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Phenylacetylene transformations in clusters with Re_2Fe and Re_2Ni_2 core. Synthesis and molecular structure of $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$ and $Cp_2Ni_2Re_2(CO)_6$-$(\mu_4\text{-}PhC{\equiv}CCH{=}CHPh)$

A.D. Shaposhnikova *, G.L. Kamalov, R.A Stadnichenko

A.V. Bogatsky Institute of Physical Chemistry of the Ukrainian Academy of Sciences,
Chernomorskaya Road 86, 270080 Odessa (USSR)

A.A. Pasynskii *, I.L. Eremenko, S.E. Nefedov

N.S. Kurnakov Institute of Inorganic Chemistry of the Academy of Sciences of the USSR,
Leninsky Prosp. 31, 117907 Moscow (USSR)

Yu.T. Struchkov and A.I. Yanovsky

A.N. Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Vavilov St. 28,
117813 Moscow (USSR)

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Abstract

Interaction of the binuclear complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ (I) with $Fe_3(CO)_{12}$ and Cp_2Ni has been studied. Reaction of I with $Fe_3(CO)_{12}$ in refluxing toluene results in formation of a heterometallic cluster $Re_2Fe(CO)_9$ $(\mu_3,\eta^4\text{-}CH{=}CH\text{-}C_6H_4)$ (II). According to the X-ray structural data, in this cluster *ortho*-metallation of the phenyl ring occurs and results in the appearance of the metalcyclopentadiene fragment. The core of the cluster II is an angular metal chain Re_2Fe with equal Re–Fe bond lengths of 2.671(2) Å and nonbonding Re(1)···Re(2) distances of 3.893(7) Å. Reaction of I with Cp_2Ni in refluxing *o*-xylene results in formation of the heterometallic cluster $Cp_2Ni_2Re_2(CO)_6(\mu_4\text{-}PhC{\equiv}CCH{=}CHPh)$ (III) (70%) along with the trinuclear cluster $Cp_3Ni_3(\mu\text{-}CO)_2$ and $Re_2(CO)_{10}$. According to the X-ray structural data cluster III contains a heterometallic Re_2Ni_2 "butterfly" core with a dihedral angle of 122° between the Re_2Ni planes. Dimerisation of the two acetylene fragments gives a ligand which is coordinated between the $ReNi_2$ "wings" only by a C≡C triple bond (with the length of 1.48(2) Å), the second hydrocarbon fragment CH=CHPh is non-coordinated.

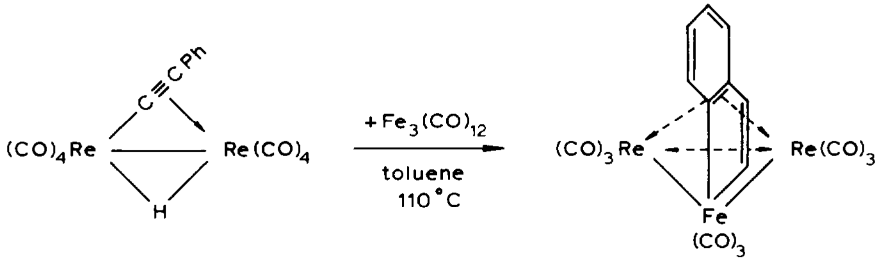
Introduction

Interest in the clusters of transition metals with acetylene ligands is a consequence of the possibility of their application as a model for activation of acetylenes on the surfaces of metal catalysts [1–3].

We have previously shown that the heterometallic cluster $Cp_2Mo_2Re_2(CO)_9(\mu\text{-}CO)(\mu_4,\eta^2\text{-}PhC{\equiv}CH)$ may be converted by decarbonylation under severe conditions into a heterometallic cluster $Cp_2Mo_2Re_2(\mu\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)(\mu\text{-}CO)(CO)_7$ which is characterized by a rearrangement of the coordinated phenylacetylene into the *ortho*-metallated bridging phenylvinylidene ligand [4]. The present paper is concerned with the transformations of phenylacetylene within the coordination sphere of its heterometallic clusters with Re_2Fe and Re_2Ni_2 cores.

