# Reactions of ( $\eta^6$-diphenylacetylene) chromiumtricarbonyl complexes with polynuclear carbonyls.
## III. Reactions of $M_4(CO)_{12}$ (M = Rh, Co) clusters with $Cr(CO)_3(\eta^6$-$PhC_2Ph)$. Crystal and molecular structure of the $Rh_4(CO)_9(\mu_5,\eta^2:\eta^6$-$PhC_2Ph)Cr(CO)_3$ cluster

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## Abstract

Reactions of two isoelectronic tetranuclear $M_4(CO)_{12}$ clusters (M = Rh,Co) (I, III) with the chromium–arenetricarbonyl complex $Cr(CO)_3(\eta^6$-$PhC_2Ph)$ (II) yield a product of metal carbonyl fragments in addition to the free triple bond of diphenylacetylene. The cobalt cluster reaction results in partial destruction of the cluster tetranuclear framework and formation of the $Co_2(CO)_6(\mu_4,\eta^2:\eta^6$-$PhC_2Ph)Cr(CO)_3$ complex, obtained earlier starting from the binuclear $Co_2(CO)_8$ compound. In the case of a rhodium cluster addition of a tetranuclear carbonyl fragment takes place, yielding the $Rh_4(CO)_9(\mu_5,\eta^2:\eta^6$-$PhC_2Ph)Cr(CO)_3$ (IV) cluster. The crystal and molecular structure of IV reveals an unusual interaction between the $Cr(CO)_3$ fragment and a rhodium atom of the tetranuclear $Rh_4$ cluster core. $^{13}C$ NMR spectroscopic data show that the solid state structure is retained in solution.

Keywords: Rhodium; Chromium; Carbonyl; Diphenylacetylene; Cluster; Crystal structure

## 1. Introduction

Reactions of tetranuclear carbonyl clusters with alkynes have attracted considerable interest over the last two decades [1–5 and references cited therein]. Various modes of alkyne coordination to tetrametal clusters have been observed, of which the most common is the symmetrical insertion of the C≡C triple bond into the "$M_4$" framework yielding the pseudo-octahedral "$M_4C_2$" structural unit.

In our previous work [6], it was shown that the triple bond in the chromium–arenetricarbonyl complex $Cr(CO)_3$ ($\eta^6$-$PhC_2Ph$) can still act as a four electron donor in the reaction with dicobaltoctacarbonyl, yielding a "$Co_2C_2$" framework, the $Cr(CO)_3$ moiety being

retained coordinated by the arene group of the diphenylacetylene ligand. Crystallographic study of $Cr(CO)_3$-($\eta^6:\eta^2$-$PhC_2Ph)Co_2(CO)_6$ [6] showed that the alkyne and arene functions of diphenylacetylene act as two independent binding sites, coordinating separately the $Co_2(CO)_6$ and $Cr(CO)_3$ carbonyl fragments; no direct Cr–Co metal–metal bonds are formed. Nevertheless, some structural distortions in "$Cr(CO)_3$ arene" and "$Co_2(CO)_6$ alkyne" moieties, caused by non-bonding interaction between the metalcarbonyl fragments, were observed.

In the present paper we report the results of the synthesis and structural characterization of the cluster $Rh_4(CO)_9(\mu_5,\eta^2:\eta^6$-$PhC_2Ph)Cr(CO)_3$ obtained by the reaction of $Rh_4(CO)_{12}$ with $Cr(CO)_3(\eta^6$-$PhC_2Ph)$. The most interesting feature of this reaction is the formation of a direct Rh–Cr bond accompanying the insertion of the diphenylacetylene alkyne function into the "$Rh_4$" framework.

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## 2. Experimental

The IR spectra were recorded on a Specord M80 spectrophotometer, the NMR spectra on a Bruker AM 500 instrument using $Cr(acac)_3$ as relaxation agent in the $^{13}C$ NMR measurements. $Cr(CO)_3(\eta^6\text{-PhC}_2Ph)$ (II) and $Rh_4(CO)_{12}$ (I) were synthesized according to the published procedures [6,7], $Co_4(CO)_{12}$ (III) was obtained by refluxing the hexane solution of $Co_2(CO)_8$. All reactions were carried out in dry hexane under argon.

