Organometallics **1986**, *5*, 1829–1833

II. The space group was uniquely assigned as *Pccn* (No. 56) on the basis of the systematic absences (0*kl*, *l* odd; *h*0*l*, *l* odd; *hk*0, *h* + *k* odd), and the correctness of this choice was confirmed by successful solution of the Patterson map, showing a ruthenium atom on one of the two twofold axes. The Molecular Structure Corp. and Enraf-Nonius SDP programs were used for solution and refinement of the structure.[19] Least-squares refinement of the ruthenium followed by a difference Fourier map revealed four peaks for the DMPE phosphorus atoms. Introduction of two of these peaks not related by an apparent mirror plane revealed all 11 non-hydrogen atoms in a subsequent difference Fourier map. Anisotropic refinement of all 11 atoms converged at $R_1 = 0.080$. A difference Fourier map showed a single large peak on an independent twofold axis corresponding to the oxygen atom of a water molecule (5.8 e/Å^3), apparently picked up from the atmosphere during recrystallization. Final refinement was carried out on all 12 atoms giving $R_1 = 0.0498$ and $R_2 = 0.0660$. Table III contains relevant bond distances and angles and Table IV positional parameters.

Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corp., and the U.S. Department of Energy (DE-AC02-83ER13095) for their partial support of this work. W.D.J. also thanks the Sloan Foundation and Camille and Henry Dreyfus Foundation for awards.

Registry No. 1, 60938-49-0; 2, 103190-62-1; 3, 103190-63-2; *cis*-4, 68878-59-1; *trans*-4, 68907-31-3; 5, 103190-64-3; Ru(DMPE)$_2$(CNEt), 103190-65-4; Ru(DMPE)$_2$(CN)$_2$·H$_2$O, 103190-66-5; Ru(DMPE)$_2$(CHCH$_2$CMe$_3$), 101519-29-3; POCl$_3$, 10025-87-3; neopentyl formamide, 78257-53-1; neopentyl isocyanide, 72243-18-6; phenyl isocyanide, 931-54-4; ethyl isocyanide, 624-79-3; *tert*-butyl isocyanide, 7188-38-7; trimethylacetonitrile, 630-18-2; isobutylene, 115-11-7; isobutane, 75-28-5.

Supplementary Material Available: Listings of anisotropic thermal parameters and bond distances and angles (3 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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(19) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum wF_o^2\}$, where $w = \{\sigma^2(F_o) + [\rho F_o^2]^2\}^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of Scattering Factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV Table 2.2B and 2.3.1.

Dynamic Behavior of the Flyover Bridge Complexes $M_2(CO)_5L\{\mu\text{-}[C(R)=C(R')]_2CO\}$ (M = Ru, Fe; L = CO, PPh$_3$, AsPh$_3$, SbPh$_3$; R, R′ = Me, Ph)

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The variable-temperature ^{1}H and ^{13}C NMR studies of a series of isomeric "flyover bridge" complexes $M_2(CO)_5L\{\mu\text{-}[C(R)=C(R')]_2CO\}$ (M = Ru, Fe; L = CO, PPh$_3$, AsPh$_3$, SbPh$_3$; R, R′ = Me, Ph) show that a fluxional process of the dienone ligand, leading to the exchange of σ- and π-bonds at the two metal centers is occurring in these compounds on the NMR time scale. The activation energy for this process in the entire series is essentially invariant ($\Delta G^{\ddagger} = (70\text{–}76) \pm 5$ kJ/mol) with the nature of M and L and is apparently independent of localized carbonyl exchange at each M(CO)$_3$ unit.

Introduction

In the last 15 years several studies concerning the intramolecular exchange of CO groups in metal carbonyl derivatives have been reported and a variety of rearrangement modes of these ligands has been shown to occur in this class of molecules.[1] Relatively less attention has been devoted to the study of the mobility of other organic ligands in these molecules. However, some novel fluxional processes have already been reported to take place on the NMR time scale. For instance, a low-energy σ–π exchange process of the bridging vinyl group in HOs$_3$(CO)$_{10}$(CH=CH$_2$) was reported by Shapley et al.,[2] and, more recently, we have shown that a "wagging" motion of the allene ligand (coupled with the "hopping" motion of the hydride on different edges of the M$_3$ triangle) is occurring in related HM$_3$(CO)$_9$(allene) (M = Ru, Os) systems.[3]