Results and discussion

The dimeric phenylacetylene complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ (I) with $Fe_3(CO)_{12}$, when refluxed in toluene for 4 h loses CO and is transformed into the $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$ (II) complex.



(I)　(II)

II has been obtained in the form of yellow-orange crystals stable in air. The mass-spectrum of II contains the peaks of the fragmentation products with the most intensive peak corresponding to $[Re_2Fe(\mu\text{-}CH{=}CHC_6H_4)]$ (m/z 529).

In the IR-spectra of the cluster II there are bands characteristic of the terminal CO groups (1915–2065 cm^{-1}).

The structure of II has been studied by X-ray structural analysis (Fig. 1). Atomic coordinates, bond lengths and bond angles are given in Tables 1, 2 and 3 respectively. The core of the cluster II is a triangular Re_2Fe with equal Re–Fe bonds of 2.671(2) Å and a non-bonding distance Re(1) · · · Re(2) of 3.893(7) Å. Each metal atom in II contains three terminal CO groups. Interaction between Re(I) and C(9) is very weak (2.85(1) Å, and the Fe(1)C(9)O(9) angle is 173°). In II *ortho*-metallation of the phenyl ring results in formation of a metalcyclopentadiene FeC(8a)C(1a)C(2a)C(7a) in which each C=C bond is coordinated with both Re atoms due to the two-electron four centered π-interaction which leads to elongation of the C(1a)–C(8a) and C(2a)–C(7a) bonds to 1.43(2) and 1.51(2) Å respectively. The whole metalcyclopentadiene system, including the arene cycle is planar and perpendicular to the plane of the Re_2Fe fragment (the dihedral angle is 90.9(1)°). Re atoms are at equal distances from the plane of the ferrol cycle (1.93(2) and 1.96(1) Å respectively). At the same time the bonds of the Re atoms with arene nuclei [Re(1)–C(2a) 2.41(1); Re(1)–C(7a) 2.40(1); Re(2)–C(2a) 2.39(1); Re(2)–C(7a) 2.45(1) Å] are significantly longer than the bonds with the vinyl part [Re(1)–C(8a) 2.26 (1) Re(1)–C(1a) 2.28(1) Re(2)–C(8a) 2.29(1), Re(2)–C(1a) 2.33(1) Å], and Fe–C(7a) and Fe–C(8a) bond lengths are practically equal (2.03(1) and 2.01(2) Å respectively).

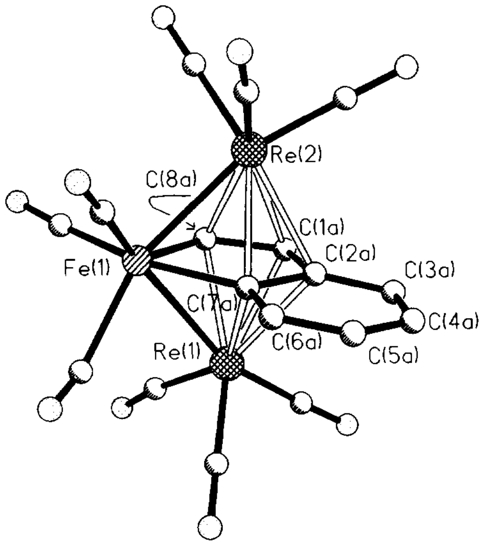
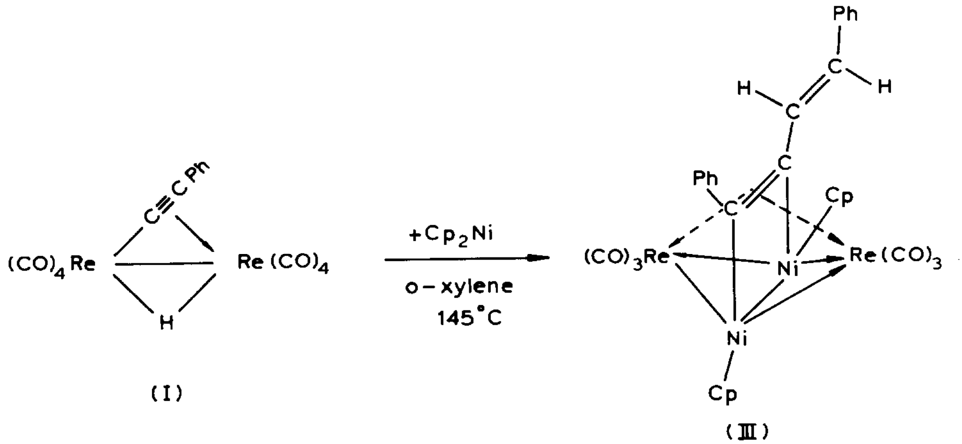


