)	−0.069 (3)	0.395 (3)							
H(16)	0.178 (4)	0.037 (3)	0.286 (3)							
H(17)	0.067 (4)	0.044 (3)	0.150 (4)							

[a] Numbers in parentheses are estimated standard deviations in the last figure quoted. [b] Equivalent isotropic B's. [c] Hydrogen atoms have the same numbers as the carbon atoms to which they are bonded. [d] Hydrogen atom temperature factors fixed at one unit in B greater than the carbon atoms to which they are bonded. [e] Anisotropic temperature factors (×10^4) are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

height 9 vs. 4 Hz). Exchange, as opposed to quadrupolar broadening, can be ruled out since the resonance actually sharpened on going from 153 to 143 K. It should be noted that the additional benefit of recording the spectrum at low temperature resides in the shortened T_1 relaxation of the metal bonded carbonyl groups thus allowing the observation of a high resolution spectrum in a very short time.[42,43] Thus the 200 K spectrum was obtained in 7 min (512 scans, pulse width = 70 μs) whereas the room temperature one was obtained in 14 min (1000 scans, pulse width = 40 μs).

Molecular Structure of μ(1-3-η:4-7-η-Cycloheptatrienyl)-tricarbonylirondicarbonylrhodium(*Fe-Rh*). Although the spectral properties of the complexes were seemingly only consistent with a cis arrangement of the metal carbonyl groups with respect to the seven-membered ring system in order to be absolutely certain about the geometry and to support some of the above conclusions with exact numbers (cf. carbonyl groups nonequivalence, length of metal-metal bond in relation to carbonyl group passage from M to M′), it was decided to investigate the structure of the Fe-Rh complex, the most thoroughly studied molecule by spectral means.

Two perspective views of the molecule $(C_7H_7)FeRh(CO)_5$, with appropriate numbering scheme, are shown in Figure 3. It is immediately obvious that the reaction between $(C_7H_7)Fe(CO)_3^-$ and $[Rh(CO)_2Cl]_2$ produces, as argued above, molecules containing bridging cycloheptatrienyl groups with a cisoid arrangement of the $Fe(CO)_3$ and $Rh(CO)_2$ moieties. The iron atom besides being bonded to three carbonyl groups, clearly separated into CO(2) trans to Fe-Rh bond and CO(1) and CO(3) trans to the allyl group, is also in bonding contact with three carbon atoms (C(13), C(14), C(15)) of the ring. The rhodium atom in addition to the two carbonyl groups is also bonded to the remaining diene (C(16), C(17), C(11), C(12)) part of the carbocycle. The final bonding interaction, satisfying the 18-electron requirement of both iron and rhodium, is obtained by the formation of a Fe-Rh metal-metal bond.[45]

The iron-rhodium bond length of 2.764 (1) Å is significantly longer than those found previously in complexes containing such bonds. The values are 2.674 (1) and 2.659 (2) Å in $[Rh\{Fe(PPh_2)(CO)_2(CH_3C_5H_4)\}_2]^+$,[47] 2.568 (3) and 2.615 (3) Å in $(C_5H_5)RhFe_3(CO)_{11}$,[48] and 2.598 (5) and 2.570 (5) Å in $(C_5H_5)_2Rh_2Fe_2(CO)_8$.[49] The reason for this lengthening can undoubtedly be traced to the presence of the bridging C_7H_7 moiety and to the resulting delicate balance between metal-metal bond length and optimum overlap between ligand and metal orbitals. As a result of these different bonding interactions the cycloheptatrienyl ring distorts, and we can easily recognize three distinct planes: the allyl fragment (C(13), C(14), C(15)), the diene part (C(11), C(12), C(16), C(17)), and the plane formed by the four carbon atoms joining the former two (C(13), C(15), C(16), C(12)). The distortion of the allyl and diene parts is such that both are bent away from the rest of the molecule, resulting in a boat conformation of the ring in contrast to *trans*-$[(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3]$[28] where metal coordination has yielded a chair conformer. The angle between these two planes is 124° (Figure 3 and Table VI), very close to 123° which is found in the analogous $Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$.[4b] It is interesting to note that the Ru-Ru bond length found in the above complex, 2.937 (2) Å, is also long (cf. $Ru_3(CO)_{12}$[50] average of 2.85 Å, $(C_8H_8)_2Ru_3(CO)_4$,[51] 2.782 (2) Å for the non-C_8H_8 bridged bond) but comparable to the C_8H_8 bridged Ru-Ru length, 2.938 (3) Å in $(C_8H_8)_2Ru_3(CO)_4$.[51]