It has also been shown, by the use of chiral derivatives, that the formal rotation of the M–M and C–C bond vectors is occurring in the (μ_2-η^2)M$_2$(alkyne) complexes[4] as well as

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0276-7333/86/2305-1829$01.50/0

Table I. Analytical Data of "Flyover Bridge" Complexes

	compd	color	anal. found[a] C	H	Fe	Ru
I_A	$Ru_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	yellow-orange	47.82 (47.62)	2.63 (2.54)		31.91 (32.06)
I_B	$Ru_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$	yellow-orange	47.75 (47.62)	2.58 (2.54)		31.88 (32.06)
II_A	$Ru_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	yellow	58.51 (58.33)	3.77 (3.59)		23.19 (23.38)
III_A	$Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	yellow	55.86 (55.51)	3.55 (3.41)		22.17 (22.25)
IV_A	$Ru_2(CO)_5(SbPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	yellow	52.91 (52.77)	3.40 (3.25)		21.02 (21.16)
I'_A	$Fe_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	red	55.80 (55.56)	2.98 (2.96)	20.53 (20.74)	
I'_B	$Fe_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$	orange	55.91 (55.56)	3.05 (2.96)	20.47 (20.74)	
II'_A	$Fe_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	turquoise	65.37 (65.12)	4.12 (4.00)	14.23 (14.47)	

[a] Calculated values are given in parentheses.

Table II. Spectroscopic Data of "Flyover Bridge" Complexes

	compd	IR[a] ν_{CO}/cm^{-1}	^1H NMR[b] δ
I_A	$Ru_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2086 m, 2063 vs, 2025 vs, 2013 m, 2007 m, 1681 m(br)	7.33–7.21 (m, 10), 1.74 (s, 6)
I_B	$Ru_2(CO_6[\mu\text{-}C(Ph){=}C\ (Me)COC(Ph){=}C(Me)]$	2086 m, 2063 vs, 2023 vs, 2021 vs(sh), 2013 m, 2005 m, 1670 m(br)	7.35–7.03 (m, 10), 2.59 (s, 3), 1.71 (s, 3)
II_A	$Ru_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2070 vs, 2019 vs, 2011 s, 1998 m, 1662 m(br)	7.35–6.93 (m, 25), 1.58 (s, 3), 1.51 (s, 3)
III_A	$Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2069 vs, 2018 vs, 2011 s, 1998 m, 1963 m, 1664 m(br)	7.46–6.96 (m, 25), 1.62 (s, 3), 1.52 (s, 3)
IV_A	$Ru_2(CO)_5(SbPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2069 vs, 2017 vs, 2010 s, 2001 m, 1964 m, 1663 m(br)	7.41–6.94 (m, 25), 1.59 (s, 3), 1.53 (s, 3)
I'_A	$Fe_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2073 m, 2046 vs, 2012 vs, 2001 m, 1991 m, 1678 m(br)	7.43–7.15 (m, 10), 1.56 (s, 6)
I'_B	$Fe_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$	2074 m, 2045 vs, 2013 vs, 2010 vs(sh), 2002 m, 1991 m, 1684 m(br)	7.46–7.10 (m, 10), 2.76 (s, 3), 1.53 (s, 3)
II'_A	$Fe_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	2053 vs, 2004 vs, 1996 s, 1981 w, 1951 m, 1657 m(br)	7.48–6.91 (m, 25), 1.38 (s, 3), 1.33 (s, 3)

[a] n-Hexane. [b] $CDCl_3$.

the C_{3v} rotation of alkyne ligands in $(\mu_3\text{-}\eta^2)M_3$(alkyne) systems.[5]

In a MO study of the electronic structures of $M_2(CO)_6$(ligand) complexes, Thorn and Hoffmann[6] suggested that "flyover" compounds could exist in enantiomeric forms and it may be possible to interconvert them via a transition state having a ring-opened (C_{2v}) structure. The dynamic behavior of some "flyover bridge" iron derivatives has already been partially investigated, but no firm conclusion was drawn at the time as to the nature of the fluxional process.[7-9]

The reactions of $M_3(CO)_{12}$ (M = Fe, Ru) with disubstituted acetylenes afford a variety of mono-, di-, tri-, and tetranuclear organometallic species; among these derivatives alkyne oligomerization and CO insertion are often observed.[10-12] The diferracycloheptadiene or "flyover" bridge complexes $M_2(CO)_6\{\mu\text{-}[C(R){=}C(R')]_2X\}$ (M = Fe, Ru; X = CH_2, CO) are an important class of such compounds. Crystal structure investigations of these molecules carried out by Piret et al. (R = R' = H, X = CH_2, M = Fe),[13] by Piron et al. (R = R' = Me, X = CO, M = Fe),[14] and by Cotton et al. (R = R' = Ph, X = CO, M = Fe)[8] revealed a twisted fulvene or dienone ligand symmetrically bridging the two equivalent $Fe(CO)_3$ units.