Fig. 1. Molecular structure of $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$.

It is noteworthy that rearrangement and coordination of the hydrocarbon ligand according to this scheme leads to formation of the formally 50-electron cluster with each metal atom achieving the electron shell of the inert gas.

Complex I interacts also with Cp_2Ni. After refluxing in xylene for 3 h tetranuclear $Cp_2Ni_2Re_2(CO)_6(\mu_4\text{-}Ph{\equiv}CCH{=}CHPh)$ (III) and trinuclear $Cp_3Ni_3(CO)_2$ clusters, with $Re_2(CO)_{10}$, are the main products.



III was isolated as black-green crystals stable in air. The characteristic stretching bands of the terminal CO groups (1868–1980 cm^{-1}) in the IR spectra of III are considerably shifted in comparison with those in the spectra of II.

The structure of III has been confirmed by X-ray structural analysis (Fig. 2). Atomic coordinates are presented in Table 4, and bond lengths and angles in Tables 5 and 6 respectively. Cluster III has a "butterfly" Re_2Ni_2 heterometallic core

Table 1

Atomic coordinates for $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$ ($\times 10^5$ for Re, $\times 10^4$ for Fe, $\times 10^3$ for O, C and H)

Atom	*x*	*y*	*z*
Re(1)	15761(7)	44079(5)	74024(5)
Re(2)	22191(7)	6428(5)	68208(5)
Fe(1)	3776(2)	2970(2)	7089(2)
O(1)	245(2)	633(1)	970(1)
O(2)	186(1)	663(1)	555(1)
O(3)	−168(2)	519(1)	736(2)
O(4)	−33(2)	−148(1)	673(1)
O(5)	421(2)	−132(1)	833(2)
O(6)	304(2)	−54(1)	434(1)
O(7)	618(1)	139(1)	829(1)
O(8)	491(2)	334(2)	471(1)
O(9)	526(2)	541(1)	829(1)
C(1)	208(2)	562(1)	883(2)
C(2)	180(2)	577(1)	620(2)
C(3)	−46(2)	492(2)	737(2)
C(4)	65(2)	−66(1)	674(1)
C(5)	344(2)	−60(1)	781(2)
C(6)	274(2)	−11(1)	524(2)
C(7)	523(2)	198(1)	779(2)
C(8)	453(2)	322(2)	567(2)
C(9)	459(2)	448(1)	779(1)
C(1a)	56(1)	235(1)	662(1)
C(2a)	91(2)	214(1)	798(1)
C(3a)	−6(2)	182(1)	882(2)
C(4a)	55(3)	172(2)	1010(2)
C(5a)	197(3)	197(2)	1051(2)
C(6a)	296(2)	230(1)	978(1)
C(7a)	250(2)	247(1)	842(1)
C(8a)	181(2)	273(1)	602(1)
H(3)	−110(19)	164(14)	872(15)
H(4)	4(17)	134(12)	1008(14)
H(5)	256(18)	193(13)	1122(15)
H(6)	431(14)	252(10)	1012(11)
H(8)	182(17)	258(12)	485(14)
H(1)	−51(15)	224(11)	611(15)

