Journal of Organometallic Chemistry, 288 (1985) 365–383
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE COORDINATION OF ALKYNES TO FOUR METAL ATOMS IN SQUARE PLANAR CLUSTERS. CRYSTAL STRUCTURE AND CLUSTER CONTRACTION AND EXPANSION REACTIONS OF $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}C_2Ph_2)$

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(Received December 21st, 1984)

Summary

The structure of the tetranuclear cluster $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}C_2Ph_2)$ (Ia) has been determined by X-ray methods. Crystals of Ia are orthorhombic, space group *Pbca*, with a 24.774(21), b 29.509(19), c 14.677(7) Å, $Z = 16$; $R = 0.063$ for 3626 observed reflections.

In the crystal structure of Ia two crystallographically independent but almost identical heteronuclear clusters are present, in which two Fe atoms and two Ni atoms are in slightly distorted square planar arrangement with the alkyne interacting with all four metals, through σ bonds to the Ni and π bonds to the Fe atoms. The structural features of Ia are compared with those of related compounds, and a discussion is presented of the square planar and flattened butterfly clusters reported to date, some of which are formally unsaturated.

The reactions of Ia (a formally 62 electron cluster which can be described in skeletal electron counting terms as a 6-vertex 8-skeletal pair *nido*-pentagonal bipyramid) with donor ligands (CO, PR_3, alkynes) and metal fragments have been examined. No evidence of Lewis acidity normally associated with unsaturation was found, but cluster expansion reactions generating pentametallic complexes from Ia via completion of the pentagonal bipyramid have been observed. The synthesis and spectroscopic characterization of these new complexes are described.

0022-328X/85/$03.30

Introduction

The potential utility of heterometallic clusters as homogeneous catalysts and as heterogeneous catalyst precursors has stimulated efforts to devise rational synthetic routes to such species [1]. With some notable exceptions, many earlier cluster syntheses were empirical and largely serendipitous. More recently the emphasis has been placed on designed strategies [2] and detailed studies of cluster reactivity. In this regard application of the ideas of skeletal electron pair theory [3] and, more recently, the concept of isolobal fragments [4] promise to have a major impact. Indeed two of the more useful synthetic strategies, particularly for heteropolymetallics, namely condensation methods between appropriate metal containing moieties [2] and the use of metal carbene or carbyne complexes as reagents for cluster synthesis [5], can in retrospect best be rationalised in terms of these theories.

Recently we reported the pyrolytic syntheses of triangular, tetrahedral, butterfly, square planar, spiked triangular, square pyramidal and capped trigonal bipyramidal clusters containing iron, ruthenium or osmium and η^5-C_5H_5-nickel moieties [6–13]. For many of these clusters alkynes, acetylides or vinylidenes were incorporated as stabilizing ligands [6]. The selectivity of these reactions could, in several cases, be improved by employing specific ruthenium hydrocarbyl clusters as reagents [7] or, more importantly, by using molecular hydrogen as a reaction atmosphere [8]. This latter approach may result in the formation of new cluster types [8,9] or in a significant increase in the yields of specific target molecules [10,11]. Dihydrogen was initially used to increase the yields of hydrido butterfly clusters [10,11], but this method also proved useful for non-hydridic species containing one or more η^5-C_5H_5-Ni units (non-bonded each to the other).

Herein we report the use of a dihydrogen atmosphere for the synthesis of the square planar mixed metal clusters $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}C_2RR')$ ($R = R' = Ph$, Ia; $R = R' = Et$, Ib; $R = H$, $R' = Me$, Bu^t, Pr^i, Ph, Ic, Id, Ie, If) previously accessible in only low yields [12,13].

The availability of Ia, in particular, in useful quantities has allowed us to study the reactivity of this formally unsaturated 62 electron species in some detail.

X-ray analysis has established that the Fe_2Ni_2 core of Ia is a distorted square, with the alkyne coordinated to all four atoms. The alternative description in terms of skeletal electron pair theory is a *nido*-pentagonal bipyramid (6 vertices, 8 skeletal pairs) with two metal atoms in axial positions and a vacant equatorial site, and with each CR fragment contributing 3 electrons to the framework.

The chemistry of Ia was examined in the context of these models. We have found that while Ia is remarkably stable towards the addition of donor ligands (CO, phosphines) and does not react with alkynes to give derivatives such as $Fe_4(CO)_{11}(\mu_4,\eta^2\text{-}HC_2Et)_2$ (complex IIa, also a 62 electron species) [14], in the presence of metal fragments expansion occurs to give moderate yields of the cluster $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_3(CO)_8(\mu_4,\eta^2\text{-}C_2Ph_2)$ (complex IIIa), formally derived from Ia by completion of the *nido*-pentagonal bipyramid. Cluster Ia also undergoes contraction reactions leading to the trimetallic $(\eta^5\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (complex IVa). On the other hand the reactions of $Ru_3(CO)_{12}$ with nickel-alkyne derivatives under H_2 lead to compounds of type III rather than I. A comparison of the reaction patterns of Ia with those of other formally unsaturated clusters is presented.

Experimental

General experimental details; materials, purification and analysis of the products

The carbonyls $Fe(CO)_5$ and $Fe_2(CO)_9$ were purchased from Fluka as was $Me_3NO \cdot 2H_2O$, which was dehydrated by sublimation in vacuo. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ were prepared by established methods. All solvents were distilled from sodium and stored over molecular sieves. Pure N_2 gas and ultrapure H_2 (S.I.A.D.) were used. The reaction mixtures were filtered under N_2, concentrated to small volume in vacuo, and purified by preparative TLC (Merck Kieselgel P.F.; eluants light petroleum and ethyl ether). Whenever possible the products were crystallized from heptane/chloroform solutions cooled at $-10°C$ and kept under nitrogen. Satisfactory elemental analyses were obtained for all of the products described below, except for those isolated only in trace amounts.

Physical measurements

The IR spectra were recorded on a Perkin–Elmer 580 B instrument. The ^1H NMR spectra were measured on a 60 MHz Varian EM360 and JEOL C 60 HL instruments; the ^{13}C NMR spectra were recorded on a Varian XL-100 in the presence of $Cr(AcAc)_3$ as a relaxation reagent. The mass spectra were determined on a single-focusing Hitachi Perkin–Elmer RMU-6H spectrometer at 70 eV, a direct inlet system being used at the lowest temperatures compatible with reasonable volatility of the samples; perfluorocarbons were used as mass markers.

Magnetic measurements were obtained by the Gouy method on a Newport Instruments magnetic balance at 20°C. Solution and solid state EPR spectra were recorded on a Varian E-109 and on a Varian GE Line; similar results were obtained with samples of different origins.

Improved syntheses and reactivity of complexes I. Cluster expansion and contraction reactions involving complexes I

The experimental details for the synthesis, reactivity and expansion or contraction of complexes I are summarized in Table 1, together with the results of reactions involving $Ru_3(CO)_{12}$.

Crystal structure determination of Ia

Suitable crystals of Ia were obtained by cooling saturated heptane/chloroform solutions (9/1) at $-10°C$ for some days under N_2. A prismatic black crystal of dimensions $0.20 \times 0.20 \times 0.25$ mm was attached to a glass fiber and mounted on a Siemens AED single-crystal diffractometer. Unit cell parameters were obtained by least-squares refinement of the values of 25 carefully centered reflections chosen from diverse regions of reciprocal space.

Crystal data. $C_{30}H_{20}Fe_2Ni_2O_6$, $M = 705.60$; orthorhombic, space group *Pbca*, *a* 24.776(21), *b* 29.509(19), *c* 14.677(7) Å; *V* 10731(12) Å^3, $Z = 16$, D_c 1.747 g cm^{-3}; Mo-K_α radiation (λ 0.71069 Å), μ(Mo-K_α) 24.94 cm^{-1}, $F(000) = 5696$.

