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The Alkyne–Cluster Interaction: Structural, Theoretical, and Mechanistic Studies on the $M_2M'(CO)_9(\mu_3\text{-}\eta^2\text{-alkyne})$ Complex ($M = Fe$; $M' = Fe$ and Ru)

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The thermal and photochemical reactions between $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and alkynes (PhC_2Ph, EtC_2Et) afford three novel heterometallic derivatives, namely, $Fe_2Ru(CO)_9$(alkyne), $Fe_2Ru(CO)_8(\text{alkyne})_2$, and $FeRu(CO)_6(\text{alkyne})_2$. The fact that $Fe_2Ru(CO)_9$(alkyne) is obtained also from the thermal reaction of $Fe_3(CO)_9$(alkyne) and $Ru_3(CO)_{12}$ suggests that a possible pathway to its formation passes through the coordinatively unsaturated $Fe_2(CO)_6$(alkyne) complex. The solid-state X-ray structure of $Fe_2Ru(CO)_9(PhC_2Ph)$ is reported, and its electronic structure is discussed on the basis of CNDO calculations.

Introduction

Among the large number of derivatives obtained in the reaction between $Fe_3(CO)_{12}$ and alkynes, it is commonly accepted[2,3] that the $\mu_3\text{-}\eta^2$ ($\perp$) alkyne complexes represent one of the first steps in the very complex pathway, which eventually leads to a variety of structural rearrangements in both the organic and the metallic moieties. In fact more than 20 types of compounds (with nuclearity ranging from one to four) have been isolated and characterized from these reactions.

However it was early recognized that a main path in this reaction involves, in two distinct mechanistic steps, the three trinuclear derivatives I, II, and III.[4]

$$\begin{array}{lll} Fe_3(CO)_9(RC_2R)\ (I) & \xrightarrow[-CO]{RC_2R}\ Fe_3(CO)_8(RC_2R)_2 & (\text{violet isomer, II}) \\ & \qquad\qquad \downarrow \triangle & \\ & \qquad\quad\ Fe_3(CO)_8(RC_2R)_2 & (\text{black isomer, III}) \end{array}$$

Furthermore since it has been reported that type I compounds are easily formed also from other iron carbonyls, i.e., $Fe(CO)_5$ and $Fe_2(CO)_9$,[2] it is conceivable that the trimetallic framework is built up by the alkyne capability to collect unsaturated metal carbonyl fragments.

The corresponding reactions of $Ru_3(CO)_{12}$ do not afford complexes of type I and II,[5] but it has been shown that type III complexes can be formed by reacting $HRu_3(CO)_9(RC \cdots CH \cdots CR)$ (the product of the oxidative addition of the alkyne to the Ru_3 cluster) with an excess of alkyne.[8] Alternative routes to $M_3(CO)_8(RC_2R)_2$ (M = Fe or Ru) are then possible. On the other hand the reaction of the mixed-metal carbonyl hydride $H_2FeRu_3(CO)_{13}$ with alkyne affords two isomers of formula $FeRu_3(CO)_{12}$(alkyne) containing a "butterfly" arrangement of the four metal atoms.[9]

In a previous paper[10] the nature of the alkyne–cluster interaction in $Fe_3(CO)_9(EtC_2Et)$ was investigated by UV-PES spectroscopy and theoretical quantum mechanical calculations. In that study the relevant role of back-donation from the two equivalent iron atoms to the alkyne as well the strong Fe–C′ bonding interaction have been stressed in complete agreement with the early qualitative picture reported by Blount et al.[4] (Figure 1).

On the basis of these results the failure to isolate stable analogous ruthenium[5] and osmium[11] derivatives can then be related to the decreased ability in back-donation in respect to the iron case. In order to test the relative importance of the electronic requirements in respect to the casual condensation of different metallic fragments around the alkyne substrate, we report here some results concerning the synthesis, reactivity, and solid, solution and electronic structures of type I compounds.

Experimental Section

Physical Measurements. All the reactions were brought about under nitrogen. Diphenylacetylene and 3-hexyne were purchased from Farchan Division. $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ were prepared according to the published procedures.[13,14]

The heterometallic complexes were analyzed by use of a F&M 185 C, H, N analyzer and a Perkin-Elmer 303 atomic absorption spectrometer. The IR spectra were recorded on a Perkin-Elmer 580 B instrument using matched 0.5-mm NaCl cells. The mass spectra were measured on a Hitachi Perkin-Elmer RMU-6H spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL C60-HL and JEOL PS-100 instruments, respectively. Chemical shifts were reported downfield positive with respect to $SiMe_4$.

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[5] A compound of formula $Ru_3(CO)_9(PhC_2Ph)$ has been reported only on the basis of elemental analysis,[6] actually we note that its IR spectrum is almost identical with that one reported for $Ru_4(CO)_{12}(PhC_2Ph)$.[7]

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[11] $Os_3(CO)_9(PhC_2Ph)$ has been recently obtained by vacuum sublimation of the coordinatively saturated $Os_3(CO)_{10}(PhC_2Ph)$ and shown to be extremely reactive.[12]

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Table I. Analysis and MS Data of the Heterometallic Complexes

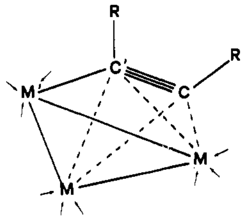
compd	physical state	elemental anal. found (calcd), % C	H	Fe	Ru	MS,[a] m/z
$Fe_2Ru(CO)_9PhC_2Ph$	dark green crystals	43.07 (42.86)	1.31 (1.55)	18.11 (17.39)	18.96 (18.63)	644 followed by loss of 9 CO's
$Fe_2Ru(CO)_9EtC_2Et$	dark green crystals	33.12 (32.85)	1.53 (1.82)	20.96 (20.44)	18.87 (18.61)	548 followed by loss of 9CO's and concommitting loss of H_2
$Fe_2Ru(CO)_8(PhC_2Ph)_2$	black crystals	53.98 (54.41)	2.24 (2.52)	14.45 (14.10)	12.97 (12.85)	794 followed by loss of 8 CO's
$FeRu(CO)_6(PhC_2Ph)$	yellow powder	60.13 (59.82)	2.85 (2.93)	8.71 (8.21)	15.12 (14.96)	682 followed by loss of 6 CO's

[a] Using an ionization energy of 70 eV.