(Ni–Re on average is 2.440(2), Re $\cdots$ Re 3.98(1) Å) with a dihedral angle of 122° between the Ni_2Re planes. Each Re atom is bonded to three terminal CO groups, while each Ni-atom is bonded to a cyclopentadienyl ligand. The acetylene bond C(1a)–C(2a) is coordinated with all four metal atoms by μ_4,η^2-type. This may be regarded as formation of two C–Ni σ-bonds (1.88(1) and 1.95(1) Å respectively), which are non-equivalent due to the substituents at the acetylene moieties being different. A two-electron four-centered bond with participation of both Re atoms is formed (the Re–C bond length is on average 2.25(1) Å); thus the acetylene bond is drastically elongated to the value of 1.48(2) Å and the electron shells of the metal atoms are formally filled. Bonding of this kind has been observed in $Co_4(CO)_{10}(EtC{\equiv}CEt)$ [5], and in the above-mentioned cluster $Cp_2Mo_2Re_2$-

Table 2

Bond lengths (Å) in $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$

Re(1)–Re(2)	3.8932(7)	O(1)–C(1)	1.15(2)
Re(1)–Fe(1)	2.671(2)	O(2)–C(2)	1.12(2)
Re(1)–O(2)	3.04(1)	O(3)–C(3)	1.17(3)
Re(1)–C(1)	1.93(2)	O(4)–C(4)	1.20(2)
Re(1)–C(2)	1.93(2)	O(5)–C(5)	1.14(2)
Re(1)–C(3)	1.89(2)	O(6)–C(6)	1.11(2)
Re(1)–C(9)	2.85(2)	O(7)–C(7)	1.15(2)
Re(1)–C(1a)	2.28(1)	O(8)–C(8)	1.14(3)
Re(1)–C(2a)	2.41(1)	O(9)–C(9)	1.17(2)
Re(1)–C(7a)	2.40(1)	C(1a)–C(2a)	1.47(2)
Re(1)–C(8a)	2.26(1)	C(1a)–C(8a)	1.43(2)
Re(2)–Fe(1)	2.671(2)	C(1a)–H(1)	1.07(1)
Re(2)–C(4)	1.90(2)	C(2a)–C(3a)	1.38(2)
Re(2)–C(5)	1.93(2)	C(2a)–C(7a)	1.51(2)
Re(2)–C(6)	1.96(2)	C(3a)–C(4a)	1.41(3)
Re(2)–C(1a)	2.33(1)	C(3a)–H(3)	1.0(2)
Re(2)–C(2a)	2.39(1)	C(3a)–H(4)	1.4(1)
Re(2)–C(7a)	2.45(1)	C(4a)–C(5a)	1.34(4)
Re(2)–C(8a)	2.29(1)	C(4a)–H(4)	0.6(2)
Fe(1)–C(7)	1.79(2)	C(5a)–C(6a)	1.32(3)
Fe(1)–C(8)	1.77(2)	C(5a)–H(5)	0.9(2)
Fe(1)–C(9)	1.76(2)	C(6a)–C(7a)	1.46(2)
Fe(1)–C(7a)	2.03(1)	C(6a)–H(6)	1.3(1)
Fe(1)–C(8a)	2.01(2)	C(8a)–H(8)	1.3(1)