The average Rh-C (carbonyl) distance of 1.879 (5) Å and the average Fe-C (carbonyl) bond length of 1.771 (5) Å are comparable to previously reported values, 1.83-1.87 Å and 1.75-1.82 Å, respectively, and require no further discussion.

The bond distances between the transition metals and the

Table V. Selected Interatomic Distances and Angles[a] in $(C_7H_7)Fe(CO)_3Rh(CO)_2$

Bond Lengths (Å)

Rh-Fe 2.7638 (7)

Rh-C(4)	= 1.884 (5)	Fe-C(1)	= 1.774 (5)	C(1)-O(1)	= 1.138 (6)
Rh-C(5)	= 1.874 (5)	Fe-C(2)	= 1.761 (4)	C(2)-O(2)	= 1.145 (6)
Rh-C(12)	= 2.217 (5)	Fe-C(3)	= 1.777 (5)	C(3)-O(3)	= 1.146 (6)
Rh-C(11)	= 2.199 (5)	Fe-C(13)	= 2.145 (4)	C(4)-O(4)	= 1.136 (6)
Rh-C(17)	= 2.197 (5)	Fe-C(14)	= 2.034 (4)	C(5)-O(5)	= 1.129 (6)
Rh-C(16)	= 2.231 (5)	Fe-C(15)	= 2.141 (5)		

C(11)-C(12)	= 1.434 (7)	C(11)-H(11)	= 0.96 (4)
C(12)-C(13)	= 1.449 (6)	C(12)-H(12)	= 0.92 (4)
C(13)-C(14)	= 1.396 (6)	C(13)-H(13)	= 0.93 (4)
C(14)-C(15)	= 1.398 (7)	C(14)-H(14)	= 0.91 (4)
C(15)-C(16)	= 1.448 (7)	C(15)-H(15)	= 0.96 (4)
C(16)-C(17)	= 1.422 (7)	C(16)-H(16)	= 0.91 (4)
C(17)-C(11)	= 1.379 (7)	C(17)-H(17)	= 0.85 (4)

Bond Angles (deg)

C(11)-C(17)-C(16)	122.1 (5)	Rh-Fe-C(1)	84.6 (2)	Fe-Rh-C(4)	111.3 (1)
C(12)-C(11)-C(17)	121.1 (5)	Rh-Fe-C(2)	178.5 (1)	Fe-Rh-C(5)	107.0 (2)
C(13)-C(14)-C(15)	120.7 (4)	Rh-Fe-C(3)	84.2 (1)	Fe-Rh-C(12)	69.4 (1)
C(11)-C(12)-C(13)	128.1 (4)	Rh-Fe-C(13)	74.9 (1)	Fe-Rh-C(11)	97.9 (1)
C(12)-C(13)-C(14)	124.9 (4)	Rh-Fe-C(14)	90.8 (1)	Fe-Rh-C(17)	97.8 (1)
C(14)-C(15)-C(16)	125.9 (4)	Rh-Fe-C(15)	74.7 (1)	Fe-Rh-C(16)	69.5 (1)
C(15)-C(16)-C(17)	127.7 (4)	Rh-C(4)-O(4)	178.0 (5)	Fe-C(1)-O(1)	176.0 (4)
		Rh-C(5)-O(5)	179.4 (5)	Fe-C(2)-O(2)	175.7 (4)
				Fe-C(3)-O(3)	176.2 (4)
C(1)-Fe-C(2)	94.5 (2)			C(4)-Rh-C(5)	91.4 (2)
C(1)-Fe-C(3)	101.0 (2)				
C(2)-Fe-C(3)	94.6 (2)				

[a] Numbers in parentheses are estimated standard deviations in last figure quoted.