Table II. IR and ^1H NMR Data

compd	IR[a] ν(CO), cm^{-1}	^1H NMR,[b,c] δ
$Fe_3(CO)_9(PhC_2Ph)$ (Ia)	2081 m, 2041 vs, 2027 vs, 2012 m, 1995 w, 1985 w	7.35 (m, 6), 6.86 (m, 2), 5.88 (m, 2)
$Fe_2Ru(CO)_9(PhC_2Ph)$ (I'a)	2093 m, 2047 vs, 2027 vs, 2005 m, 1990 w, 1983 w	7.30 (m, 6), 6.87 (m, 2), 6.10 (m, 2)
$Fe_3(CO)_9(EtC_2Et)$ (Ib)	2078 m, 2031 vs, 2023 vs, 2006 m, 1994 w, 1991 w	3.60 (q, 2), 1.72 (t, 3), 1.63 (q, 2), 0.48 (t, 3)
$Fe_2Ru(CO)_9(EtC_2Et)$ (I'b)	2088 m, 2040 vs, 2022 vs, 2005 m, 1988 w, 1978 w	3.56 (q, 2), 1.87 (q, 2), 1.74 (t, 3), 0.58 (t, 3)
$Fe_3(CO)_8(PhC_2Ph)_2$ (IIIa)	2058 m, 2020 m, 2014 vs, 2005 m, 1975 m, 1869 m, 1856 m	7.45 (m, 4), 7.20 (m, 6), 6.87 (m, 6), 6.29 (m, 4)
$Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III'a)	2065 m, 2019 m, 2013 vs, 2003 m, 1973 m, 1875 m, 1975 m, 1852 m	7.47 (m, 4), 7.18 (m, 6), 6.83 (m, 6), 6.38 (m, 4)
$Fe_2(CO)_6(PhC_2Ph)_2$ (IVa)	2070 s, 2031 vs, 2011 s, 1992 s	6.98 (m, 20)
$FeRu(CO)_6(PhC_2Ph)_2$ (IV'a)	2068 s, 2027 vs, 2007 s, 1990 s	6.92 (m, 20)

[a] n-Hexane. [b] $CDCl_3$. [c] Multiplicity and integrated intensities in parentheses.



(I)

Figure 1. Structure of the $M_2M'(CO)_9(RC_2R)$ complex: M = M' = Fe, R = Ph, Ia; M = M' = Fe, R = Et, Ib; M = Fe, M' = Ru, R = Ph, I'a; M = Fe, M' = Ru, R = Et, I'b.

$Cr(acac)_3$ ($\sim 10^{-3}$ M) was added as a shiftless relaxation agent for ^{13}C NMR measurements.

The physical properties and analytical and MS data for the heterometallic compounds are listed in Table I and IR and ^1H NMR data in Table II.

Calculations. Quantum mechanical calculations were performed by a version of the CNDO method[15] suitable for transition-metal complexes. Semiempirical parameters were obtained[15] from atomic spectroscopical data, whereas C, O, and H parameters are Pople's standard ones.[16] Gross atomic charges and overlap populations were obtained by Mulliken's population analysis[17] of the deorthogonalized[18] eigenvectors.

X-ray analysis: $C_6H_5C_2C_6H_5Ru_1Fe_2(CO)_9$; M_r = 643.09; triclinic; a = 9.146 (3) Å, b = 9.137 (3) Å, c = 16.321 (4) Å, α = 80.81 (3)°, β = 75.84 (3)°, γ = 62.58 (3)°; V = 1172.1 (7) Å^3, D_{calcd} = 1.822 g cm^{-3}, D_{measd} = 1.82 g cm^{-3} (by flotation in iodobenzene–benzene solutions); $\mu_{Mo\ K\alpha}$ = 18.95 cm^{-1}; Z = 2; $F(000)$ = 632; space group $P\bar{1}$; the choice of the centric space group was confirmed by the structural determination.

A needle-shaped crystal, dark green color, of 0.05 × 0.05 × 0.25 mm in size was used for data collection on a Philips PW 1100 four-circle diffractometer: Mo Kα radiation monochromatized by a graphite plate; θ–2θ scan mode; scan width 1.5° at a speed of 0.03 s^{-1}; background measured for 7 s at each extremity; θ from 2° up to 25°; two standard intensity and orientation reflections were measured at 3-h intervals; no decomposition of the crystal was noticed during data collection.

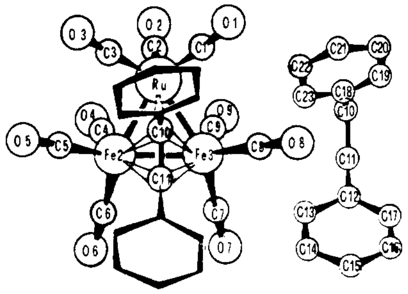


Figure 2. View of the molecular shape of the complex $Fe_2Ru(CO)_9(PhC_2Ph)$ (I'a) with the atomic numbering scheme.

Of the 4125 independent reflections 2696 were considered observed with $I \geq 2.5\sigma(I)$. Intensities were corrected for Lorentz and polarization effects but not for absorption.