### 2.1. Reaction of $Cr(CO)_3(\eta^6\text{-PhC}_2Ph)$ (II) and $Rh_4(CO)_{12}$ (I)

A mixture of I (65 mg, 0.087 mmol) and II (55 mg, 0.175 mmol) in hexane (40 ml) was allowed to stand for four days at room temperature. Dark brown crystals of the product. $Rh_4(CO)_9(\mu_5,\eta^2:\eta^6\text{-PhC}_2Ph)Cr(CO)_3$ (IV), insoluble in hexane, were decanted, washed with pentane and dried in argon flow. Yield 62 mg, 83.8%. Anal. Found. C, 32.03; H, 1.25 $C_{26}H_{10}O_{12}Rh_4Cr$ Calc.: C, 31.93; H, 1.03%. The IR spectrum and TLC spot test of the mother liquor showed no other products apart from some unreacted starting compounds.

### 2.2. Reaction of $Cr(CO)_3(\eta^6\text{-PhC}_2Ph)$ (II) and $Co_2(CO)_8$ (III)

A mixture of III (70 mg, 0.122 mmol) and II (40 mg, 0.127 mmol) in hexane (50 ml) was allowed to stand for four days at room temperature. The residue of some decomposition products was decanted and the solution obtained was separated with column chromatography (silica, 40/100, 2 × 15 cm). Elution with hexane gave a brown band of $Co_2(CO)_8$ (20 mg). Subsequent elution with a hexane/ether (8/1) mixture gave a yellow band of unreacted II (19 mg) and a violet band of $Co_2(CO)_6(\mu_3,\eta^2:\eta^6\text{-PhC}_2Ph)Cr(CO)_3$ (5 mg), identified by its IR spectrum [6].
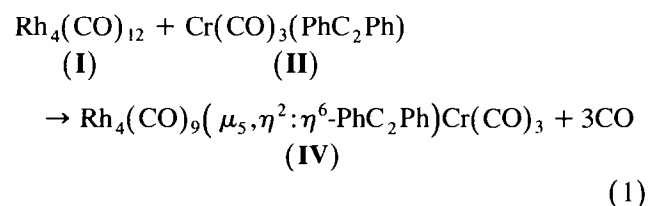
### 2.3. Structure determination

A single crystal of IV suitable for X-ray study was selected from the sample crystallized from the reaction solution. Crystal data for IV: $C_{26}H_{10}O_{12}CrRh_4$, $M = 977.98$, triclinic, at 186 K $a = 10.003(3)$, $b = 11.347(3)$, $c = 14.061(4)$ Å, $\alpha = 74.51(2)$, $\beta = 74.78(2)$, $\gamma = 75.47(2)°$, $V = 1455.8(7)$ Å$^3$, $Z = 2$, space group $P\bar{1}$, $d_c = 2.231$ g cm$^{-3}$, $\mu = 26.43$ cm$^{-1}$, $F(000) = 932$.

X-ray diffraction study was carried out with a Siemens P3/PC diffractometer ($T = 186$ K, graphite monochromated Mo K$\alpha$ radiation, $\lambda = 0.71069$ Å, $\theta$–$2\theta$ scan technique, $2\theta < 56°$). The structure was solved by direct methods using the SHELXTL PLUS programs (PC version) [8] and refined in anisotropic ap-

proximation by the SHELXL-93 program [9]; no absorption correction was applied. All hydrogen atoms were located in the difference synthesis and included in the refinement in the isotropic approximation. The final discrepancy factors are $R = 0.061$, $wR2 = 0.141$ for 4787 independent reflections with $I > 2\sigma(I)$, and $R1 = 0.111$ and $wR2 = 0.162$ for all 6958 unique reflections. The atomic coordinates of the structure IV are given in Table 1. A table of anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

## 3. Results and discussion

The reaction of the tetranuclear rhodium cluster I with II:

$$Rh_4(CO)_{12} + Cr(CO)_3(PhC_2Ph)$$
$$\qquad (I) \qquad\qquad (II)$$

$$\rightarrow Rh_4(CO)_9(\mu_5,\eta^2:\eta^6\text{-PhC}_2Ph)Cr(CO)_3 + 3CO$$
$$\qquad\qquad (IV)$$

$$(1)$$

readily affords the dark brown crystalline product IV in high yield. The crystal and molecular structure of IV was determined by X-ray study and is shown in Fig. 1, selected bond lengths and angles are given in Table 2.