Table 3

Bond angles (°) in $Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$

Fe(1)Re(1)C(1a)	73.8(3)	Re(1)C(2a)C(7a)	71.4(7)
Fe(1)Re(1)C(2a)	73.2(3)	Re(2)C(2a)C(1a)	69.6(7)
Fe(1)Re(1)C(7a)	46.8(3)	Re(2)C(2a)C(3a)	128 (1)
Fe(1)Re(1)C(8a)	47.3(4)	Re(2)C(2a)C(7a)	73.9(7)
C(1a)Re(1)C(2a)	36.3(5)	C(1a)C(2a)C(3a)	127 (1)
C(1a)Re(1)C(7a)	62.8(5)	C(1a)C(2a)C(7a)	110 (1)
C(1a)Re(1)C(8a)	36.8(5)	Re(1)C(7a)Re(2)	106.6(5)
Re(1)C(1a)Re(2)	115.1(6)	Re(1)C(7a)Fe(1)	73.6(4)
Re(1)C(1a)C(2a)	76.8(8)	Re(1)C(7a)C(2a)	72.1(7)
Re(1)C(1a)C(8a)	71.0(8)	Re(1)C(7a)C(6a)	127.4(9)
Re(2)C(1a)C(2a)	74.2(8)	Re(2)C(7a)Fe(1)	72.5(4)
Re(2)C(1a)C(8a)	70.2(8)	Re(2)C(7a)C(2a)	69.8(7)
C(2a)C(1a)C(8a)	114 (1)	Re(2)C(7a)C(6a)	125.0(9)
C(2a)Re(1)C(8a)	62.6(5)	Fe(1)C(7a)C(2a)	117.5(9)
C(7a)Re(1)C(8a)	66.9(5)	Fe(1)C(7a)C(6a)	128 (1)
Fe(1)Re(2)C(1a)	73.0(3)	C(2a)C(7a)C(6a)	115 (1)
Fe(1)Re(2)C(2a)	73.5(3)	Re(1)C(8a)Re(2)	117.6(6)
Fe(1)Re(2)C(7a)	46.5(3)	Re(1)C(8a)Fe(1)	77.0(5)
Fe(1)Re(2)C(8a)	47.2(4)	Re(1)C(8a)C(1a)	72.2(8)
Re(1)C(2a)Re(2)	108.2(5)	Re(2)C(8a)Fe(1)	76.4(5)
Re(1)C(1a)C(2a)	66.9(7)	Re(2)C(8a)C(1a)	73.6(8)
Re(1)C(2a)C(3a)	124 (1)	Fe(1)C(8a)C(1a)	119.2(9)

Dihedral angle 90.09(1)

Table 4

Atomic coordinates for $Cp_2Re_2Ni_2(CO)_6(\mu_4\text{-}Ph{\equiv}CCH{=}CHPh)$ ($\times 10^5$ for Re and Ni, $\times 10^4$ for O, C H)

Atom	*x*	*y*	*z*
Re(1)	10584(5)	18995(3)	7975(3)
Re(2)	38993(5)	19477(3)	25019(3)
Ni(1)	18419(17)	27864(9)	18961(8)
Ni(2)	14106(18)	13535(9)	20805(8)
O(1)	1008(12)	3261(6)	−300(5)
O(2)	879(11)	688(6)	−415(5)
O(3)	−2189(9)	1858(7)	744(5)
O(4)	3417(12)	2423(6)	4044(5)
O(5)	6671(11)	2887(8)	2590(6)
O(6)	5523(13)	426(7)	2993(6)
C(1)	998(17)	2731(8)	100(7)
C(2)	900(16)	1140(8)	62(7)
C(3)	−959(14)	1898(8)	726(6)
C(4)	3610(15)	2240(7)	3478(8)
C(5)	5562(15)	2521(9)	2557(7)
C(6)	4932(14)	1020(8)	2819(7)
C(1a)	2853(14)	1379(7)	1455(6)
C(2a)	3202(13)	2236(7)	1348(6)
C(3a)	4303(13)	2565(8)	881(7)
C(4a)	4831(14)	3350(8)	921(7)
C(5a)	−4183(14)	3663(8)	446(7)
C(6a)	−3650(18)	4433(9)	567(8)
C(7a)	−2606(20)	4766(9)	146(9)
C(8a)	2130(17)	4304(11)	−361(8)
C(9a)	−2638(18)	3557(9)	−482(8)
C(10a)	−3657(15)	3240(9)	−99(7)
C(11a)	3722(14)	658(7)	1206(6)
C(12a)	3031(16)	−69(7)	1045(7)
C(13a)	3832(18)	−724(7)	818(8)
C(14a)	5236(17)	−659(8)	765(7)
C(15a)	4060(15)	−46(8)	−933(7)
C(16a)	−4784(14)	708(8)	1163(7)
C(11)	1747(15)	4041(7)	1741(8)
C(12)	358(16)	3729(9)	1602(8)
C(13)	19(16)	3339(8)	2214(9)
C(14)	1179(20)	3461(8)	2723(7)
C(15)	2262(17)	3884(8)	2425(9)
C(21)	115(16)	1306(8)	2936(7)
C(22)	1266(17)	735(9)	3044(7)
C(23)	1161(18)	186(7)	2491(8)
C(24)	−77(16)	416(9)	2041(7)
C(25)	−700(15)	1095(9)	2321(8)
H(6a)	4060	−223	4021
H(7a)	2238	4653	−237
H(8a)	−1371	4517	−655
H(9a)	−2260	3204	−893
H(10a)	−4040	2663	−214
H(12a)	1928	−119	1086
H(13a)	−3303	1250	−677
H(14a)	4213	1156	−610
H(15a)	−2988	73	883
H(16a)	5774	1236	1305