First structure factor calculations were computed with coordinates of the isostructural compound $C_6H_5C_2C_6H_5Fe_3(CO)_9$, with the Ru atom replacing the Fe(1) one, as predicted by theoretical calculations, R = 10.5.

Positional and anisotropic thermal parameters of the nonhydrogen atoms were refined by the block least-squares program with unitary weights; H atoms were introduced in fixed calculated positions (B = 6.0 Å^2) as the mean of equivalent isotropic thermal parameters of the phenyl carbon atoms.

Refinement converged to R = 0.081, the mean shift/esd was about 0.02, and the final difference map revealed no peak > 0.7 e Å^{-3}.

Atomic scattering factors were derived from ref 28, and the program SHELX[19] was used.

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Table III. Final Atomic Parameters with Esd's in Parentheses

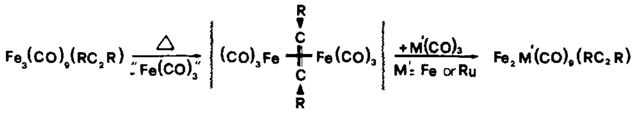
	x	y	z	B_{eq}, Å^2
Ru	0.5662 (1)	0.7320 (1)	0.1691 (1)	3.65 (3)
Fe(2)	0.8642 (2)	0.5453 (2)	0.1952 (1)	3.36 (6)
Fe(3)	0.7763 (2)	0.8551 (2)	0.1522 (1)	3.54 (6)
C(1)	0.3689 (19)	0.9330 (21)	0.1863 (9)	5.1 (5)
O(1)	0.2497 (16)	1.0488 (15)	0.2042 (9)	5.6 (4)
C(2)	0.5016 (19)	0.6998 (21)	0.0718 (11)	5.5 (6)
O(2)	0.4718 (18)	0.6800 (21)	0.0132 (9)	5.1 (5)
C(3)	0.4785 (17)	0.5875 (20)	0.2403 (11)	4.9 (5)
O(3)	0.4353 (17)	0.5025 (18)	0.2798 (9)	8.5 (5)
C(4)	0.8503 (20)	0.4853 (21)	0.1007 (13)	5.1 (6)
O(4)	0.8601 (16)	0.4188 (18)	0.0422 (8)	7.1 (6)
C(5)	0.8638 (20)	0.3785 (19)	0.2614 (11)	4.9 (5)
O(5)	0.8635 (21)	0.2672 (19)	0.3093 (11)	8.8 (6)
C(6)	1.0894 (21)	0.4671 (21)	0.1711 (14)	6.0 (6)
O(6)	1.2285 (15)	0.4267 (21)	0.1538 (11)	8.5 (6)
C(7)	0.9771 (25)	0.8589 (22)	0.1117 (14)	6.5 (6)
O(7)	1.1041 (18)	0.8547 (22)	0.0836 (13)	11.0 (7)
C(8)	0.6672 (23)	1.0731 (22)	0.1703 (12)	6.1 (6)
O(8)	0.6145 (22)	1.2121 (16)	0.1744 (12)	9.2 (6)
C(9)	0.7293 (22)	0.8583 (19)	0.0531 (12)	5.6 (5)
O(9)	0.7228 (20)	0.8674 (18)	−0.0815 (9)	8.8 (5)
C(10)	0.6910 (16)	0.7521 (16)	0.2631 (8)	3.2 (4)
C(11)	0.8615 (15)	0.7189 (15)	0.2512 (8)	3.0 (4)
C(12)	0.9530 (15)	0.7238 (18)	0.3118 (8)	3.4 (4)
C(13)	1.0313 (22)	0.5816 (24)	0.3643 (11)	6.5 (6)
C(14)	1.1024 (24)	0.5934 (26)	0.4264 (12)	7.5 (7)
C(15)	1.1207 (21)	0.7390 (27)	0.4302 (11)	6.6 (7)
C(16)	1.0627 (21)	0.8635 (24)	0.3768 (13)	6.4 (6)
C(17)	0.9739 (20)	0.8645 (19)	0.3188 (10)	4.7 (5)
C(18)	0.5781 (15)	0.7972 (17)	0.3474 (9)	3.3 (4)
C(19)	0.4618 (20)	0.9630 (22)	0.3624 (12)	6.3 (6)
C(20)	0.3630 (20)	0.9988 (27)	0.4435 (14)	7.4 (8)
C(21)	0.3830 (29)	0.8728 (30)	0.5061 (13)	7.9 (8)
C(22)	0.4941 (23)	0.7143 (27)	0.4936 (11)	7.3 (7)
C(23)	0.5955 (20)	0.6724 (20)	0.4140 (9)	5.1 (5)
H(13)	1.034	0.479	0.356	
H(14)	1.140	0.504	0.467	
H(15)	1.175	0.745	0.471	
H(16)	1.082	0.957	0.378	
H(17)	0.927	0.961	0.283	
H(19)	0.451	1.048	0.319	
H(20)	0.283	1.109	0.456	
H(21)	0.315	0.900	0.561	
H(22)	0.503	0.632	0.538	
H(23)	0.676	0.561	0.404	