Intensity data were collected at 295 K using niobium-filtered Mo-K_α radiation. The θ-2θ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. The scan range was ± 0.5 from the peak centre. The pulse-height descriminator was set to accept 90% of the Mo-K_α peak. A standard reflection was remeasured after 20 reflections as a check on crystal and instrument stability. No

(Continued on p. 371)

TABLE 1

STOICHIOMETRY, CONDITIONS AND PRODUCTS OF THE REACTIONS DESCRIBED IN THIS PAPER [a]

(i) *Reactions of $M_3(CO)_{12}$ with $(\eta^5\text{-}C_5H_5)_2Ni_2(RC_2R')$ and H_2. Improved syntheses of clusters I; Synthesis of new $(\eta^5\text{-}C_5H_5)_2Ni_2M_3(CO)_8(RC_2R')$ (clusters III) (M = Fe, Ru)*			
M = Fe			
R = R′ = Ph	$\xrightarrow{(\text{N}_2)}$	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (10%) [b] [Ia]	Ref. 12
	$\xrightarrow[\text{30 min, (1.5/1)}^{c}]{\text{H}_2\text{, heptane}}$	$Ni(CO)_4$, $Fe_3(CO)_{12}$, $[(Cp)Fe(CO)_2]_2$ (10%), $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (30%) [IVa] [7], $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (35%) [Ia], $(Cp)_2Ni_2Fe_2(CO)_7$ (2%) [12], $(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (nc) (15%) [IIIa]	this work
R = R′ = Et	$\xrightarrow{(\text{N}_2)}$	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (20%) [b] [Ib]	Ref. 12
	$\xrightarrow[\text{30 min, (1.5/1)}]{\text{H}_2\text{, heptane}}$	$Fe_3(CO)_{12}$, $[(Cp)Fe(CO)_2]_2$ (7%), $(Cp)_2Ni_2Fe(CO)_3(C_2Et_2)$ (15%) [IVb] [7], $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (40%) [Ib], $(Cp)_2Ni_2Fe_3(CO)_8(C_2Et_2)$ (nc) (9%) [IIIb], iron-alkyne products	this work
M = Ru			
R = R′ = Ph	$\xrightarrow{(\text{H}_2)}$	$(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$ (10%) [b] [IIIc] [8]	Ref. 7,8
R = R′ = Et	$\xrightarrow[\text{30 min, (1/1)}]{\text{H}_2\text{, octane}}$	$(Cp)NiRu_3(CO)_8(C_6H_9)$ (isomers, 15%) [7], $(Cp)_2Ni_2Ru(CO)_3(C_2Et_2)$ (10%) [IVd], $(Cp)_2Ni_2Ru_3(CO)_8(C_2Et_2)$ (nc) (6%) [IIId], ruthenium-alkyne products	this work
(ii) *Reactions of $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (IVa); cluster expansion leading to clusters I and III*			
with $Fe(CO)_5$	$\xrightarrow[\text{150 min, (1/3)}]{\text{N}_2\text{ heptane}}$	$Fe_3(CO)_{12}$ (15%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (nc) (3%) [Ia], $(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (1%) [IIIa], unreacted [IVa] (30%)	this work
with $Fe(CO)_5$ and Me_3NO [d]	$\xrightarrow[\text{30 min, (1/3)}]{\text{N}_2\text{, heptane}}$	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (8%) [Ia], unreacted IVa (80%)	this work

with $Fe_2(CO)_9$	$\xrightarrow[30\ \text{min},\ (1/2)]{H_2,\ \text{octane}}$	no reaction	
with $Fe_2(CO)_9$ and Me_3NO	$\xrightarrow[60\ \text{min},\ (1/2)]{H_2,\ \text{octane}}$	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (12%) [Ia], $(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (2%) [IIIa], unreacted [IVa] (60%), iron-alkyne products	this work
(iii) *Reaction of $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (Ia) and $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (Ib)* *Cluster expansion and contraction reactions leading to clusters III and IV*			
Complex Ia			
Δ	$\xrightarrow[120\ \text{min}]{N_2,\ \text{heptane}}$	unreacted Ia (50%), $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (nc) (30%) [IVa], $[(Cp)Fe(CO)_2]_2$ (15%), decomposition	this work
with $Fe(CO)_5$	$\xrightarrow[60\ \text{min},\ (1/3)]{H_2,\ \text{heptane}}$	unreacted Ia (60%), $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (10%) [IVa], iron-alkyne products, decomposition	this work
with $Fe(CO)_5$ and Me_3NO	$\xrightarrow[60\ \text{min},\ (1/3)]{N_2,\ \text{heptane}}$	unreacted Ia (50%), $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (10%) [IVa], $(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (5%) [IIIa], $[(Cp)Fe(CO)_2]_2$ (15%).	this work
with neat [e] H_2SO_4	$\xrightarrow[10\ \text{min}]{N_2,\ \text{ethanol}}$	$[(Cp)Fe(CO)_2]_2$ (tr), $(Cp)_2Ni_2Fe_2(CO)_7$ [12] (tr), decomposition, stilbene [f], diphenylethane [f]	this work
Complex Ib			
with $Fe(CO)_5$	$\xrightarrow[60\ \text{min},\ (1/3)]{H_2,\ \text{heptane}}$	unreacted Ib (60%), $[(Cp)Fe(CO)]_2$ (10%), decomposition	this work
with $Fe(CO)_5$ and Me_3NO	$\xrightarrow[300\ \text{min},\ (1/3)]{N_2,\ \text{heptane}}$	$(Cp)_2Ni_2Fe_3(CO)_8(C_2Et_2)$ (4%) [IIIb], $(Cp)_2Ni_2Fe(CO)_3(C_2Et_2)$ (10%) [IVb], $[(Cp)Fe(CO)_2]_2$ (5%)	this work
(iv) *Reaction of $(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (IIIa); cluster contraction to Ia and IVa*			
Δ	$\xrightarrow[90\ \text{min}]{CO\text{-}H_2,\ \text{heptane}}$	unreacted IIIa (6%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (10%) [Ia], $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (15%) (IVa), iron-alkyne products, metal powder	this work

TABLE 1 (continued)

(v) *Reactions of Ia with donor ligands and hydrogen*			
with PPh_3	$\xrightarrow[40\ \text{min},\ (1/2)]{N_2,\ \text{heptane}}$	unreacted Ia (15%), *$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$* (10%) [IVa], *$(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$* (12%) IIIa, $[(Cp)Fe(CO)_2]_2$ (15%), four low nuclearity phosphine derivatives (5% each; under investigation)	this work
with PPh_3 and Me_3NO	$\xrightarrow[70\ \text{min},\ (1/2)]{N_2,\ \text{hexane}}$	unreacted Ia (90%), *$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$* (1%) [IVa], $[(Cp)Fe(CO)_2]_2$ (2%)	this work
with C_2Ph_2	$\xrightarrow[90\ \text{min},\ (1/2)]{H_2\ \text{or}\ N_2,\ \text{heptane}}$	*$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$* (15%) [IVa], $[(Cp)Fe(CO)_2]_2$ (20%), $Fe_2(CO)_6(C_2Ph_2)_2$ (40%).	this work

[a] The figures in parentheses are the averaged yields of the products, based on the iron or ruthenium; (tr) = trace amounts. Numbers in square brackets correspond to those complexes discussed in the text. nc denotes new compound; products in italics denote expansion or contraction products. Only a limited range of reaction conditions were examined for the cluster expansion and contraction reactions because at lower temperatures there is no reaction, and at higher temperatures ready decomposition occurs. [b] yields of I reported by comparison. [c] Moles of reactants; the first figure is referred to the first reactant. [d] The reactions in the presence of anhydrous Me_3NO were always performed by suspending or dissolving the cluster reactant, $Fe(CO)_5$ and Me_3NO in cold hydrocarbons, then bringing the mixtures to the reflux temperature; addition of $Fe(CO)_5$ to hot solutions of clusters and Me_3NO caused immediate formation of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. [e] No reaction in 24 h at RT. [f] GC-MS analysis.

significant change in the measured intensities of this reflection was observed during data collection. A total of 7746 independent reflections ($3 \leqslant \theta \leqslant 23°$) were measured, of which 3626, having $I \geqslant 2\sigma(I)$, were employed in the analysis; the remaining 4120 were considered unobserved. Data were corrected for Lorentz and polarisation effects, but no absorption correction was applied in view of the low absorbance of the sample.