Table 4 (continued)

Atom	*x*	*y*	*z*
H(11)	2287	4351	1379
H(12)	−302	3761	1120
H(13)	−889	3021	2295
H(14)	1226	3273	3233
H(15)	3246	4048	2686
H(21)	−86	1781	3260
H(22)	2050	740	3475
H(23)	1834	−310	2422
H(24)	−461	128	1575
H(25)	−1613	1388	2090
H(3a)	−5319	2181	510
H(4a)	4512	3719	1299

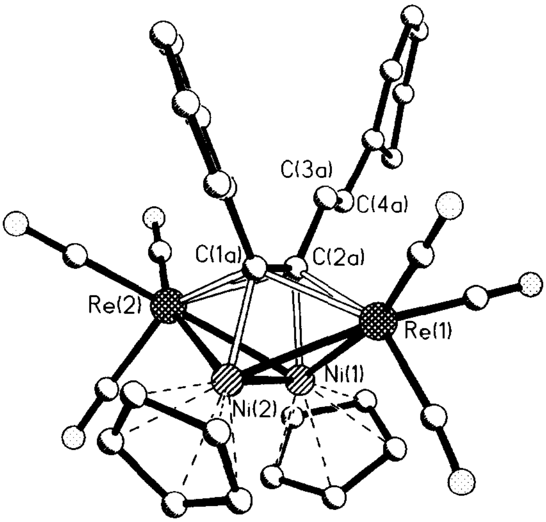


Fig. 2. Molecular structure of $\mathrm{Cp_2Ni_2Re_2(CO)_6(\mu_4\text{-}PhC{\equiv}CCH{=}CHPh)}$.

Table 5

Bond lengths (Å) in $\mathrm{Cp_2Re_2Ni_2(CO)_6(\mu_4\text{-}Ph{\equiv}CCH{=}CHPh)}$

Re(1)–Ni(1)	2.591(2)	Ni(1)–Ni(2)	2.440(2)
Re(1)–Ni(2)	2.578(2)	Ni(1)–C(2a)	1.95(1)
Re(1)–C(1a)	2.17(1)	Ni(2)–C(1a)	1.88(1)
Re(1)–C(2a)	2.25(1)	C(1a)–C(2a)	1.48(2)
Re(2)–Ni(1)	2.560(2)	C(1a)–C(11a)	1.55(2)
Re(2)–Ni(2)	2.591(2)	C(2a)–C(3a)	1.52(2)
Re(2)–C(1a)	2.32(1)	C(3a)–C(4a)	1.39(2)
Re(2)–C(2a)	2.26(1)	C(4a)–C(5a)	1.45(2)