Table IV. Intramolecular Distances (Å) with with Esd's in Parentheses

Ru-Fe(2)	2.564 (2)	Ru-C(10)	2.198 (17)
Ru-Fe(3)	2.582 (3)	Fe(2)-C(10)	2.088 (12)
Fe(2)-Fe(3)	2.588 (3)	Fe(3)-C(10)	2.052 (13)
Ru-C(1)	1.890 (13)	Fe(2)-C(11)	1.941 (16)
Ru-C(2)	1.930 (21)	Fe(3)-C(11)	1.961 (12)
Ru-C(3)	1.941 (18)	C(10)-C(11)	1.413 (20)
Fe(2)-C(4)	1.768 (23)	C(11)-C(12)	1.461 (23)
Fe(2)-C(5)	1.723 (17)	C(12)-C(13)	1.422 (21)
Fe(2)-C(6)	1.801 (18)	C(13)-C(14)	1.373 (34)
Fe(3)-C(7)	1.808 (23)	C(14)-C(15)	1.428 (38)
Fe(3)-C(8)	1.807 (18)	C(15)-C(16)	1.300 (26)
Fe(3)-C(9)	1.765 (22)	C(16)-C(17)	1.387 (31)
C(1)-O(1)	1.129 (17)	C(17)-C(12)	1.409 (28)
C(2)-O(2)	1.118 (28)	C(10)-C(18)	1.491 (17)
C(3)-O(3)	1.083 (25)	C(18)-C(19)	1.412 (20)
C(4)-O(4)	1.176 (28)	C(19)-C(20)	1.399 (26)
C(5)-O(5)	1.180 (24)	C(20)-C(21)	1.387 (31)
C(6)-O(6)	1.122 (22)	C(21)-C(22)	1.345 (29)
C(7)-O(7)	1.125 (28)	C(22)-C(23)	1.392 (21)
C(8)-O(8)	1.139 (24)	C(23)-C(18)	1.424 (20)
C(9)-O(9)	1.172 (26)		

Final coordinates are listed in Table III, bond lengths in Table IV, and bond angles in Table V. Figure 2 shows a view of the title compound with the labeling scheme.

Scheme I



Preparation of $Fe_2Ru(CO)_9(PhC_2Ph)$ (I′a) by Photochemical Activation. In a typical run 500 mg (0.8 mmol) of $Ru_3(CO)_{12}$, 400 mg (0.8 mmol) of $Fe_3(CO)_{12}$, and 285 mg (1.6 mmol) of PhC_2Ph in 200 mL of cyclohexane were photolyzed at room temperature with an unfiltered Italquartz 500-W medium-pressure Hg lamp (immersion system). After 10 h the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2, and the solution chromatographed on TLC preparative plates (SiO_2, eluent petroleum ether and 10% diethyl ether).

Besides the well-known acetylenic derivatives of iron[2] and ruthenium,[3,7] $Fe_2Ru(CO)_9(PhC_2Ph)$ (I′a) (~20%), $Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III′a) (trace), and $FeRu(CO)_6(PhC_2Ph)_2$ (IV′a) (~10%) were eluted.

Reactions of $Ru_3(CO)_{12}$ with $Fe_3(CO)_9(PhC_2Ph)$ (Ia) and $Fe_3(CO)_9(EtC_2Et)$ (Ib). $Fe_3(CO)_9(PhC_2Ph)$ (500 mg, 0.8 mmol) and $Ru_3(CO)_{12}$ (400 mg, 0.8 mmol) were heated in refluxing cyclohexane for 8 h. Similar separation workup gave $Fe_2Ru(CO)_9(PhC_2Ph)$ (I′a) in ~30% yield. Analogous reaction using $Fe_3(CO)_9(EtC_2Et)$ afforded $Fe_2Ru(CO)_9(EtC_2Et)$ (I′b) in ~20% yield.

Reaction of I′a with PhC_2Ph. I′a and diphenylacetylene in 1:5 molar ratio were heated in refluxing cyclohexane for 4 h. From the plates, $Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III′a) and $FeRu(CO)_6(PhC_2Ph)$ (IV′a) were recovered in ~30% and ~20% yields, respectively. No homometallic derivatives of iron or ruthenium were found.

Attempt To React $Fe_3(CO)_8(PhC_2Ph)_2$ with $Ru_3(CO)_{12}$. A mixture of IIIa and $Ru_3(CO)_{12}$ in equimolar ratio was photolyzed in cyclohexane for 24 h, and no detectable amount of III′a or IV′a was found. The same behavior was observed when an identical mixture was heated under reflux for 48 h.

Preparation of Carbon-13 Enriched Samples of I′a, III′a, and IV′a. The ^{13}CO enrichment was performed on Ia by stirring a solution of the compound in cyclohexane in a sealed ampule for 5 days at +40 °C in the presence of <1 atm of ^{13}CO. Ia was then thermally reacted with $Ru_3(CO)_{12}$ previously enriched in ^{13}CO (sealed vial, 50 °C for 4 days) to give I′a. III′a and IV′a were then obtained from I′a according to the procedure described above.

Results and Discussion

Formation of Type I Complexes. It has been shown that both $Fe_3(CO)_{12}$[20] and $Ru_3(CO)_{12}$[21] undergo photochemical declusterification to produce mononuclear fragments. In the absence of any electronic or steric factor the photoreaction of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ with PhC≡CPh in 1:1:2 molar ratio would generate all the possible type I clusters $M_xM'_y(CO)_9(PhC_2Ph)$ (M = Fe; M′ = Ru; $x + y = 3$) as well as the tetrametallic "butterfly" $M_xM'_y(CO)_{12}(PhC_2Ph)$ complexes (M = Fe; M′ = Ru; $x + y = 4$) among a "cascade" of other products.

On the contrary from the above reaction only $Fe_3(CO)_9(PhC_2Ph)$ (Ia) and $Fe_2Ru(CO)_9(PhC_2Ph)$ (I′a) have been obtained, besides the well-known homonuclear derivatives of iron and ruthenium and two novel mixed-metal complexes of formula $Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III′a) and $FeRu(CO)_6(PhC_2Ph)_2$ (IV′a).

The observed behavior suggests then that, in its main features, this reaction follows a pathway analogous to that one reported for iron carbonyls. Interestingly no derivative containing the Ru_2Fe moiety is obtained in this reaction.