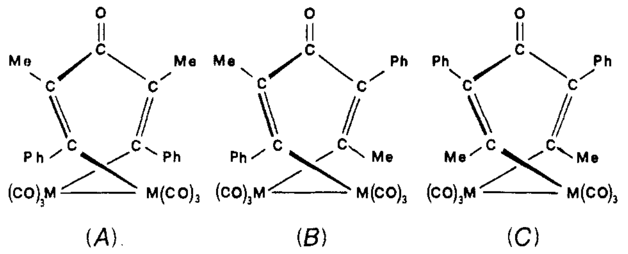

Figure 1. Proposed structure of "flyover bridge" isomers obtained from reaction of $M_3(CO)_{12}$ (M = Ru, Fe) with PhC≡CMe. Structure A: M = Ru, I_A; M = Fe, I'_A. Structure B: M = Ru, I_B; M = Fe, I'_B. Structure C: no isomer in detectable yield.

Results and Discussion

We have synthesized a series of flyover bridge complexes of general formula $M_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (M = Ru, Fe) which are formed by reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with methylphenylacetylene in apolar solvents. Analytical, IR, and NMR data for these complexes are given in Tables I and II. Only two of the three possible isomeric forms deriving from the permutation of the substituents of the unsymmetrical acetylene (A, B, and C) are obtained for each metal (Figure 1). We assign the structures of these two isomers to type A and B. Structures I_B and I'_B (the unsymmetrical isomers from $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$, respectively) are assigned on the basis of the observation of two methyl group resonances at δ 1.77 (s, 3) and 2.59 (s, 3) (M = Ru, I_B) and δ 1.53 (s, 3) and 2.76 (s, 3) (M = Fe, I'_B). Both in I_B and I'_B the most deshielded

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Table III. Activation Energies for Process ii

	compd	$\Delta\nu$,[a] Hz	T_c, K	$\Delta G^\ddagger$ kJ/mol[d]
II_A	$Ru_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	5.4[b]	330	74.3 ± 5.0
III_A	$Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	14.6[b]	332	72.0 ± 5.0
IV_A	$Ru_2(CO)_5(SbPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	7.9[b]	341	75.8 ± 5.0
II'_A	$Fe_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	4.6[b]	311	70.3 ± 5.0
I_B	$Ru_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$	76.2[c]	370	75.5 ± 5.0
I'_B	$Fe_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$	145.1[c]	374	74.3 ± 5.0
III_A	$Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$	183.1[c]	353	69.3 ± 5.0

[a] Toluene-d_8. [b] $\Delta\nu$ refers to methyl resonances. [c] $\Delta\nu$ refers to $M(CO)_3$ resonances. [d] Evaluated by using the approximate equation $\Delta G^\ddagger = 4.567T_c[9.97 + \log T_c/\Delta\nu]$.

methyl signal is assigned to the methyl substituent on the ring carbon atom adjacent to the $M(CO)_3$ unit.

It is well-known, based on experimental correlation, that hydrogen atoms bound to carbon atoms σ bonded to one metal atom and π bonded to a second one, $C(\sigma,\pi)$, are greatly deshielded and that the effect is still felt, though to lesser extent, for hydrogen atoms in β-position with respect to such $C(\sigma,\pi)$ interaction.[15]

Structures I_A and I'_A (the symmetrical isomers) are assigned on the basis of the chemical shifts of the single methyl resonances observed (δ 1.74 (s, 6; M = Ru, I_A), δ 1.56, (s, 6; M = Fe, I'_A)). Structures I_C and I'_C would then be expected to show methyl resonances of relative intensity 6 but in the methyl downfield range of δ 2.5–2.8. Thus I_C and I'_C having the two methyl groups on the carbon atoms σ bound to the metal centers were not obtained in detectable amount.[16]