Structure solution and refinement for Ia. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares using the SHELX system of computing programs [15] initially with isotropic and then, in two blocks, with

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH e.s.d.'s IN PARENTHESES FOR Ia

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Fe(11)	329(1)	3987(1)	1996(1)	C(131)	1799(8)	2776(7)	3715(13)
Fe(21)	−122(1)	3075(1)	2873(1)	C(141)	1262(7)	2896(6)	3484(12)
Fe(12)	2706(1)	1441(1)	1615(1)	C(151)	331(6)	3853(5)	4224(10)
Fe(22)	3146(1)	536(1)	2534(1)	C(161)	416(6)	3548(5)	4923(11)
Ni(11)	−504(1)	3829(1)	2818(1)	C(171)	485(6)	3695(6)	5830(11)
Ni(21)	439(1)	3199(1)	1547(1)	C(181)	475(6)	4159(6)	6001(11)
Ni(12)	2548(1)	648(1)	1255(1)	C(191)	397(7)	4469(6)	5306(12)
Ni(22)	3556(1)	1274(1)	2362(1)	C(201)	336(7)	4316(6)	4400(11)
O(11)	1294(6)	4221(5)	946(9)	C(211)	877(8)	2604(7)	1086(13)
O(21)	189(6)	4952(4)	2382(9)	C(221)	1123(9)	2985(8)	740(15)
O(31)	−406(6)	4004(5)	447(9)	C(231)	747(9)	3225(8)	199(15)
O(41)	−777(5)	2884(5)	4491(9)	C(241)	257(9)	2977(8)	208(15)
O(51)	260(5)	2144(4)	2867(8)	C(251)	348(8)	2591(7)	781(13)
O(61)	−952(6)	2939(4)	1492(9)	C(261)	−1277(8)	3963(7)	2290(14)
O(12)	2893(7)	2403(5)	1910(10)	C(271)	−1338(8)	3725(7)	3056(14)
O(22)	1695(6)	1671(6)	720(10)	C(281)	−1136(9)	3961(8)	3821(14)
O(32)	3355(6)	1396(6)	−48(9)	C(291)	−941(8)	4343(8)	3504(15)
O(42)	2757(6)	−390(4)	2669(9)	C(301)	−1018(9)	4372(8)	2561(16)
O(52)	3872(6)	392(5)	4095(9)	C(92)	2763(6)	1353(5)	3852(10)
O(62)	3905(5)	340(4)	1066(9)	C(102)	2803(6)	1819(6)	4030(11)
C(11)	927(7)	4109(5)	1349(11)	C(112)	2713(7)	1987(6)	4912(11)
C(21)	243(7)	4562(6)	2255(11)	C(122)	2584(7)	1690(6)	5600(11)
C(31)	−122(9)	3979(8)	1070(13)	C(132)	2548(7)	1214(6)	5447(11)
C(41)	−527(7)	2966(6)	3853(12)	C(142)	2643(6)	1052(5)	4565(10)
C(51)	125(6)	2516(6)	2862(11)	C(152)	1886(6)	865(5)	2853(10)
C(61)	−624(7)	3007(6)	2040(13)	C(162)	1744(7)	444(6)	3252(12)
C(71)	603(5)	3443(4)	2754(9)	C(172)	1229(8)	393(7)	3656(13)
C(81)	221(5)	3685(4)	3259(9)	C(182)	869(7)	754(7)	3617(12)
C(12)	2825(8)	2019(7)	1817(12)	C(192)	1000(7)	1150(6)	3241(12)
C(22)	2101(9)	1578(7)	1074(12)	C(202)	1524(7)	1224(6)	2890(12)
C(32)	3119(7)	1395(7)	603(14)	C(212)	4219(9)	1435(7)	3245(14)
C(42)	2896(7)	−22(6)	2627(12)	C(222)	4017(9)	1835(8)	2894(15)
C(52)	3596(8)	449(6)	3501(11)	C(232)	4065(8)	1804(7)	1910(13)
C(62)	3601(7)	427(6)	1630(12)	C(242)	4307(7)	1372(6)	1717(12)
C(72)	2857(6)	1170(4)	2891(9)	C(252)	4401(7)	1151(6)	2548(13)
C(82)	2442(5)	912(4)	2447(9)	C(262)	2656(8)	415(7)	−94(13)
C(91)	1156(6)	3326(5)	3082(9)	C(272)	2624(7)	43(6)	491(11)
C(101)	1580(7)	3608(6)	2961(11)	C(282)	2101(8)	52(7)	884(12)
C(111)	2113(7)	3502(6)	3179(11)	C(292)	1833(9)	424(8)	558(15)
C(121)	2221(7)	3070(7)	3521(12)	C(302)	2163(9)	660(8)	−40(15)

TABLE 3

SPECTROSCOPIC DATA FOR COMPLEXES I, III AND IV

Complex	ν(CO) (cm^{-1}) (C_6H_{14} sol.)	NMR (δ(ppm); $CDCl_3$)		Mass spectra
		^{1}H	^{13}C [a]	
$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (IVa, dark green crystals)	Ref. 7	Ref. 7	90.4 (Cp) [b], 126.2–128.3 (t, Ph), 147.8, 155.7 (C alkyne), 211.5 (CO_{ax}) 213.2 (CO_{eq}) [c]	Ref. 7
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (Ia, dark blue crystals)	Ref. 12 2080w [d], 1990vs(b), 1950vs(sh), 1935vs(b) 1585w, 1485m, 1435m-s, 1380w	Ref. 12	91.5 (Cp), 121.0–124.9 (t, Ph), 146.3, 174.9 (C alkyne)	Ref. 12
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (Ib, dark blue crystals)	Ref. 12	Ref. 12	16.2, 37.3, 75.5, 75.8, 76.2, 78.0, 78.3 (Et), 89.15 (Cp), 199.6 (C alkyne or CO's)	Ref. 12
$(Cp)_2Ni_2Fe_3(CO)_8(C_2Ph_2)$ (IIIa, dark blue-grey solid)	2018vs, 1988vs, 1960m-s, 1842m, 1820m	7.30m (10H, Ph), 5.25s, 4.80s (10H, Cp)	decomposes during the measurement [f]	$P^+ = 648$ m/e (Fe_2Ni_2)
$(Cp)_2Ni_2Fe_3(CO)_8(C_2Et_2)$ (IIIb, dark blue-grey solid)	2008vs, 1994s, 1960s(b), 1845m-w, 1818m	5.30s, 5.45s (10H, Cp), 3.55m, 2.70m (10H, Et)	decomposes during the measurement	$P^+ = 552$ m/e (Fe_2Ni_2)
$(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$ (IIIc, dark brown solid)	2030s, 2004vs, 1974s, 1962s, 1865mw, 1835m [e]	6.90–7.10m (10H, Ph) 5.40s (10 H, Cp) [e]	–	$P^+ = 740$ m/e (Ru_2Ni_2) [e]
$(Cp)_2Ni_2Ru_3(CO)_8(C_2Et_2)$ (IIId, dark brown solid)	2024s, 2002s, 1994m(b), 1863m, 1845m	5.30s, 5.40s (10H, Cp) 3.50m, 2.45m (10H, Et)	–	$P^+ = 700$ m/e (Ru_2Ni_2)

[a] Downfield shift positive with respect to internal TMS T 313 K. $Cr(AcAc)_3$ added. [b] Proposed attributions in parentheses. [c] Integration 1/2. [d] KBr disc. [e] Already reported (Ref. 8); by comparison with the newly synthesized complexes III. [f] $CDCl_3$ solution under nitrogen for 24 h; the solution contains ca. 1% of Ia, 5% of IIIa, unidentified products and metal powder.

anisotropic thermal parameters for the metal atoms, the carbon and oxygen atoms of the carbonyl groups and the C(7) and C(8) atoms of the alkynes. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. Refinement to convergence gave $R = 0.063$. The atomic scattering factors used, corrected for the anomalous dispersion for iron and nickel, were taken from ref. 16.