Table 6

Bond angles (°) in $Cp_2Re_2Ni_2(CO)_6(\mu_4\text{-}PhC{\equiv}CCH{=}CHPh)$

Ni(1)Re(1)Ni(2)	56.33(5)	Ni(1)C(1a)Ni(2)	61.7(3)
Ni(1)Re(1)C(1a)	67.8(3)	Ni(1)C(1a)C(2a)	45.2(6)
Ni(1)Re(1)C(2a)	46.8(3)	Ni(2)C(1a)C(2a)	106.9(8)
Ni(2)Re(1)C(1a)	45.7(3)	Re(1)C(2a)Re(2)	123.8(5)
Ni(2)Re(1)C(2a)	67.9(3)	Re(1)C(2a)Ni(1)	75.9(4)
Ni(1)Ni(2)C(1a)	75.5(4)	Re(1)C(2a)C(1a)	67.8(6)
C(1a)Re(1)C(2a)	39.0(4)	Re(1)C(2a)C(3a)	116.7(8)
Ni(1)Re(2)Ni(2)	56.53(5)	Re(2)C(2a)Ni(1)	74.4(4)
Ni(1)Re(2)C(1a)	66.4(3)	Re(2)C(2a)C(1a)	73.4(7)
Ni(1)Re(2)C(2a)	47.1(3)	Re(2)Ni(1)C(2a)	58.4(3)
Re(1)C(1a)Re(2)	124.5(5)	Re(2)Ni(1)C(1a)	52.6(3)
Ni(2)Re(2)C(1a)	44.6(4)	Ni(2)Ni(1)C(1a)	42.8(3)
Ni(2)Re(2)C(2a)	67.4(3)	Ni(2)Ni(1)C(2a)	75.3(3)
C(1a)Re(2)C(2a)	37.5(4)	Re(2)C(2a)C(3a)	118.9(8)
Re(1)Ni(1)Re(2)	101.19(6)	Ni(1)C(2a)C(1a)	102.2(8)
Re(1)Ni(1)Ni(2)	61.56(5)	Ni(1)C(2a)C(3a)	131.1(8)
Re(1)Ni(1)C(1a)	48.7(3)	C(1a)C(2a)C(3a)	127 (1)
Re(1)Ni(1)C(2a)	57.3(3)	C(2a)C(3a)C(4a)	124(1)
Re(1)C(1a)Ni(1)	63.5(3)	C(3a)C(4a)C(5a)	123 (1)
Re(2)Ni(1)Ni(2)	62.39(5)	C(1a)Ni(1)C(2a)	32.5(4)
Re(1)C(1a)Ni(2)	78.6(4)	Re(1)Ni(2)Re(2)	100.69(6)
Re(1)C(1a)C(2a)	73.2(7)	Re(1)Ni(1)Ni(2)	62.11(5)
Re(2)C(1a)Ni(1)	61.0(3)	Re(1)Ni(2)C(1a)	55.7(4)
Re(2)C(1a)Ni(2)	75.3(4)	Re(2)Ni(2)Ni(1)	61.08(5)
Re(2)C(1a)C(2a)	69.1(6)	Re(2)Ni(2)C(1a)	60.1(4)

$(CO)_{10}(\mu_4,\eta^2\text{-}PhC{\equiv}CH)$ [4]. However in this case one more phenylacetylene molecule is added leading to a non-coordinated phenylvinyl substituent at the C(2a) atom (the C(3a)=C(4a) bond length is 1.39(2) Å). The mechanism of dimerization of the phenyl-acetylene molecule is unknown, but it may be noted that small quantities (8%) of $Re_2(CO)_{10}$ are formed presumably as a result of decay of I.