Table VI. Weighted[a] Least-Squares Planes in $(C_7H_7)Fe(CO)_3Rh(CO)_2$ of the form $Ax + By + Cz + D = 0$[b]

Plane no.	Atoms	A	B	C	D
1. (allyl)	C(13), C(14), C(15)	0.9420	0.1137	0.3159	2.9246
2. (diene)	C(11), C(12), C(16), C(17)	−0.7332	0.6017	0.3169	0.4816
3. (joining)	C(12), C(13), C(16), C(15)	0.9747	−0.2167	0.0543	1.3021

Distances of Atoms from Planes, Å

Plane 1				Plane 2				Plane 3			
C(13)	0.000	H(13)	0.11	C(11)	0.003	H(11)	−0.13	C(12)	0.002	H(12)	0.19
C(14)	0.000	H(14)	0.16	C(12)	−0.001	H(12)	−0.28	C(13)	−0.002	H(13)	−0.08
C(15)	0.000	H(15)	0.14	C(16)	0.002	H(16)	−0.20	C(15)	0.002	H(15)	−0.07
				C(17)	−0.004	H(17)	−0.19	C(16)	−0.002	H(16)	0.110

Dihedral Angles between Planes

Plane 1-Plane 3	155°36′	Plane 2-Plane 3	145°53′	Plane 1-Plane 2	123°55′

[a] Atoms are weighted by the reciprocals of their variances. [b] Coordinates are referred to as a right-handed Angstrom orthogonal system with y and z directed along b and c^*, respectively.

carbon atoms of the ring closely resemble those previously found in related complexes. Thus we can compare the iron-to-ring carbon bond lengths of 2.145 (4), 2.034 (4), and 2.141 (5) Å to other complexes containing such symmetrical (η^3-allyl)iron bonding combination: 2.141 (4), 2.043 (3), 2.178 (3) Å and 2.168 (3), 2.041 (4), 2.116 (4) Å in $(C_7H_8)Fe_2(CO)_6$;[52] 2.14 (1), 2.11 (1), 2.12 (1) Å in $C_8H_8Fe_2(CO)_5$;[31] 2.11 (2), 2.12 (2), 2.12 (2) Å and 2.07 (2), 2.11 (2), 2.13 (2) Å in $[(CH_3)_4(C_8H_4)]Fe_2(CO)_5$.[53] We may also note that in this complex just like in almost exclusively all other compounds containing an allyl-Fe moiety[52-55] the central carbon atom, C(14), lies significantly closer to the metal than the end carbon atoms, C(13) and C(15). The rhodium to diene carbon distances of 2.231 (5), 2.197 (5), 2.199 (5), and 2.217 (5) Å compare favorably with those found in $(C_5H_5)Rh[C_4H_4(CH_3)_2]$[56] (2.17 (1), 2.11 (1), 2.10 (2), and 2.14 (1) Å), $(C_5H_5)Rh[C_6(CF_3)_6]$,[57] (2.04 (3) Å for inner carbons and 2.15 (3) Å for outer ones), and $(C_4H_6)_2RhCl$[58] (2.15 (1) Å for inner carbons and 2.21 (1) Å for outer ones). Although the usually observed difference[56-58] (0.06-0.10 Å) between the metal-to-outer and metal-to-inner carbon distances has been reduced in the present complex (∼0.02 Å), the generally observed longer rhodium-to-outer carbon bond lengths are still being maintained.

As was mentioned before the organic ligand is far from being planar and hence complete delocalization of the π electrons and subsequently equal C-C bond lengths are not expected and indeed not found. It is gratifying to see that, as expected, the longest bond lengths, 1.449 (7) and 1.448 (7) Å, are associated with the bonds (C(12), C(13) and C(15), C(16)) that link the