The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analyzing the variation of ΔF with respect to F_0.

Final atomic coordinates for the non-hydrogen atoms are listed in Table 2. Calculated coordinates for hydrogen atoms, thermal parameters for the non-hydrogen atoms and a list of structure factors are available from the authors on request.

All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and discussion

Spectroscopic (and magnetic) properties of Ia, Ib, IVa and of the new IIIa, IIIb, and IIId complexes

IR, ^{1}H and ^{13}C NMR and mass spectral data for the complexes are listed in Table 3.

The colours of and physical data for the new clusters correspond closely with the properties of previously characterized complexes of the type $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}RC_2R)$ [12,13] and together with the X-ray structure for Ia confirm that the two sets of complexes have similar structures.

The mass spectra of complexes I and III deserve comment. Several of the complexes decompose extensively in the mass spectrometer; this was particularly evident for the clusters I. The parent ion was not observed for many of the complexes I, but studies of metastable ions conclusively showed that I fragments via consecutive loss of two CO groups, affording a high intensity ion of m/e corresponding to $[M - 2CO]^+$. Subsequent fragmentation seems to result in preferential loss of an iron or ruthenium atom [17]. The facile loss of CO molecules under electron impact or FAB contrasts with the difficulty of substituting CO ligands by phosphines or alkynes in these molecules (vide infra). However, facile loss of one metal atom accords with the observed cluster contraction reactions. Complexes of type III decompose in the mass spectrometer to give M_2Ni_2 fragments, in accord with the subsequently observed cluster contractions. For these species, when parent ions were observed, ready loss of an $M(CO)_2$ unit occurs, to give $[(C_5H_5)_2Ni_2M_2(CO)_4(RC_2R')]^+$ as the first observable fragment. Again this mechanism was established by observation of metastable ions corresponding to the fragmentation.

The assignment of the ^{13}C resonances is based on literature data for analogous or closely related clusters [6]. For Ia no signals for the CO ligands could be detected at 40°C, and the low solubility at or below 0°C prevented variable temperature studies; such behaviour is often indicative of CO fluxionality. For IVa however, sharp signals of the expected integrated intensity were found in the region of the terminal CO ligands, indicating that this compound has a static structure in solution.

Solutions of Ia and Ib in CCl_4 gave no EPR signals. However, solid samples of Ia or Ib, prepared in various reactions and purified, all gave EPR signals. Although we cannot completely rule out the presence of trace metallic impurities, extensive recrystallization of Ia did not affect the EPR resonance. Observation of this effect prompted an X-ray analysis of the structure of Ia.

Crystal structure of Ia. The structure of Ia consists of two crystallographically independent but very similar complexes; these are shown in Fig. 1 and 2, together with the atom numbering schemes. Bond distances and angles are given in Table 4.

The metal framework. The complexes are characterized by a tetranuclear cluster of two Fe and two Ni atoms coordinated by six terminal carbonyls (through the Fe atoms), by two cyclopentadienyl groups (through the Ni atoms) and by a diphenylacetylene ligand interacting with all four metal atoms. The Fe and Ni atoms alternate at the vertices of a distorted square (0.25 Å above or below the mean plane passing through the four metals). The Fe–Ni bond lengths are very similar in the two complexes, being in the range 2.419–2.436 Å (molecule **1**) and 2.414–2.431 Å (molecule **2**). The nonbonding Fe–Fe and Ni–Ni distances are 3.186(4) and 3.521(4) Å respectively in **1**, and 3.184(4) and 3.506(4) Å in **2**. A distortion of the square planar cluster towards a flattened butterfly is also indicated by the dihedral angle between the Ni(1)Fe(1)Fe(2) and Ni(2)Fe(1)Fe(2) triangles, 148.1(1)° (**1**) and 147.8(1)° (**2**). This makes plausible the alternative description of this cluster as a *nido*-pentagonal bipyramid, with a vacant equatorial site.

The set of 6 CO and two C_5H_5 ligands is sterically and electronically equivalent to the 11 CO's found in clusters $M_4(CO)_{11}(\mu_4\text{-}PR)_2$ (M = Fe, Ru) [18] and in $Fe_4(CO)_{11}(NEt)(ONEt)$ [19]. Complexes $Fe_4(CO)_{11}(\mu_4\text{-}PR)_2$, however, easily add donor ligands, whereas complexes I do not undergo similar reactions.

A variety of homo- and hetero-metallic square planar clusters with and without

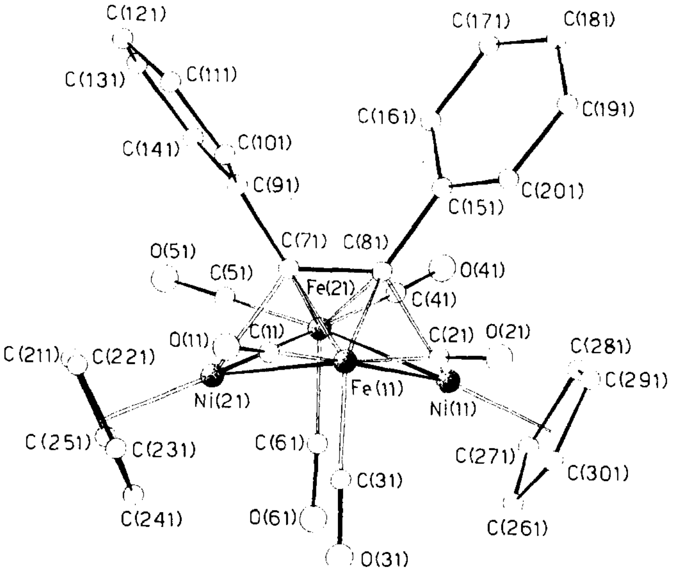


Fig. 1. Structure of the complex $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}C_2Ph_2)$ (molecule **1**) with the atom numbering scheme.

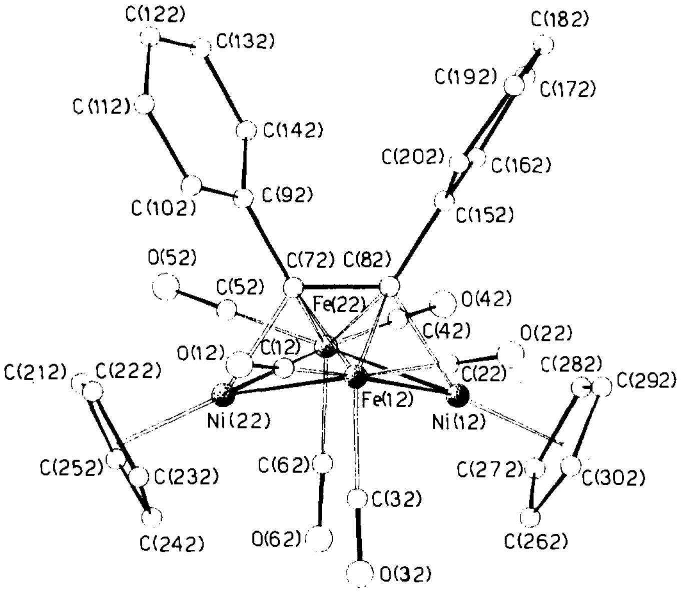


Fig. 2. Structure of the complex $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}C_2Ph_2)$ (molecule **2**) with the atom numbering scheme.

bridging and semi-bridging CO's are known. These clusters are worthy of discussion in the context of the structure and reactivity of complexes I. The principal types are shown in Fig. 3, and the most relevant structural features in Table 5.