The ^{13}C NMR spectrum at +21 °C of a ^{13}CO-enriched sample (~20%) of I_A shows two peaks in the carbonyl region, at 201.6 and 194.6 ppm, in the relative intensity ratio of 1:6. As the temperature is lowered (Figure 2), the signal of intensity 6 broadens and then gives rise, at −40 °C, to three absorptions of equal intensity at 194.4, 194.5, and 194.8 ppm. This behavior allows us to assign the resonance at 194.6 ppm in the room-temperature spectrum to the six terminally bonded carbonyls which are involved in a rearrangement process which can eventually be frozen out at low temperature. The downfield peak at 201.6 ppm can then be assigned to the ketonic carbonyl. From line-shape analysis the activation energy of the CO-localized scrambling process is estimated to be 61.7 ± 5 kJ/mol.

The variable-temperature ^{13}C NMR of analogues of I'_A, i.e., $Fe_2(CO)_6\{\mu\text{-}[C(PH){=}C(Ph)]_2CO\}$, have already been investigated showing a dynamic behavior identical with that of I_A with only slight differences in the activation energy.[7-9]

In I_B the ^{13}C NMR spectrum at −35 °C shows, in the carbonyl region, six resonances at δ 197.1, 195.9, 195.8, 195.5, 195.2, and 194.8 of relative intensity 1:1:1:1:1:1. As the sample is heated to room temperature, these resonances broaden and coalesce to two peaks of equal intensity at δ 196.1 and 195.0. The ketonic carbonyl group in I_B is found at 199.4 ppm.[17] This pattern can easily be assigned to the two different $Ru(CO)_3$ sets involved in a fast localized scrambling process at each ruthenium center. Line-shape analysis shows that the two CO-localized scrambling processes have the same activation energy within the experimental error ($\Delta G^\ddagger$ = 60.6 ± 5 kJ/mol). As the temperature is increased, these two resonances broaden again and coalesce; at 110 °C a new single peak at 195.3 ppm is observed. With the assumption of a coalescence temperature of 97 °C, the $\Delta G^\ddagger$ for this process is about 75.5 ± 5 kJ/mol (Table III). The equivalence of all the terminal CO resonances observed in the high-temperature limiting spectrum of I_B can be accounted for both in terms of (i) a delocalized intermetallic CO exchange or (ii) a motion of the dienone through a transition state possessing mirror symmetry which renders equivalent the two different $Ru(CO)_3$ units.

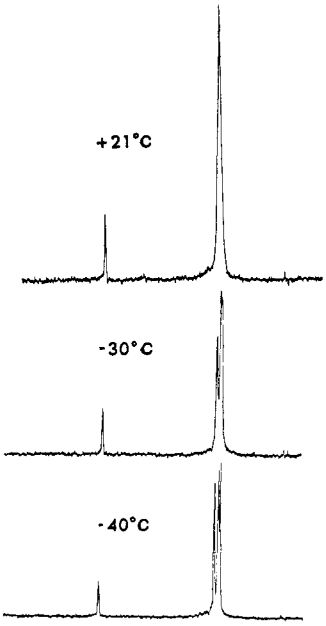

Figure 2. Variable-temperature ^{13}C NMR spectra of $Ru_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (I_A) in $CDCl_3$ containing 0.05 M $Cr(acac)_3$.

In I'_B six carbonyl resonances are observed at room temperature at δ 211.8, 211.2, 209.8, 208.9, 208.1, and 206.1 of relative intensity 1:1:1:1:1:1. As the temperature is increased to +62 °C, these resonances broaden and collapse to two humps at 211.4 and 209.3 ppm. This initial exchange process again arises from the localized scrambling of the COs at the two iron centers. The activation energy, estimated by line-shape analysis, is about 59.7 ± 5 kJ/mol. As the temperature of the solution of I'_B is increased, the two peaks at δ 211.4 and 209.3 broaden further and coalesce to a single absorption at δ 210.2 at 105 °C. With use of a coalescence temperature of 101 °C, we estimate a $\Delta G^\ddagger$ = 74.3 ± 5 kJ/mol. The fact that this second stage which makes all carbonyl groups in I_B and I'_B equivalent has approximately the same activation energy lends support to the idea that this process does not involve inter-

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[16] The reaction of $Fe_2(CO)_9$ with methylphenylacetylene (molecular ratio 1:2) in cyclohexane at room temperature under N_2 for 24 h, besides I'_A and I'_B, affords also in small amount a dark yellow compound whose spectroscopic properties indicate to be the third isomer $Fe_2(CO)_6\{\mu\text{-}[C(Me){=}C(Ph)]_2CO\}$ (I'_C) (MS, m/e 540 (M^+) followed by stepwise loss of six CO; IR (n-hexane, cm^{-1}) ν(CO) 2075 m, 2044 vs, 2010 vs, 2001 m, 1991 m, 1680 m (b); ^1H NMR ($CDCl_3$, δ) 8.00–6.93 (m, 10), 2.74 (s, 6).