Another route to the synthesis of $Fe_2Ru(CO)_9$(alkyne) complexes (I′a and I′b) has been found by thermally reacting the preformed $Fe_3(CO)_9$(alkyne) (Ia and Ib) and $Ru_3(CO)_{12}$ in cyclohexane. We think that a possible

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Table V. Bond Angles (deg) with Esd's in Parentheses

Ru-Fe(2)-Fe(3)	60.2 (0.8)	C(7)-Fe(3)-Ru	153.5 (0.6)	Ru-C(10)-Fe(2)	73.4 (0.5)
Ru-Fe(3)-Fe(2)	59.5 (0.8)	C(7)-Fe(3)-Fe(2)	102.1 (0.6)	Ru-C(10)-Fe(3)	74.7 (0.5)
Fe(2)-Ru-Fe(3)	60.4 (0.8)	C(8)-Fe(3)-Ru	110.8 (0.7)	C(10)-C(11)-C(12)	129.1 (1.2)
Ru-C(1)-O(1)	173.7 (1.3)	C(8)-Fe(3)-Fe(2)	154.4 (0.6)	Fe(2)-C(10)-Fe(3)	77.4 (0.5)
Ru-C(2)-O(2)	176.6 (1.8)	C(9)-Fe(3)-Ru	69.9 (0.7)	Fe(2)-M-Fe(3)	86.8
Ru-C(3)-O(3)	177.4 (1.6)	C(9)-Fe(3)-Fe(2)	98.2 (0.5)	Fe(2)-C(11)-Fe(3)	83.1 (0.5)
Fe(2)-C(4)-O(4)	168.4 (1.6)	C(1)-Ru-C(10)	98.6 (0.6)	C(10)-Fe(2)-Fe(3)	50.7 (0.4)
Fe(2)-C(5)-O(5)	177.4 (1.6)	C(2)-Ru-C(10)	168.2 (0.7)	C(10)-Fe(3)-Fe(2)	51.9 (0.4)
Fe(2)-C(6)-O(6)	176.1 (1.7)	C(3)-Ru-C(10)	95.4 (0.6)	C(10)-Fe(2)-C(11)	40.9 (0.6)
Fe(3)-C(7)-O(7)	177.2 (1.9)	C(4)-Fe(2)-C(10)	127.6 (0.7)	C(10)-Fe(3)-C(11)	41.2 (0.6)
Fe(3)-C(8)-O(8)	171.4 (2.0)	C(5)-Fe(2)-C(10)	105.0 (0.6)	C(11)-Fe(2)-Fe(3)	48.8 (0.4)
Fe(3)-C(9)-O(9)	167.5 (2.0)	C(6)-Fe(2)-C(10)	127.1 (0.7)	C(11)-Fe(3)-Fe(2)	48.1 (0.4)
C(1)-Ru-C(2)	89.9 (0.7)	C(7)-Fe(3)-C(10)	130.7 (0.8)	Fe(2)-C(10)-C(11)	64.0 (0.7)
C(2)-Ru-C(3)	91.4 (0.7)	C(8)-Fe(3)-C(10)	102.6 (0.7)	Fe(3)-C(10)-C(11)	66.0 (0.7)
C(3)-Ru-C(1)	98.1 (0.7)	C(9)-Fe(3)-C(10)	124.9 (0.7)	Fe(2)-C(11)-C(10)	75.2 (0.8)
C(4)-Fe(2)-C(5)	99.3 (0.8)	C(4)-Fe(2)-C(11)	146.2 (0.7)	Fe(3)-C(11)-C(10)	72.9 (0.8)
C(5)-Fe(2)-C(6)	95.0 (0.8)	C(5)-Fe(2)-C(11)	114.2 (0.7)	C(11)-C(12)-C(13)	120.4 (1.4)
C(6)-Fe(2)-C(4)	95.3 (0.9)	C(6)-Fe(2)-C(11)	86.2 (0.7)	C(11)-C(12)-C(17)	122.4 (1.2)
C(7)-Fe(3)-C(8)	93.6 (0.8)	C(7)-Fe(3)-C(11)	89.7 (0.8)	C(12)-C(13)-C(14)	119.4 (1.7)
C(8)-Fe(3)-C(9)	99.9 (0.8)	C(8)-Fe(3)-C(11)	112.8 (0.7)	C(13)-C(14)-C(15)	120.3 (1.8)
C(9)-Fe(3)-C(7)	96.6 (0.9)	C(9)-Fe(3)-C(11)	146.2 (0.6)	C(14)-C(15)-C(16)	119.6 (2.0)
C(1)-Ru-Fe(2)	149.2 (0.5)	C(4)-Fe(2)-M[a]	139.8	C(15)-C(16)-C(17)	122.2 (1.9)
C(1)-Ru-Fe(3)	96.6 (0.5)	C(5)-Fe(2)-M	110.7	C(16)-C(17)-C(12)	120.5 (1.5)
C(2)-Ru-Fe(2)	118.9 (0.5)	C(6)-Fe(2)-M	107.4	C(17)-C(12)-C(13)	117.1 (1.4)
C(2)-Ru-Fe(3)	121.1 (0.5)	C(7)-Fe(3)-M	110.7	C(10)-C(18)-C(19)	120.4 (1.3)
C(3)-Ru-Fe(2)	92.1 (0.5)	C(8)-Fe(3)-M	108.8	C(10)-C(18)-C(23)	119.1 (1.3)
C(3)-Ru-Fe(3)	144.2 (0.5)	C(9)-Fe(3)-M	138.2	C(18)-C(19)-C(20)	118.0 (1.6)
C(4)-Fe(2)-Ru	73.1 (0.6)	Ru-C(10)-C(11)	126.6	C(19)-C(20)-C(21)	119.7 (2.0)
C(4)-Fe(2)-Fe(3)	98.1 (0.6)	Ru-C(10)-C(18)	112.9 (1.0)	C(20)-C(21)-C(22)	123.5 (2.0)
C(5)-Fe(2)-Ru	109.3 (0.7)	C(18)-C(10)-C(11)	120.5 (1.3)	C(21)-C(22)-C(23)	119.0 (1.9)
C(5)-Fe(2)-Fe(3)	155.7 (0.6)	Fe(2)-Ru-C(10)	51.3 (0.4)	C(22)-C(23)-C(18)	119.5 (1.6)
C(6)-Fe(2)-Ru	154.3 (0.6)	Fe(3)-Ru-C(10)	50.1 (0.4)	C(23)-C(18)-C(19)	120.3 (1.4)
C(6)-Fe(2)-Fe(3)	100.2 (0.6)				