Complexes I and III belong to the non-bridged type **A**, although in III there are also CO bridges out of the square plane; $Ru_5(CO)_{15}(\mu_4\text{-PR})$ (R = Ph, Et) [20] are also apparently unbridged, although some of the M–C–O angles are close to 170°. Type **B** is represented by $Fe_4(CO)_{11}[P(OMe)_3](P\text{-}p\text{-tolyl})_2$ obtained by ligand addition to the **D**-type complex $Fe_4(CO)_{11}(P\text{-}p\text{-tolyl})_2$ [18]; type **C** is represented only by $Ru_4(CO)_{11}(\mu_4,\eta^2\text{-MeC}_2Ph)_2$ (complex IIb) [21], its iron homologue, IIa, being a **D**-type.

Several type-**D** structures are known; complex IIa, $Fe_4(CO)_{11}(NEt)(ONEt)$ [19], $Fe_4(CO)_{10}(L)(\mu_4\text{-P-}p\text{-tolyl})_2$ (L = CO, $P(OMe)_3$, complexes V) [2,18], $Ru_4(CO)_{11}(\mu_4\text{-PR})_2$ (complexes VI) [22], $Fe_2Co_2(CO)_{11}(\mu_4\text{-PPh})_2$(2 isomers, complexes VII) and $Fe_2Co_2(CO)_{11}(\mu_4\text{-S})$ (complex VIII). The presence of 11 CO's (corresponding to the two C_5H_5 and six CO's in complexes I) and the formally unsaturated 62 electron counts are not easily explainable. The same is true for the apparently unnecessary presence of bridging and semi-bridging CO's when it is noted that all the metals could have the same substitution and electron count. This behaviour and the reactivity of complexes V and VII have been recently explained in terms of the presence of a double M–M bond along the CO-bridged edge; indeed, three long and one markedly shorter metal–metal distances are observed for IIa, V and VII (Table 5) [23]. However, the metal–metal distances in complexes I are very close each to the other.

Only one example of type **E**, $Ru_4(CO)_{11}(\mu_4\text{-PPh})(C_2Ph_2)$ has been reported [24], complexes $Co_4(CO)_{10}(\mu_4\text{-L})_2$ (L = PPh, S) [25] belong to type **F**, whose structures are readily rationalized; finally, the only example of type **G**, $Ru_5(CO)_{13}(\mu\text{-}$

(Continued on p. 380)

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR COMPLEX Ia

(i) In the coordination sphere of the heterometals

Fe(11)–Ni(11)	2.436(4)	Fe(12)–Ni(12)	2.431(4)
Fe(11)–Ni(21)	2.432(4)	Fe(12)–Ni(22)	2.425(4)
Fe(21)–Ni(11)	2.419(4)	Fe(22)–Ni(12)	2.414(3)
Fe(21)–Ni(21)	2.419(3)	Fe(22)–Ni(22)	2.416(4)
Fe(11)–C(11)	1.796(17)	Fe(12)–C(12)	1.756(21)
Fe(11)–C(21)	1.752(18)	Fe(12)–C(22)	1.744(21)
Fe(11)–C(31)	1.760(20)	Fe(12)–C(32)	1.809(20)
Fe(11)–C(71)	2.068(13)	Fe(12)–C(72)	2.070(13)
Fe(11)–C(81)	2.074(13)	Fe(12)–C(82)	2.087(13)
Fe(21)–C(41)	1.783(18)	Fe(22)–C(42)	1.764(18)
Fe(21)–C(51)	1.760(18)	Fe(22)–C(52)	1.823(18)
Fe(21)–C(61)	1.755(18)	Fe(22)–C(62)	1.770(18)
Fe(21)–C(71)	2.106(13)	Fe(22)–C(72)	2.071(13)
Fe(21)–C(81)	2.070(12)	Fe(22)–C(82)	2.071(13)
Ni(11)–C(81)	1.956(13)	Ni(12)–C(82)	1.933(13)
Ni(21)–C(71)	1.955(13)	Ni(22)–C(72)	1.923(15)
Ni(11)–Fe(11)–Ni(21)	92.6(1)	Ni(12)–Fe(12)–Ni(22)	92.4(2)
Ni(11)–Fe(21)–Ni(21)	93.4(1)	Ni(12)–Fe(22)–Ni(22)	93.1(1)
Fe(11)–Ni(11)–Fe(21)	82.0(1)	Fe(12)–Ni(12)–Fe(22)	82.2(1)
Fe(11)–Ni(21)–Fe(21)	82.1(1)	Fe(12)–Ni(22)–Fe(22)	82.3(1)
Ni(11)–Fe(11)–C(11)	177.6(5)	Ni(12)–Fe(12)–C(12)	177.1(6)
Ni(11)–Fe(11)–C(21)	88.6(6)	Ni(12)–Fe(12)–C(22)	89.2(7)
Ni(11)–Fe(11)–C(31)	80.9(7)	Ni(12)–Fe(12)–C(32)	80.8(7)
Ni(11)–Fe(11)–C(71)	82.1(4)	Ni(12)–Fe(12)–C(72)	81.6(4)
Ni(11)–Fe(11)–C(81)	50.6(4)	Ni(12)–Fe(12)–C(82)	50.0(3)
Ni(21)–Fe(11)–C(11)	87.5(5)	Ni(22)–Fe(12)–C(12)	88.6(6)
Ni(21)–Fe(11)–C(21)	176.8(5)	Ni(22)–Fe(12)–C(22)	178.3(7)
Ni(21)–Fe(11)–C(31)	81.3(7)	Ni(22)–Fe(12)–C(32)	82.2(6)
Ni(21)–Fe(11)–C(71)	50.7(3)	Ni(22)–Fe(12)–C(72)	49.9(4)
Ni(21)–Fe(11)–C(81)	81.1(3)	Ni(22)–Fe(12)–C(82)	81.7(4)
C(11)–Fe(11)–C(21)	91.2(8)	C(12)–Fe(12)–C(22)	89.8(9)
C(11)–Fe(11)–C(31)	96.8(8)	C(12)–Fe(12)–C(32)	96.7(9)
C(11)–Fe(11)–C(71)	99.7(6)	C(12)–Fe(12)–C(72)	101.1(7)
C(11)–Fe(11)–C(81)	131.7(7)	C(12)–Fe(12)–C(82)	132.9(7)
C(21)–Fe(11)–C(31)	95.9(9)	C(22)–Fe(12)–C(32)	97.5(9)
C(21)–Fe(11)–C(71)	132.5(7)	C(22)–Fe(12)–C(72)	131.1(8)
C(21)–Fe(11)–C(81)	101.9(7)	C(22)–Fe(12)–C(82)	99.8(8)
C(31)–Fe(11)–C(71)	127.8(8)	C(32)–Fe(12)–C(72)	127.7(7)
C(31)–Fe(11)–C(81)	127.1(8)	C(32)–Fe(12)–C(82)	127.0(7)
C(71)–Fe(11)–C(81)	39.5(5)	C(72)–Fe(12)–C(82)	40.4(5)
Ni(11)–Fe(21)–C(41)	88.4(6)	Ni(12)–Fe(22)–C(42)	88.4(6)
Ni(11)–Fe(21)–C(51)	176.4(5)	Ni(12)–Fe(22)–C(52)	179.8(6)
Ni(11)–Fe(21)–C(61)	78.7(6)	Ni(12)–Fe(22)–C(62)	80.4(6)
Ni(11)–Fe(21)–C(71)	81.8(4)	Ni(12)–Fe(22)–C(72)	82.0(4)
Ni(11)–Fe(21)–C(81)	50.9(3)	Ni(12)–Fe(22)–C(82)	50.3(4)
Ni(21)–Fe(21)–C(41)	178.2(6)	Ni(22)–Fe(22)–C(42)	175.4(8)
Ni(21)–Fe(21)–C(51)	86.2(5)	Ni(22)–Fe(22)–C(52)	87.2(6)
Ni(21)–Fe(21)–C(61)	82.2(6)	Ni(22)–Fe(22)–C(62)	79.5(6)
Ni(21)–Fe(21)–C(71)	50.6(4)	Ni(22)–Fe(22)–C(72)	50.0(3)
Ni(21)–Fe(21)–C(81)	81.5(4)	Ni(22)–Fe(22)–C(82)	82.2(3)
C(41)–Fe(21)–C(51)	91.9(8)	C(42)–Fe(22)–C(52)	91.3(8)
C(41)–Fe(21)–C(61)	98.2(8)	C(42)–Fe(22)–C(62)	96.4(8)