[17] This assignment is further supported by the observation that the addition of ^{13}CO to a chloroform solution of I_B in a sealed NMR tube leads, under heating at +65 °C for 2 h, to the increase of the resonances at 196.1 and 195.0 ppm, whereas the signal at 199.4 ppm remains unaffected.

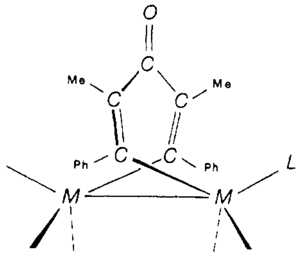


Figure 3. Proposed solution structures of group V-substituted derivatives of symmetrical "flyover bridge" complexes I_A and I'_A. M = Ru: L = PPh_3, II_A; L = $AsPh_3$, III_A; L = $SbPh_3$, IV_A. M = Fe: L = PPh_3, II'_A.

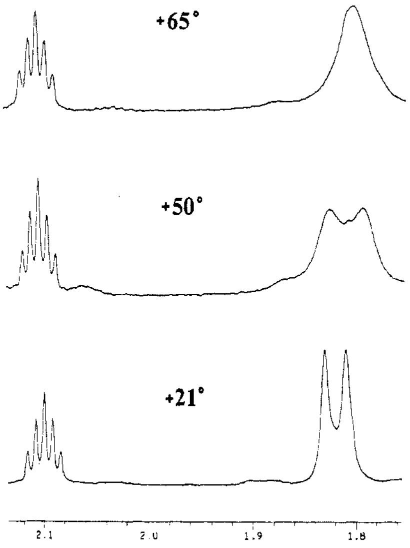


Figure 4. Variable-temperature ^1H NMR spectra of $Ru_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (II_A) in toluene-d_8. The methyl group resonance of the solvent represents a useful check of the resolution level at the various temperatures.

metallic carbonyl exchange (process i). Indeed the required carbonyl-bridged intermediate is expected to have a lower $\Delta G^{\ddagger}$ for the iron case.[1]

In order to demonstrate the occurrence of process ii unambiguously, the synthesis of group V substituted derivatives of I_A and I'_A was undertaken. The thermal reaction of I_A and photochemical reaction of I'_A with PPh_3, $AsPh_3$, or $SbPh_3$ in 1:1 molecular ratio give rise to main products, whose spectral data correspond to the monosubstituted derivatives (Figure 3). Analytical, infrared, and ^1H NMR data for these complexes are listed in Table I and II.

On going from the unsubstituted I_A to its monophosphine derivative II_A the two methyl groups are no longer equivalent; at +21 °C, the ^1H NMR spectrum of II_A in toluene-d_8 shows two resonances at δ 1.83 and 1.81 (Figure 4). When the temperature is increased, the two methyl signals average to a single resonance (coalescence temperature = 57 °C; estimated $\Delta G^{\ddagger} = 74.3 \pm 5$ kJ/mol). Since the nonequivalence of the methyl groups derives from the presence of the phosphine ligand on one ruthenium atom and this ligand cannot migrate from one metallic center to the other, it follows that the equivalence can arise only from a motion of the dienone (process ii).

All the other substituted derivatives (II'_A, III_A, IV_A) show similar behavior (Table III). Interestingly the activation energies for the averaging of the two sets of $M(CO)_3$ in I_B and I'_B is the same, within the experimental error, as that for the averaging of the methyl groups in II_A, II'_A, III_A, and IV_A. This demonstrates that only path ii can be responsible for all these averaging processes.

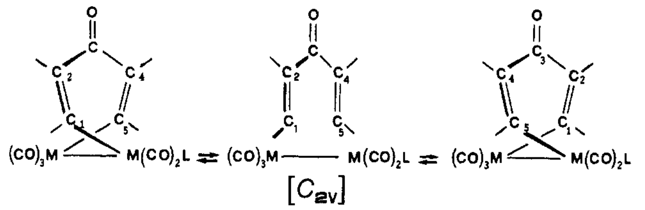
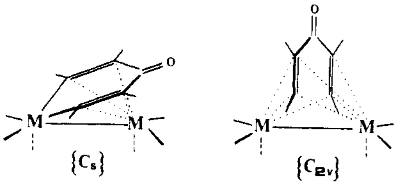


Figure 5. Proposed scheme for interchanging the "flyover bridge" helicity.