[a] M is the midpoint between C(10) and C(11).

mechanism (Scheme I) for the formation of type I complexes passes through an unsaturated $Fe_2(CO)_6(RC_2R)$ species, which has been isolated and characterized only for R = *t*-Bu.[22] It is likely that this binuclear unsaturated intermediate is a possible precursor in the formation of type I complexes in the reaction between iron carbonyls and alkynes. In order to get some experimental evidence for the displacement of a "$Fe(CO)_3$" unit from $Fe_3(CO)_9$(alkyne), we recorded the carbon-13 NMR spectra of a mixture of $Fe_3(CO)_9(C_2Et_2)$ (^{13}CO enriched)/$Fe_3(CO)_9(C_2Ph_2)$ in toluene at +60 °C. Unfortunately the incorporation of ^{13}CO into the unenriched species occurs to a similar extent at the two structurally different iron centers, thus indicating that, at this temperature, an eventual "$Fe(CO)_3$" exchange process would be masked by an incipient carbonyl equilibration over all the molecule.

Spectroscopic and Structural Data of $Fe_2Ru(CO)_9$(alkyne). The IR and ^1H NMR spectra of $Fe_2Ru(CO)_9(PhC_2Ph)$ (I′a) and $Fe_2Ru(CO)_9(EtC_2Et)$ (I′b) are very similar to those of corresponding iron derivatives (see Table II) apart from small changes in frequencies and chemical shifts induced by the heteroatom, suggesting that the Cs symmetry has been retained (Ru in M′ position). More diagnostic has been the variable-temperature ^{13}C NMR spectra of an enriched sample of I′a.

At +25 °C, two CO absorptions are observed at 211.8 and 189.4 ppm in the relative intensity ratio of 2:1. On going down to −50 °C the high-field signal broadens and at −65 °C it is split into two signals at 191.7 and 187.9 ppm. It follows that at this temperature the spectrum consists of three resonances in the relative intensity ratio of 6:1:2. This result parallels that found for Ib,[10] indicating that the ruthenium atom is σ bonded to the C′ atom of the alkyne (see Figure 1). A localized exchange at each $M(CO)_3$ unit is occurring, which can be "frozen out" only for the $Ru(CO)_3$ unit. The higher field shift of these resonances as well as the higher coalescence temperature for this scrambling process in respect to Ib are in accord with this assignment.[23]

In order to assess the possible minor changes that occurred in the structural parameters on going from Ia to I′a, an X-ray structure determination of I′a has been undertaken. The intramolecular distances and bond angles with the estimated standard deviations of I′a are reported in Tables IV and V. For comparison purposes the same numbering convention used in the structural determination of Ia[4] has been adopted (Figure 2). An identical geometrical arrangement has been found for I′a with respect to Ia. Minor variations are present in the metallic framework as a consequence of the larger atomic dimension of the Ru atom replacing the Fe one [Ru–Fe(2) = 2.56 Å and Ru–Fe(3) = 2.58 Å vs. Fe(1)–Fe(2) = 2.48 Å and Fe(1)–Fe(3) = 2.50 Å in Ia]. The Fe(2)–Fe(3) bond length is equal in the two molecules; the Ru–Fe bond distance (average 2.57 Å), however, is significantly shorter than the Ru–Fe distances found in other heteronuclear carbonyl complexes (average 2.70 Å).[24] This fact is consistent with the already suggested hypothesis[10] that the interactions between the alkyne ligand and the metal–carbonyl fragments play the leading role in the determination of the cluster geometry; i.e., the metal–metal bond lengths can adapt themselves in order to optimize the alkyne–cluster interaction. The dimensions and bond angles of the coordinated diphenylacetylene and the alkyne–Fe distances are similar

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(22) Cotton, F. A.; Frenz, B. A.; Troup, J. M.; Deganello, G. *J. Organomet. Chem.* **1975**, *94*, C53.

(23) Aime, S.; Milone, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 149.

(24) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 40.

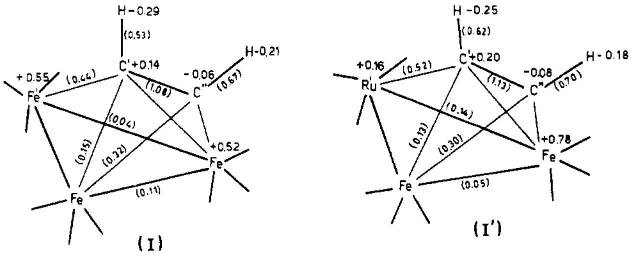

Figure 3. CNDO gross atomic charges and bond overlap populations of $Fe_3(CO)_9(HC_2H)$ (I) and $Fe_2Ru(CO)_9(HC_2H)$ (I′).

to those of Ia whereas the Ru–C(10) distance (2.20 Å) is 0.15 Å longer than the corresponding Fe(1)–C(10) one.