TABLE 4 (continued)

C(41)–Fe(21)–C(71)	129.8(7)	C(42)–Fe(22)–C(72)	134.6(7)
C(41)–Fe(21)–C(81)	99.6(7)	C(42)–Fe(22)–C(82)	102.1(7)
C(51)–Fe(21)–C(61)	97.6(8)	C(52)–Fe(22)–C(62)	99.7(8)
C(51)–Fe(21)–C(71)	100.7(6)	C(52)–Fe(22)–C(72)	98.1(7)
C(51)–Fe(21)–C(81)	132.5(6)	C(52)–Fe(22)–C(82)	129.7(7)
C(61)–Fe(21)–C(71)	127.3(7)	C(62)–Fe(22)–C(72)	125.0(7)
C(61)–Fe(21)–C(81)	125.5(7)	C(62)–Fe(22)–C(82)	126.0(7)
C(71)–Fe(21)–C(81)	39.1(5)	C(72)–Fe(22)–C(82)	40.6(5)
Fe(11)–Ni(11)–C(81)	55.1(4)	Fe(12)–Ni(12)–C(82)	55.7(4)
Fe(21)–Ni(11)–C(81)	55.2(4)	Fe(22)–Ni(12)–C(82)	55.6(4)
Fe(11)–Ni(21)–C(71)	54.9(4)	Fe(12)–Ni(22)–C(72)	55.4(4)
Fe(21)–Ni(21)–C(71)	56.4(4)	Fe(22)–Ni(22)–C(72)	55.6(4)

(ii) In the carbonyl groups

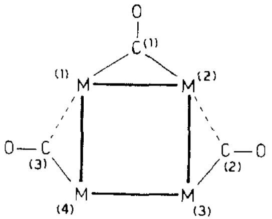
O(11)–C(11)	1.134(22)	O(12)–C(12)	1.154(25)
O(21)–C(21)	1.173(21)	O(22)–C(22)	1.165(26)
O(31)–C(31)	1.156(24)	O(32)–C(32)	1.120(24)
O(41)–C(41)	1.148(22)	O(42)–C(42)	1.141(21)
O(51)–C(51)	1.148(21)	O(52)–C(52)	1.121(22)
O(61)–C(61)	1.161(23)	O(62)–C(62)	1.148(22)
Fe(11)–C(11)–O(11)	174.6(14)	Fe(12)–C(12)–O(12)	176.8(16)
Fe(11)–C(21)–O(21)	176.6(14)	Fe(12)–C(22)–O(22)	179.4(16)
Fe(11)–C(31)–O(31)	175.2(20)	Fe(12)–C(32)–O(32)	174.6(18)
Fe(21)–C(41)–O(41)	177.7(16)	Fe(22)–C(42)–O(42)	176.7(16)
Fe(21)–C(51)–O(51)	176.5(14)	Fe(22)–C(52)–O(52)	179.5(16)
Fe(21)–C(61)–O(61)	176.6(15)	Fe(22)–C(62)–O(62)	176.9(15)

(iii) In the organic ligands

C(71)–C(81)	1.398(18)	C(72)–C(82)	1.436(18)
C(71)–C(91)	1.493(19)	C(72)–C(92)	1.528(20)
C(81)–C(151)	1.525(20)	C(82)–C(152)	1.507(19)
Fe(11)–C(71)–Fe(21)	99.5(5)	Fe(12)–C(72)–Fe(22)	100.5(6)
Fe(11)–C(71)–Ni(21)	74.3(4)	Fe(12)–C(72)–Ni(22)	74.7(5)
Fe(11)–C(71)–C(81)	70.5(7)	Fe(12)–C(72)–C(82)	70.4(7)
Fe(11)–C(71)–C(91)	130.9(9)	Fe(12)–C(72)–C(92)	132.1(9)
Fe(21)–C(71)–Ni(21)	73.0(4)	Fe(22)–C(72)–Ni(22)	74.4(4)
Fe(21)–C(71)–C(81)	69.0(7)	Fe(22)–C(72)–C(82)	69.7(7)
Fe(21)–C(71)–C(91)	129.5(9)	Fe(22)–C(72)–C(92)	127.3(9)
Ni(21)–C(71)–C(81)	121.8(9)	Ni(22)–C(72)–C(82)	123.1(9)
Ni(21)–C(71)–C(91)	113.4(9)	Ni(22)–C(72)–C(92)	117.0(9)
C(81)–C(71)–C(91)	124.6(9)	C(82)–C(72)–C(92)	119.8(9)
Fe(11)–C(81)–Fe(21)	100.5(6)	Fe(12)–C(82)–Fe(22)	99.9(5)
Fe(11)–C(81)–Ni(11)	74.3(5)	Fe(12)–C(82)–Ni(12)	74.3(5)
Fe(11)–C(81)–C(71)	70.0(7)	Fe(12)–C(82)–C(72)	69.2(7)
Fe(11)–C(81)–C(151)	131.9(9)	Fe(12)–C(82)–C(152)	125.9(9)
Fe(21)–C(81)–Ni(11)	73.8(4)	Fe(22)–C(82)–Ni(12)	74.1(4)
Fe(21)–C(81)–C(71)	71.9(7)	Fe(22)–C(82)–C(72)	69.7(8)
Fe(21)–C(81)–C(151)	127.6(9)	Fe(22)–C(82)–C(152)	134.1(9)
Ni(11)–C(81)–C(71)	123.9(9)	Ni(12)–C(82)–C(72)	121.8(9)
Ni(11)–C(81)–C(151)	113.6(8)	Ni(12)–C(82)–C(152)	116.4(9)
C(71)–C(81)–C(151)	122.5(9)	C(72)–(82)–C(152)	121.6(9)