In principle two mechanisms are possible for path ii: the organometallic molecule traverses either the symmetrical transition-state structure C_s or C_{2v}.



Although we cannot rigorously exclude a C_s intermediate with two σ bonds to one metal atom and two π bonds to the other metal atom, i.e., a ferrole-type structure, Hoffmann calculations suggest that in the case of the fulvene homologous $Fe_2(CO)_6\{\mu\text{-}[C(H){=}C(H)]_2CH_2\}$, this is a much higher energy intermediate than the C_{2v} intermediate because of the large antibonding interaction between the vinyl carbon and the π-bonded iron atom.[6] Recently EHMO calculations have shown that the overall electric features of the fulvene $Fe_2(CO)_6\{\mu\text{-}[C(H){=}C(H)]_2CH_2\}$ and dienone $Fe_2(CO)_6\{\mu\text{-}[C(H){=}C(H)]_2CO\}$ are very similar and furthermore that the oxygen atom bears much more electronic density in respect to the vinyl carbon counterpart.[17]

The most likely mechanism for path ii is that the organometallic molecule traverses the symmetrical ring-opened transition-state structure (C_{2v}) as suggested by Thorn and Hoffmann for the homologous "fulvene" complex[6] in order to average the magnetic environments (Figure 5).

The activation energy for interchanging the flyover bridge helicity should depend only on the rearrangement of the geometry of the organic chain, and it is thus expected to be almost independent of the electronic and steric properties of M and L, as experimentally found.

The interchange of the helicity of the flyover bridge is apparently independent of localized carbonyl groups exchange at each $M(CO)_3$ unit, which always occurs at lower activation energy.

Finally, at +21 °C, the ^{13}C-nmr spectrum of $Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (III_A) shows four resonances in the carbonyl region at 204.9 (1, ketonic carbonyl), 201.2 (1), 198.5 (1), and 195.6(3) ppm, respectively. When a highly ^{13}CO-enriched ($\sim$40%) sample of III_A was examined by ^{13}C nmr, the resonances at 201.2 and 198.5 showed a $^2J_{CC}$ coupling of 3.5 Hz, which is in the range observed for carbonyls in a cis arrangement.[18] These data are consistent with a structure where the arsine ligand is either in a position cis or trans to the metal–metal bond and with the three COs at the unsubstituted ruthenium being already involved in a fast localized exchange at room temperature. However, an examination of molecular models shows that the latter position is sterically favored.

We then propose a solution structure for III_A (and probably for II_A, II'_A, and IV_A as well) having the $AsPh_3$ ligand in a position trans to the metal–metal bond (Figure 3), in which the three COs at the unsubstituted ruthenium

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(18) Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* 1981, 300.

are already involved in a fast localized exchange at room temperature.

As the temperature is increased, the resonances at δ 201.2 and 198.5, assigned to the COs on the arsine-substituted ruthenium atom, broaden and collapse into the base line (+80 °C): above 100 °C an averaged signal at 199.8 ppm is observed ($\Delta G^{\ddagger} = 69.3 \pm 5$ kJ/mol).

In principle, the proposed motion of the organic ligand would make the CO resonances on the arsine-substituted Ru atom equivalent without any direct exchange of these two diastereotopic carbonyl groups. However, we cannot exclude the possibility that a concomitant localized exchange of the CO groups at the arsine-substituted metal center occurs, although these experiments give no direct evidence for such a process.

Experimental Section

$Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ were prepared according to published procedures.[19,20] The ligands were purchased from Strem Chemicals and used without further purification.

Elemental analyses were carried out with a F&M Model 185 CHN analyzer and a Perkin-Elmer 303 atomic absorption spectrophotometer.

IR spectra were recorded on a Perkin-Elmer 580 B instrument, ^1H and ^{13}C NMR spectra on a JEOL GX 270/89 spectrometer, and MS spectra on a Hitachi Perkin-Elmer RMH-6 machine with an ionizing voltage of 70 eV. TLC was carried out on commercial Merck plates (SiO_2), eluant n-hexane and diethyl ether (9:1 v/v).