In the light of the above reported structural data, which rule out any metallic steric effect in the formation of I′a, the experimental evidence regarding the isolation of just one isomer of I′a may be accounted for in terms of electronic driving factors. In Figure 2 the CNDO-computed gross atomic charges and bond overlap populations of I and I′ (when R = R′ = H) are compared. The reported data show what is expected on the basis of the metallic electronegativity differences (Pauling values: Fe, 1.8; Ru, 2.2): the unique Ru atom draws charge from both the alkyne (charge of the alkyne: −0.42 e in I and −0.31 e in I′) and the two Fe atoms. The increased positive charge on the iron atoms results in turn from a reduction of the overlap populations of both Fe–alkyne and Fe–Fe interactions. The overall bonding scheme previously discussed for I,[10] however, is adequate for I′, in particular as far as the leading role of the back-bonding interaction between the two equivalent iron atoms and the alkyne π^* levels is concerned. As a consequence, the nonformation of different $RuFe_2$ and Ru_2Fe isomers in these reactions can be traced back to the tendency to maintain the strong $Fe_2 \rightarrow$ alkyne back-donation.

The I → III Transformation. Although the role of the type I compound in the formation of III (with the intermediacy of II)[4] was recognized early, we were interested in getting a more detailed picture of this transformation. Thermal reaction of I′a with an excess of PhC_2Ph gives only one isomer of formula $Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III′a); this compound is also obtained—as the unique representative of type III molecules—from the photolytic reaction of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and PhC_2Ph. The preformed $Fe_3(CO)_8(PhC_2Ph)_2$ (IIIa) does not react at all with $Ru_3(CO)_{12}$ via both thermal or photolytic activation but just slowly decomposes to $Fe_2(CO)_6(PhC_2Ph)_2$ (IVa).

These findings suggests that the I → III transformation does occur without any cluster breakdown/cluster reforming path. The structure of $RuFe_2(CO)_8(PhC_2Ph)_2$ (III′a) was assessed on the basis of the IR and carbon-13 NMR spectra. As shown in Figure 3, its IR spectrum is very similar to that of $Fe_3(CO)_8(PhC_2Ph)_2$, both displaying five absorptions in the CO terminal region as expected on the basis of the idealized C_{2v} symmetry.

The carbon-13 NMR spectrum of a ^{13}CO-enriched sample at 0 °C of IIIa shows three absorptions at 251.2, 205.0, and 190.1 ppm in the relative intensity ratio of 2:4:2. The highest field peak is assigned to the two terminally bonded carbonyls on the Ru atom, whereas the remaining two resonances are due to two bridging and four terminal carbonyls bonded to the iron centers. The chemical shifts of the latter resonances are in the range already reported for the corresponding homometallic iron derivative.[25] As the temperature is increased to +40 °C, the two low-field resonances broaden and eventually at +75 °C are completely collapsed into the base line. An incipient decomposition of the sample prevented the possibility to record spectra at higher temperatures. The observed behavior parallels that already found in $Fe_3(CO)_8(PhC_2Ph)_2$, but unexpectedly it occurs in a higher temperature range.

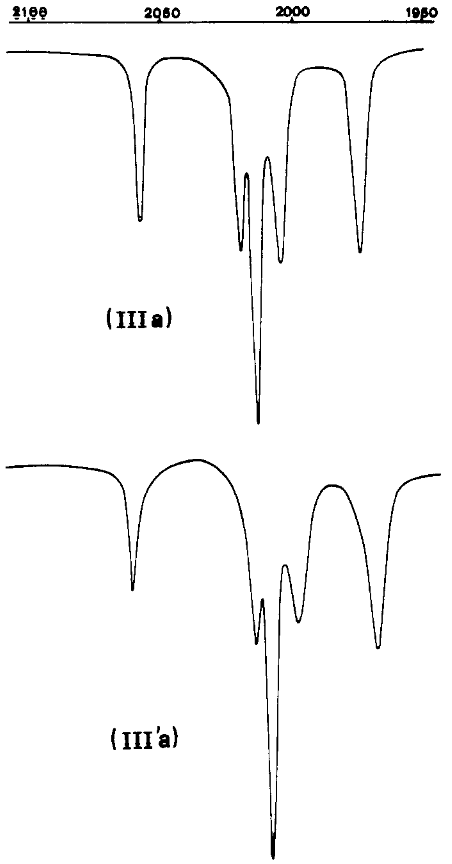

Figure 4. Terminal carbonyl region IR spectra of $Fe_3(CO)_8(PhC_2Ph)_2$ (IIIa) and $Fe_2Ru(CO)_8(PhC_2Ph)_2$ (III′a) measured in *n*-hexane solution.

The pattern detected in the carbonyl region unambiguously indicates that the Ru atom is involved in the formation of the metallacyclopentadienyl system whereas the Fe atoms are symmetrically π bonded to the unsaturated moiety. Further support for this structure comes from the preservation of the ruthenium cyclopentadienyl ring in $FeRu(CO)_6(PhC_2Ph)_2$ (IV′a), the major product of the pyrolysis of III′a. The structure of IV′a has been assessed on the basis of the variable-temperature ^{13}C NMR spectra of an enriched (~30%) sample.[26]

Conclusions

This study has shown that only a limited number of products can be obtained from the photochemical reaction of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and PhC_2Ph; their characterization has allowed us to suggest that the occurring reaction

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[25] Aime, S.; Milone, L.; Sappa, E. *Inorg. Chim. Acta* **1976**, *16*, L7.