TABLE 5

BONDING PARAMETERS IN SQUARE METAL ATOM ARRANGEMENTS



Complex	M–M [a] (Å)	M–M–M [b] (°)	M–C(1) (Å) M–C(1)–O(1) (°)	M–C(2) (Å) M–C(2)–O(2) (°)	M–C(3) (Å) M–C(3)–O(3) (°)	References
Structure A						
$Ru_5(CO)_{15}(PPh)$ [c]	2.837(3), 2.900(3)	89.4(1)–91.4(1) [e]	–	–	–	20
	2.838(3), 2.882(3) [d]					
	2.848(3), 2.886(3)	89.1(1)–91.0(1) [e]	–	–	–	20
	2.835(3), 2.896(3) [d]					
$Ru_5(CO)_{15}(PEt)$	2.882(2), 2.817(2)	89.2(1)–90.9(1) [e]	–	–	–	20
	2.873(3), 2.910(3) [d]					
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$	2.426(3), 2.417(3)	91.0(1)–83.0(1)	–	–	–	12
	2.414(3), 2.422(3)	91.2(1)–82.7(1)				
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ [c]						
molecule **1**	2.419(4), 2.436(4)	82.0(1), 92.6(1)	–	–	–	this work
	2.432(4), 2.419(4)	82.1(1), 93.4(1)				
molecule **2**	2.414(3), 2.431(4)	82.2(1), 92.4(2)	–	–	–	this work
	2.425(4), 2.416(4)	82.2(1), 93.1(1)	–	–	–	
$(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$	2.545(2), 2.598(3)	94.9(1), 84.0(1)	–	–	–	8
	2.547(2), 2.589(3)	95.1(1), 84.2(1)				
Structure B						
$Fe_4(CO)_{11}P(OMe)_3$-	2.668(2), 2.687(2)	–	–	–	–	2, 18
(P-*p*-tolyl)$_2$	2.710(2), 2.666(2)			178(1)	175(1)	

Structure C						
$Ru_4(CO)_{11}(MeC_2Ph)_2$	2.748(4), 2.829(3) 2.739(5), 2.829(3)	86.6(1)–86.8(1) ^{e}	2.035(10), 2.035(10) 137.5(3), 137.5(3)	–	–	11
Structure D						
$Fe_4(CO)_{11}(HC_2Et)_2$	2.515(5), 2.633(4) 2.644(4), 2.608(4)	87.5(1), 84.7(1) 85.4(1), 87.9(1)	1.936(13), 1.976(14) 142.3(10), 138.3(9)	1.789(13), 2.705 169.3(15)	1.780(11), 2.586 169.0(11)	14
$Fe_4(CO)_{11}(NEt)(ONEt)$	2.552(3), 2.485(3) 2.531(3), 2.488(3)	90.5(1), 89.5(1) 90.9(1), 88.9(1)	1.91(1), 1.95(1) 139.5(1), 137.7(1)	1.81(2), 2.47(2) 163.3(14)	1.78(2), 2.44(2) 165.2(13)	19
$Fe_4(CO)_{10}P(OMe)_3$- (P-*p*-tolyl)$_2$	2.458(3), 2.671(3) 2.755(3), 2.642(3)	–	–	– 171(2)	– 168(2)	2, 18
$Fe_4(CO)_{11}$(P-*p*-tolyl)$_2$	2.440(3), 2.685(2) 2.694(3), 2.685(2)	92.72(7)–87.28(7) ^{e}	1.93(1), 1.93(1) 141(1), 141(1)	– 169(1)	– 169(1)	2, 18
$Fe_2Co_2(CO)_{11}(PPh)_2$ $Ph_{\parallel}$	2.515(3), 2.635(2) 2.724(3), 2.597(2)	91.76(7), 87.40(7) 88.02(7), 92.82(7)	– 134 (1), 143(1)	– 170(1)	– 168(1)	2, 18
$Ph_{\perp}$	2.514(4), 2.664(5) 2.705(4), 2.659(4)	92.1(1), 87.8(1) 88.1(1), 92.0(1)	– 141(2), 137(2)	– 172(2)	– 171(2)	2, 18
$Fe_2Co_2(CO)_{11}S_2$	2.495(2), 2.58(3) 2.604(3), 2.58(3)	–	–	–	–	2, 18
$Ru_4(CO)_{11}(PPh)_2$	2.717(5), 2.874(5) 2.878(5), 2.854(5)	91.5(2), 88.0(1) 88.7(1), 91.6(1)	–	–, 2.7	–, 2.7	22
Structure F						
$Co_4(CO)_{10}(PPh)_2$	2.519(2) ^{f}, 2.697(2) ^{g}	–	1.928(8)–1.959(9) ^{e}	–	–	25
$Co_4(CO)_{10}S_2$	2.480(9) ^{f}, 2.598(10) ^{g}	–	1.86(3)–1.91(3) ^{e}	–	–	25
Structure G						
$Ru_5(CO)_{13}(PPh_2)(C_2Ph)$	2.696(1), 2.874 2.816, 2.857	–	–	–	–	26

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[a] For numbering of the atoms see the formula. The values are in the order: M(1)–M(2), M(2)–M(3), M(3)–M(4), M(4)–M(1). [b] In the order, the central metal is: M(2), M(3), M(4), M(1). [c] Two independent molecules. [d] Symmetrical edges, not distinguishable. [e] Maximum and minimum values. [f] Mean of the bridged edges. [g] Mean of the non-bridged edges.

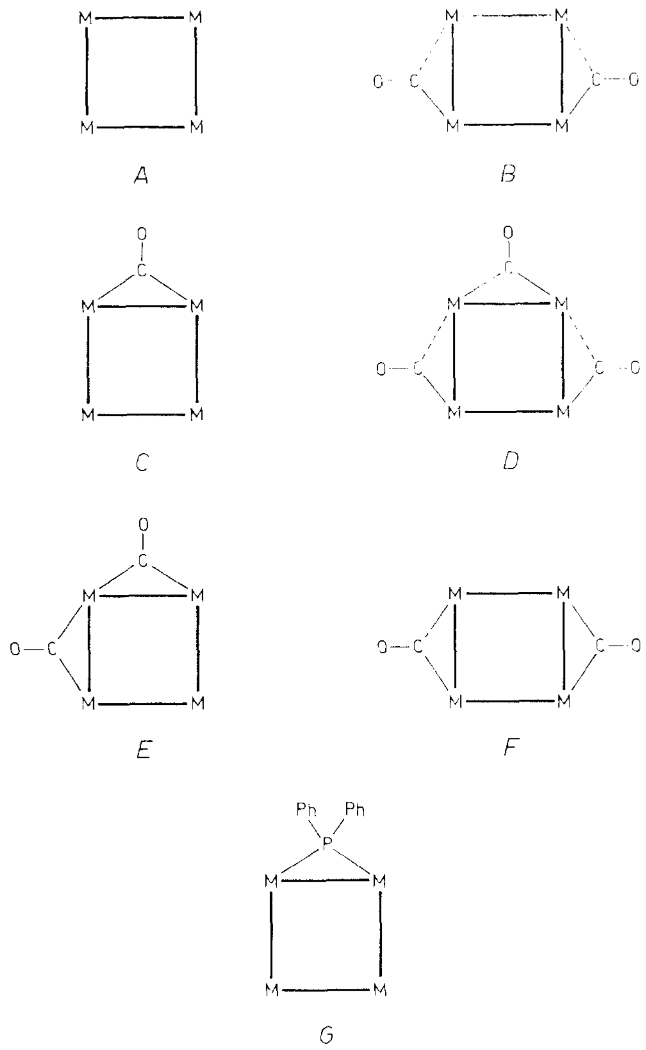

Fig. 3. Schematic representation of the square or quasi-planar square arrangements of metal atoms in complexes with structures of types A–G (see text).

$PPh_2)(\mu_4,\eta^2\text{-}C_2Ph)$ (complex IX) [26] again corresponds to an unsaturated system [27].

The alkyne ligand. The PhC_2Ph ligand is bonded to the Ni atoms through σ bonds (Ni–C 1.956(13) and 1.955(13) Å in **1**, 1.933(13) and 1.923(15) Å in **2**), and to the Fe atoms through π bonds (Fe–C 2.086(13), 2.074(13), 2.106(13) and 2.070(12) Å in **1**, and 2.070(13), 2.087(13), 2.071(13) and 2.071(13) Å in **2**). The acetylenic C(7)–C(8) bond distances (1.398(18) and 1.436(18) Å in the two independent molecules) are in the range of values found for other μ_4,η^2-bound alkynes [21,28–31].