In summary it may be concluded that the driving force of the rearrangement of the coordinated phenylacetylene molecules is their trend to compensation of electron deficiency, which arises from attachment to I of the electron-unsaturated fragments ($Fe(CO)_3$ or Cp_2Ni_2 for II and III respectively) or from partial decarbonylation of the acetylene-containing clusters, e.g. $Cp_2Mo_2Re_2(CO)_{10}(\mu_4,\eta^2\text{-}PhC{\equiv}CH)$ with formation of $Cp_2Mo_2Re_2(\mu\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)(CO)_8$ [4].

Experimental

All operations associated with synthesis and isolation of the initial and the final complexes were carried out under argon flow, including the purification of the hydrocarbon solvents by distillation over dispersed sodium. The initial complex I has been synthesized earlier [6], $Fe_3(CO)_{12}$ and Cp_2Ni were obtained in accordance with well-known techniques [7,8]. IR spectra were measured with a Specord IR 75 instrument, in KBr pellets. X-ray structural data for complexes II and III were obtained on a Hilger & Watts four-circle automatic diffractometer (λ(Mo-K_α), $\theta/2\theta$-scan). The crystal data are in Table 7.

Table 7

Crystal data of compounds II and III

	II	III
Crystal structure	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.276(9)	9.399(9)
b, Å	9.961(9)	16.572(28)
c, Å	10.667(1)	18.886(23)
β, deg	97.97(8)	95.542(9)
V, Å^3	974.9	2928.1
Z	4	4
2θ(0°)	56	56
Number of reflections measured	5232	4127
Number of reflections used in refinement with $I \geqslant 4\sigma$	4157	2239
R	0.052	0.045
R_W	0.053	0.024

Structures II and III were solved by the direct methods and refined in anisotropic full-matrix approximation for all non-hydrogen atoms (for II, hydrogen atoms were refined isotropically). For the structure III hydrogen atoms at C(3a) and C(4a) were located by difference Fourier synthesis and no refinement was performed.

$Re_2Fe(CO)_9(\mu_3,\eta^4\text{-}CH{=}CHC_6H_4)$ (II)

0.40 g (0.7 mmol) of $Fe_3(CO)_{12}$ was added to the solution of 0.50 g (0.7 mmol) of I in 50 ml of toluene and the dark-green solution was refluxed for 8 h. The red-brown solution thus obtained was concentrated under vacuum to 6 ml and cooled to −5°C. Yellow-orange crystals were precipitated and isolated by decantation, washed in pentane and dried under vacuum. The yield of the product was 0.68 g (70%). IR spectrum (ν, cm^{-1}): 700 m, 750 s, 1915 s, 1945 vs, 2010 vs, 2065 s.

$Cp_2Ni_2Re_2(CO)_6(\mu_4,\eta^2\text{-}PhC{\equiv}CCH{=}CHPh)$ (III)

0.22 g (1.0 mmol) of Cp_2Ni was added to the solution of 0.80 g (1.0 mmol) of I in 50 ml of *o*-xylene; the green reaction mixture was refluxed for 4 h until the solution acquired a stable black-green colour. A small amount 0.07 g (8%) of the precipitated $Re_2(CO)_{10}$ was washed in pentane and dried under vacuum (IR spectra, ν(CO), cm^{-1}: 1950 vs, 2060 s). The mother liquor was evaporated under vacuum and the residue chromatographed on a column with Al_2O_3. The zones were eluted in the following succession: green (1) (by a hexane–benzene 4:1 mixture) and brown (2) (by benzene). After concentration of fraction 2 black crystals of $Cp_3Ni_3(CO)_2$ precipitated to an amount of 0.12 g (15%), (IR spectrum (ν(CO), cm^{-1}): 1750 vs). Fraction 1 was concentrated to a volume of 6–8 ml; 4–5 ml of heptane was added and it was kept at −5°C for 24 h. The precipitated black-green crystals of III were isolated from the solution by decantation, washed in pentane and dried under vacuum. Yield of the crystals was 0.49 g (60%). IR-spectrum (ν, cm^{-1}): 685 w, 745 m, 805 m, 820 m, 1868 s, 1868 s, 1885 vs, 1900 s, 1980 s.

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