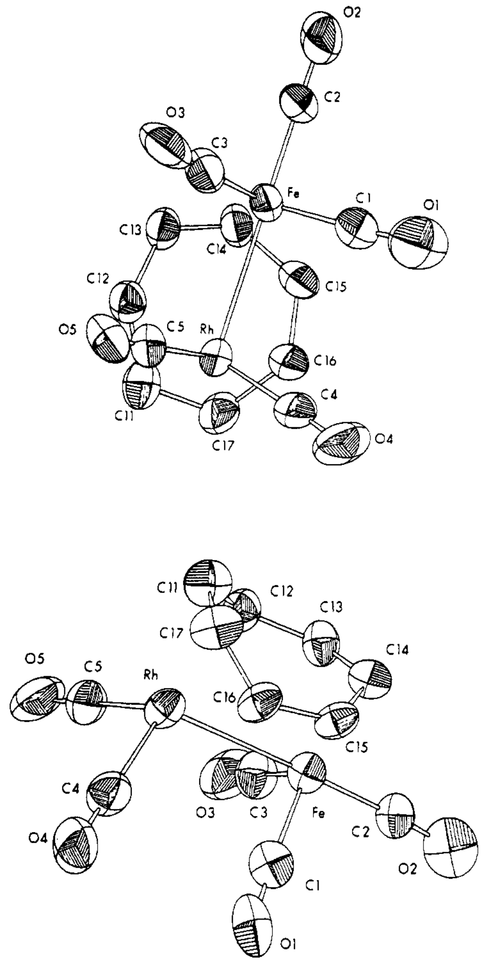


Figure 3. ORTEP drawings of $(C_7H_7)Fe(CO)_3Rh(CO)_2$ showing the atom-numbering scheme used in this paper and 50% probability thermal ellipsoids for all non-hydrogen atoms.

two Fe and Rh bound fragments together. It is noteworthy that in the related dimetallic cycloheptatrienyl complex, $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$, having the transoid arrangement of the two metals, the corresponding bond lengths are 1.50 (1) and 1.49 (1) Å, respectively.[28] The considerably longer distances presumably indicate even more drastic breakdown of the π electron delocalization than in the present case. Indeed, Cotton[28] has concluded that in the above compound "there is little, if any, significant structural interdependence between the two parts of the dinuclear molecule". Obviously the same cannot be said for the compounds of this study, and the interdependence of the two parts of the molecule has implications as far as the fluxionality of the molecules is concerned (vide infra). The C–C bond distances within the allyl fragments, 1.396 (7) and 1.398 (8) Å, are comparable to many previously reported values[52-55] (1.38–1.42 Å), and indeed their identical nature observed in this structure without a crystallographically imposed symmetry is remarkable. The alteration of the C–C bond lengths, long–short–long, in the bound diene fragment in this molecule has many counterparts, the tabulation being most extensive for (diene)$Fe(CO)_3$[59] complexes. The change in the pattern of these distances from what is found in the free diene has been attributed to a combination of electron donation from the HOMO of the diene to empty metal d orbitals and back-acceptance of electron density into the LUMO of the ligand from filled metal d orbitals,[60] there being a quantitative one-to-one correlation between the strength of the metal–diene interaction and the difference between "inner" C–C distance, C(11)C(17), and the average value of the "outer" C–C bond lengths, C(11)C(12) and C(16)C(17). The observed value of 0.049 Å when compared to other known Rh–diene complexes, −0.07 Å in $(C_4H_6)_2RhCl$,[58] 0.0 Å in $(C_5H_5)Rh[C_4H_4(CH_3)_2]$[56] and $(C_5H_5)Rh[C_4H_4Cl_2]$,[56] and 0.08 Å in $(C_5H_5)Rh[C_6(CF_3)_6]$,[58] thus indicates rather strong bonding between rhodium and the cycloheptatrienyl ring.

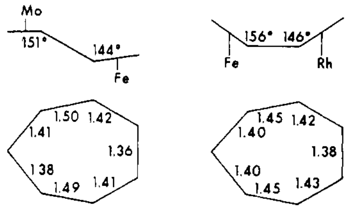


Figure 4. Diagrams summarizing the conformations and dimensions of the C_7H_7 rings in $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$ (left) and $(C_7H_7)Fe(CO)_3Rh(CO)_2$ (right). The standard derivations on the C–C bond lengths are ca. 0.01 Å for both compounds.