All the ^{13}CO-enriched "flyover bridge" compounds were synthesized from the parent clusters $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$, previously ~20% enriched by exchange with <1 atm of ^{13}CO for 4 days at +60 and +40 °C, respectively.

Simulations of the variable-temperature ^{13}C NMR spectra concerning the localized COs exchange at each $M(CO)_3$ unit were performed by using the Poly program obtained from Darensbury NMR Program Library.

$Ru_2(CO)_6[\mu\text{-}(PhC_2Me)_2CO]$ Isomers. A solution of $Ru_3(CO)_{12}$ (0.50 g) and PhC_2Me (0.15 mL) in cyclohexane (200 mL) was refluxed under N_2 for 4 h. After cooling, the solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and separated by TLC, giving $Ru_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (I_A, symmetrical isomer) in ~45% yield and $Ru_2(CO)_6[\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)]$ (I_B, asymmetrical isomer) in ~7% yield among several other well-known products, namely, $Ru_4(CO)_{12}(PhC_2Me)$,[21] $Ru_4(CO)_{11}(PhC_2Me)_2$,[22] $Ru_3(CO)_8(PhC_2Me)_2$,[23] and $Ru_2(CO)_6(PhC_2Me)_2$.[23] Both isomers I_A and I_B gave MS spectra having m/e 632 (M^+) (based on ^{102}Ru), followed by stepwise loss of six COs.

$Fe_2(CO)_6[\mu\text{-}(PhC_2Me)_2CO]$ Isomers. A solution of $Fe_3(CO)_{12}$ (0.50 g) and PhC_2Me (0.20 mL) in n-hexane (200 mL) was refluxed under N_2 for 8 h. Separation workup as reported above gave $Fe_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (I'_A, symmetrical isomer, red powder, ~10% yield) and $Fe_2(CO)_6\{\mu\text{-}C(Ph){=}C(Me)COC(Ph){=}C(Me)\}$ (I'_B, asymmetrical isomer, ~35% yield) among several other well-known products, namely, $Fe_3(CO)_9(PhC_2Me)$, $Fe_3(CO)_8(PhC_2Me)_2$, and $Fe_2(CO)_6(PhC_2Me)_2$.[24,25] Both isomers I'_A and I'_B gave MS spectra having m/e 540 (M^+), followed by stepwise loss of six COs.

$Ru_2(CO)_5L\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (L = PPh_3, $AsPh_3$, $SbPh_3$). A solution of $Ru_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (I_A, 0.30 g) and PPh_3 (0.13 g) in cyclohexane (200 mL) was refluxed under N_2 for 3 h. TLC workup afforded $Ru_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (II_A) as a yellow powder (~50% yield).

Similar procedures gave $Ru_2(CO)_5(AsPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (III_A) and $Ru_2(CO)_5(SbPh_3)\}\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (IV_A) in 45% and 35% yields, respectively.

$Fe_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$. A solution of $Fe_2(CO)_6\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (I'_A, 0.30 g) and PPh_3 (0.15 g) in n-hexane (50 mL) under N_2 atmosphere was irradiated at room temperature for 8 h with an unfiltered 100-W mercury lamp (immersion system). Separation workup gave $Fe_2(CO)_5(PPh_3)\{\mu\text{-}[C(Ph){=}C(Me)]_2CO\}$ (II'_A) as a turquoise powder (~20% yield).

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Registry No. I_A, 101916-53-4; I'_A, 101916-55-6; I_B, 101916-54-5; I'_B, 101916-56-7; II_A, 101916-58-9; II'_A, 101916-61-4; III_A, 101916-59-0; IV_A, 101916-60-3; $Ru_4(CO)_{12}(PhC_2Me)$, 56801-95-7; $Ru_4(CO)_{11}(PhC_2Me)_2$, 91236-64-5; $Ru_3(CO)_8(PhC_2Me)_2$, 101932-62-1; $Ru_2(CO)_6(PhC_2Me)_2$, 101932-63-2; $Fe_3(CO)_9(PhC_2Me)$, 101315-99-5; $Fe_3(CO)_8(PhC_2Me)_2$, 101916-57-8; $Fe_2(CO)_6(PhC_2Me)_2$, 12569-92-5; $Ru_3(CO)_{12}$, 15243-33-1; PhC_2Me, 673-32-5; $Fe_3(CO)_{12}$, 17685-52-8.

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