A comparison of the extent of "activation" as measured by the distortion of the alkyne on coordination to a butterfly or square planar framework may be of interest for the "modelling approach" to surface chemistry. Structural parameters for

μ_4,η^2-bound alkynes (with alternating σ and π bonds) for selected examples of butterfly clusters and for the known square planar clusters are listed in Table 6.

The "activation" or "distortion" of the triple bond is apparently independent of the cluster size and shape; only slightly longer values for the C–C bonds are observed in the butterfly clusters with respect to those found in the square planar clusters. However, complexes IV (derived from the cluster contraction of complexes I) show a considerably shorter C–C bond in the coordinated C_2Ph_2. In the recently obtained spiked triangular $(Cp)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}C_2Ph)$ cluster, the acetylide C–C distance is 1.313(8) Å [22]; this can be compared with the 1.342(11) Å value found for $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}C_2Ph)$ [26].

Reactivity of clusters I, III and IV. Cluster expansion and contraction reactions

Compounds I (and III) were found to be unreactive towards and unaffected by proton acids. In contrast, cluster modification on protonation is well documented for other systems [28b,d]. It is noteworthy that the clusters I are quite unreactive towards Lewis bases, including CO, phosphines, and alkynes, under the conditions used here. Although only four M–M bonds are present in I, with a total electron count of 62, there is apparently little tendency to add another electron pair. In contrast the *closo* clusters V, which also have a planar M_4 array, readily add donors. This behaviour is unlikely to be due to steric hindrance, especially when it is considered that I (although in low yields) may expand to the *closo* structure III. Complexes I readily lose $Fe(CO)_3$ in solution to form the 48 electron *nido* structure

TABLE 6

μ_4-η^2-ALKYNES IN SQUARE PLANAR AND SELECTED BUTTERFLY CLUSTERS

Complex	M–M [a]	(Hinge) [b]	M–C(σ) [c]	M–C(π) [c]	C–C	Reference
Square-planar, square-pyramidal and "very flat" butterfly clusters						
$Fe_4(CO)_{11}(HC_2Et)_2$	2.600(4)	–	2.005(11)	2.168(13)	1.374(15)	14
			1.994(12)	2.166(13)	1.397(16)	
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$	2.419(3)	–	1.936(16)	2.067(16)	1.431(23)	12
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$	2.426(4)	–	1.955(13)	2.079(13)	1.398(18)	this work
molecule **2**	2.421(4)	–	1.928(14)	2.075(13)	1.435(19)	this work
$Ru_4(CO)_{11}(MeC_2Ph)_2$	2.786(4)	–	2.156(11)	2.323(10)	1.40(1)	21
$(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$	2.569(3)	–	1.92(1)	2.26(1)	1.41(1)	8
Selected examples of trimetallic clusters						
$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$	2.391(4)	–	1.85(2)	2.02(2)	1.34(2)	12
$(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$	2.469(3)	–	1.91(2)	2.18(2)	1.40(3)	12
Selected examples of butterfly clusters						
$Co_4(CO)_{10}(C_2Et_2)$	2.457(5)	2.552(5)	2.01(14)	2.10(14)	1.44(2)	29
$FeCo_3(CO)_9(C_2Ph_2)[PhC_2(H)Ph]$	2.432(4)	2.670(4)	2.033(10)	2.079(12)	1.41(2)	30
$[RuCo_3(CO)_{10}(C_2Ph_2)]^-$	2.504(2)	2.725(2)	2.13(1)	2.10(1)	1.34(1)	28b
$RuCo_3(CO)_9(PPh_2)(HC_2Bu^t)$	2.504(1)	2.776(1)	2.098(4)	–	1.424(5)	31
$Ru_2Co_2(CO)_{11}(C_2Ph_2)$	2.595(1)	2.757(1)	2.222(3)	2.069(3)	1.432(5)	28c
$Ru_4(CO)_{12}(C_2Ph_2)$	2.73(1)	2.85(1)	2.16(1)	2.25(1)	1.46(2)	28d
$FeRu_3(CO)_{12}(C_2Ph_2)$ [d]	2.681(1)	2.780(1)	2.120(3)	2.241(3)	1.460(3)	28a
$FeRu_3(CO)_{12}(C_2Ph_2)$ [e]	2.678(1)	2.849(1)	2.177(3)	2.178(3)	1.458(4)	28a

[a] Mean values (metal in the square, square base of pyramids, or four metals in butterflies). [b] Only for butterfly clusters. [c] Mean values. [d] Iron in the hinge. [e] Iron on wingtip.

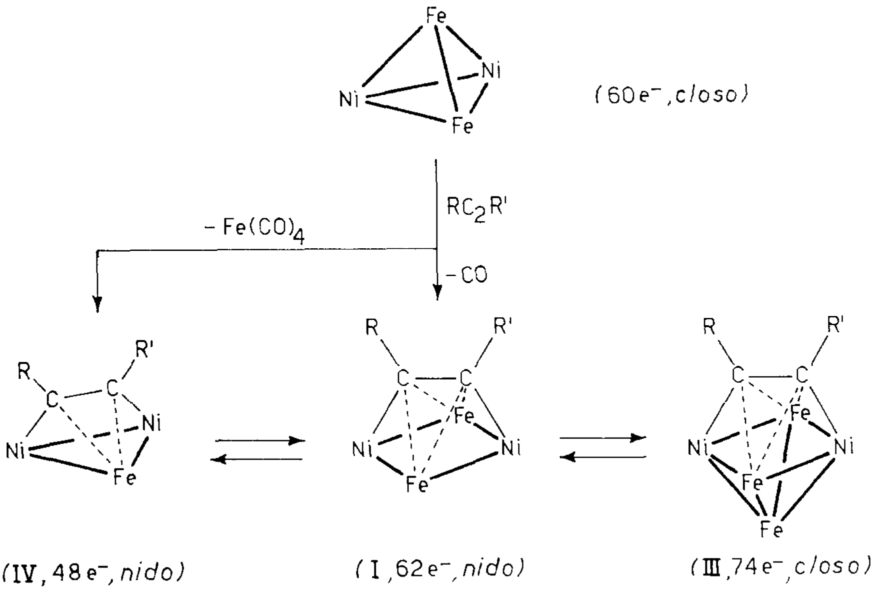

Fig. 4. Cluster expansion and contraction reactions involving clusters I.

IV. In turn, IV undergoes expansion to clusters I and then to III, although in low yields, thermal decomposition being the main process in all these reactions. Cluster growth occurs in the presence of H_2; occasionally spontaneous decomposition gives higher clusters in very low yields.

All the evidence obtained in this work points to the occurrence of metal fragment condensation in these cluster reactions. The alkyne ligands play a major role in facilitating the capture of metal fragments and stabilizing the polyhedral framework. These results appear to confirm recent observations by Vahrenkamp [33] for other mixed metal systems.

Overall the reactions reported in this work can be described as "reversible" expansions from a 48 electron *nido*, IV, to a 62 electron *nido*, I, and finally to a 74 electron, *closo*, III structure. These transformations are illustrated in Fig. 4.

A reaction sequence leading to complexes I has been reported by Bruce [34]; the trimetallic cluster which undergoes expansion is, however, the anionic $[(Cp)NiFe_2(CO)_6(\mu_3,\eta^2\text{-}\|\text{-}C_2Ph_2)]^-$ and not $(Cp)_2Ni_2Fe(CO)_6(C_2Ph_2)$, stated in ref. 23.

We are currently exploring the wider implications of these cluster expansion and contraction reactions.

Acknowledgements

We are indebted to Professor C. Giori (Unità Risonanze Magnetiche, G.N.S.M., Parma) and R.P. Ferrari (Università di Torino) for the EPR measurements. C.N.R. (Rome) is thanked for financial support of this work, and N.S.E.R.C. (Canada) for an international scientific exchange award (to E.S.).

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