Finally we turn our attention to the question of the rather dramatic increase in fluxionality of these dinuclear cycloheptatrienyl complexes as the geometry of the two metal carbonyl moieties changes from trans to cis and to the possibility of correlating it with some structural feature(s) of these complexes as observed in the solid state. In this regard, we note that in their respective study, both Lipscomb[61] and Cotton[28] have observed that the enhanced rate of rearrangement on going from *trans*-$(C_8H_8)[Fe(CO)_3]_2$ to $(C_8H_8)Fe(CO)_3$ and from *trans*-$(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$ to $(C_5H_5)(CO)_2Mo(C_7H_7)$ is accompanied by an increased pπ–pπ overlap between the localized bonding fragments of the cyclic polyenes. Since the overlap is a function of both the C–C distance and the angle ϕ between the respective pπ orbitals, it varies as the *cosine* of this angle, increased overlap means shorter C–C bond length and a smaller value of the angle ϕ. For instance, in the above compounds, by assuming that the pπ orbital was perpendicular to the plane defined by the atom at the junction of the two bonding units and its two neighboring carbon atoms, the values of ϕ were calculated to be 98° and 60.2°, 61°, and 14.7°, respectively.

Figure 4 summarizes the distances and the conformations of the seven-membered rings in the two compounds we wish to compare. The observation of both shorter C–C distance, 1.45 vs. 1.50 Å, and smaller ϕ angle,[62] 22.8 vs. 61.0°, in our compound is indeed in accord with increased pπ–pπ overlap between allyl and diene portions of the ring and hence with the observed faster rate of rearrangement.

Conclusion

The present study was undertaken to investigate the utility of $[(C_7H_7)Fe(CO)_3]^-$ as a starting material toward the synthesis of dimetallic cycloheptatrienyl complexes of the transition metals. Although the yields of the reported complexes are rather disappointing, they do represent the first preparation of such compounds and as such demonstrate the synthetic usefulness of the above anion. Indeed the realization of the cis disposition of the metal carbonyl moieties with respect to the cycloheptatrienyl ring besides offering a rationale for the higher yield obtained from $[Re(CO)_3BrTHF]_2$ as compared to $[Mn(CO)_4Br]_2$ reaction[63] also identifies the ability of the central metal ion to easily accept five electrons as a desirable quality in order to enter into a successful reaction with the anion. We are currently exploring the reactivity of a logical candidate, $Mo(NO)_2Cl_2$. The success of this reaction, in addition to the utility, should also establish the synthetic versatility of $[(C_7H_7)Fe(CO)_3]^-$.

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Supplementary Material Available: Tables I (mass spectra) and IV (root-mean-square amplitudes) and final values of $|F_o|$ and $|F_c|$ (12 pages). Ordering information is given on any current masthead page.

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(35) (a) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, **14**, 511 (1975), (acenaphthylene)Fe$_2$(CO)$_5$, (C$_7$H$_8$)Fe$_2$(CO)$_6$; (b) *J. Am. Chem. Soc.*, **97**, 1046 (1975), (C$_8$H$_{10}$)Fe$_2$(CO)$_6$; (c) F.. Cotton and D. L. Hunter, *ibid.*, **97**, 5739 (1975), (C$_8$H$_{12}$)Fe$_2$CO$_6$; (d) (C$_9$H$_{10}$)Fe$_2$(CO)$_6$, Li Shing Man, unpublished observation; (e) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Organomet. Chem.*, **87**, C42 (1975), (guaiazulene)Mo$_2$(CO)$_6$.

(36) Although the possibility that the singlets are a result of accidental chemical shift equivalence of the carbonyl groups cannot be ruled out, unequivocally, since we did not obtain the expected limiting spectra. The observations[35] that the resonances due to the carbonyl groups trans to an allyl group and trans to a metal–metal bond are well resolved in all cases so far studied indicates that this is highly unlikely.

(37) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 1233 (1974).

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(63) The rhenium complex is all set up to accept the five electrons that the anion is desirous to donate since THF is an easily displaceable ligand; however, in the case of the manganese complex a carbonyl group must be eliminated before the reaction is completed, an obviously higher energy process.