[26] The ^{13}C NMR spectrum of IV′a in freon/CD_2Cl_2 solution shows three absorptions at 217.3 (3), 197.2 (1), and 193.2 (1) ppm. The downfield peak is very broad at −115 °C, but it was not possible to go further down in temperature to "freeze out" the exchange process. This peak is assigned to the COs of the $Fe(CO)_3$ unit π bonded to the metallacyclopentadienyl system on the basis of the similarity of its chemical shift with those found for the same $Fe(CO)_3$ moiety in homologous homometallic derivatives.[27] The remaining two resonances are assigned to the carbonyl group bonded to the ruthenium atom in the metallacyclopentadienyl ring; their chemical shifts fall in the expected region.[23]

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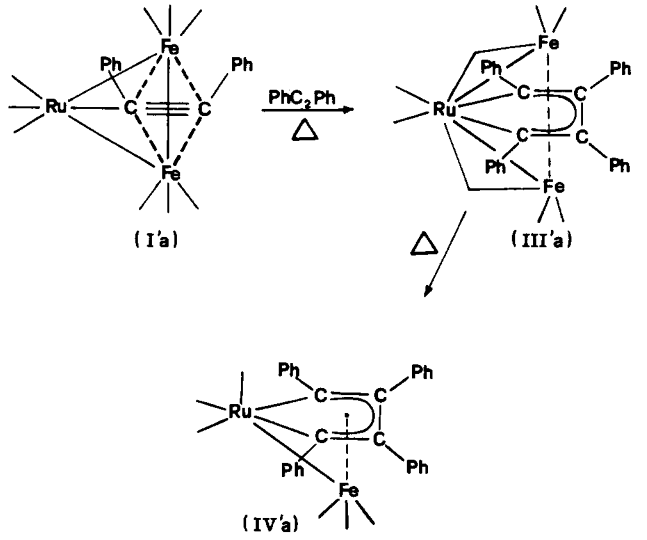

path corresponds to the main one found when $Fe_3(CO)_{12}$ alone is reacted with PhC_2Ph.

The detection of just one isomer of formula $Fe_2Ru(CO)_9$(alkyne) has been accounted for in terms of the leading role of the electronic effects with respect to the steric factors. Furthermore its formation by thermal reaction of $Fe_3(CO)_9$(alkyne) with $Ru_3(CO)_{12}$ suggests that a possible pathway in the reaction of $Fe_3(CO)_{12}$ with alkynes passes through a binuclear intermediate containing an iron-iron double bond. It has also been shown that the I → III transformation occurs with the preservation of the cluster integrity.

Finally we wish to emphasize that, apart from the intrinsic interest to synthesize novel heterometallic clusters, the study of reactions involving different metal carbonyl substrates can provide a fruitful source of mechanistic information in the reaction between $M_3(CO)_{12}$ and alkynes.

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Registry No. I, 83802-15-7; I', 90991-62-1; Ia, 12171-93-6; I'a, 90991-63-2; Ib, 69402-19-3; I'b, 91002-48-1; IIIa, 90991-65-4; III'a, 90991-66-5; IVa, 33310-05-3; IV'a, 90991-67-6; $Ru_3(CO)_{12}$, 15243-33-1; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Tables of structure factor amplitudes, fractional coordinates, and thermal parameters for $(C_6H_5C_2C_6H_5)Ru_1Fe_2(CO)_9$ (19 pages). Ordering information is given on any current masthead page.

A Rarely Encountered Class of Stable Mononuclear 17-Electron Rhenium(II) Complexes: *trans*-$[Re(CNR)_2(NCCH_3)L(PPh_3)_2](BF_4)_2$ (R = *i*-Pr or *t*-Bu and L = CH_3CN or py)

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The reactions of $[ReH(NCCH_3)_3L(PPh_3)_2](BF_4)_2$ (L = CH_3CN, py, $C_6H_{11}NH_2$, or *t*-$BuNH_2$) with RNC (R = *i*-Pr or *t*-Bu) proceed in a stepwise fashion to afford $[ReH(NCCH_3)_2(CNR)L(PPh_3)_2](BF_4)_2$ (I), $[Re(CNR)_2(NCCH_3)L(PPh_3)_2]BF_4$ (II), and $[Re(CNR)_4(PPh_3)_2]BF_4$ (III). Complexes of the type II are oxidized to the corresponding paramagnetic 17-electron dications. The crystal structure of the dichloromethane solvate of $[Re(CN\text{-}t\text{-}Bu)_2(NCCH_3)_2(PPh_3)_2](BF_4)_2$ shows it to be the all-trans isomer. It crystallizes in a unit cell with a = 44.729 (2) Å, b = 12.170 (1) Å, c = 21.018 (2) Å, β = 106.15 (2)°, V = 10.989 Å^3, Z = 8, and monoclinic space group $C2/c$.

Introduction

Well-defined and structurally characterized *mononuclear* coordination complexes of Re(II) are rare,[2,3] although the stability of this oxidation state can be engendered through the formation of rhenium-rhenium multiple bonds as in the dirhenium(II) complexes $Re_2X_4(PR_3)_4$ (X = halide).[4,5] The rarity of such mononuclear species is especially surprising in view of the stability of other d^5 complexes such as those of Mn(II) and Os(III). In this report we describe details of the isolation of members of a new class of mononuclear paramagnetic 17-electron rhenium(II) complex, viz., $[Re(CNR)_2(NCCH_3)L(PPh_3)_2](BF_4)_2$, where R = *i*-Pr or *t*-Bu and L = CH_3CN or py, that we have obtained during our investigations into the reactivity of the rhenium(III) monohydrides $[ReH(NCCH_3)_3L(PPh_3)_2](BF_4)_2$, where L = CH_3CN, py, $C_6H_{11}NH_2$, or *t*-$BuNH_2$,[6] a group of molecules that are isoelectronic with several related cationic hydrido species of Mo(IV), W(IV), and Ir(III).[7-10] Details of the crystal

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(10) The closely related seven-coordinate rhenium(III) monohydride complex $[ReHCl(PMe_3)_5]BF_4$ has recently been the subject of a study by Wilkinson and co-workers; see: Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

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