The main feature of this structure is the direct metal–metal bond between the Cr(1) and Rh(3) atoms. The $Cr(CO)_3Ph$ group is an electronically and coordinatively saturated moiety, and only a few examples of similar bonding are described in the literature [10–15]. In the heterobimetallic indenyl complex $cis$-$Cr(CO)_3$-(indenyl)RhL$_2$ [10], the $Cr(CO)_3$ and RhL$_2$ fragments bound to $C_6$ and $C_5$ aromatic rings respectively form a Cr–Rh bond, with bond length 3.181(1) Å for L$_2$ = norbornadiene and 3.077(1) Å for L$_2$ = (CO)$_2$. However, this Rh–Cr interaction results in such large distortions in the $(CO)_3Cr$–arene and L$_2$Rh–Cp bonding, that these can be considered as $\eta^6 \rightarrow \eta^4$(arene) and $\eta^5 \rightarrow \eta^3$ (Cp) hapticity changes. The subsequent coordinative unsaturation of the $(CO)_3Cr(\eta^4$-arene) and L$_2$Rh($\eta^3$-Cp) fragments results in the onset of direct Cr–Rh interaction. However, this bonding pattern differs from the interaction observed in IV because in the latter case a phenyl ring of diphenylacetylene is unambiguously bound to a chromium atom in $\eta^6$-mode. All Cr–C$_{Ph}$ bonds are similar in length, ranging from 2.202(8) to 2.254(7) Å, and the configuration of the phenyl ring is nearly planar.

Other examples of metal–$Cr(CO)_3$(arene) bonding are more closely related to the Cr–Rh interaction found in IV. In the binuclear $(C_5Me_5)Rh(CO)$–$Cr(CO)_3$ arene

[11] compounds the Cr–Rh bond is considered as a donor Cr to Rh bond of order 1, with bond length 2.757(2) Å. The Cr(CO)$_3$arene group in this complex acts as a two electron donor for the Rh atom to meet 18e requirements. Moreover, the starting (C$_5$Me$_5$)Rh-

Table 1

Atomic coordinates ($\times 10^4$, $\times 10^3$ for H atoms) and equivalent isotropic (for H) displacement parameters ($\text{Å}^2 \times 10^3$) for IV

| Atom | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Rh(1) | 1183(1) | 7877(1) | 3479(1) | 25(1) |
| Rh(2) | 2025(1) | 8111(1) | 1485(1) | 24(1) |
| Rh(3) | 2918(1) | 5835(1) | 2710(1) | 24(1) |
| Rh(4) | 1864(1) | 10184(1) | 2366(1) | 29(1) |
| Cr(1) | 5895(1) | 4763(1) | 2245(1) | 26(1) |
| O(1) | 1566(8) | 6863(7) | 5637(5) | 58(2) |
| O(2) | −1685(8) | 7176(8) | 3779(6) | 64(2) |
| O(3) | −966(8) | 9291(8) | 1150(6) | 65(2) |
| O(4) | 3473(9) | 8337(8) | −729(5) | 68(2) |
| O(5) | −812(7) | 10159(6) | 4024(5) | 50(2) |
| O(6) | 1018(7) | 5861(6) | 1435(6) | 50(2) |
| O(7) | 1596(8) | 3611(7) | 3917(6) | 60(2) |
| O(8) | 3596(9) | 10879(7) | 233(5) | 62(2) |
| O(9) | 579(8) | 12932(6) | 2087(7) | 69(2) |
| O(10) | 4807(8) | 3842(7) | 4476(5) | 56(2) |
| O(11) | 7720(7) | 2220(6) | 2387(7) | 64(2) |
| O(12) | 4144(6) | 3709(6) | 1341(5) | 46(2) |
| C(1) | 1406(9) | 7278(8) | 4832(6) | 36(2) |
| C(2) | −615(10) | 7414(9) | 3671(6) | 40(2) |
| C(3) | 143(9) | 8864(8) | 1278(6) | 39(2) |
| C(4) | 2963(9) | 8239(8) | 93(6) | 35(2) |
| C(5) | 252(9) | 9751(8) | 3519(6) | 31(2) |
| C(6) | 1630(9) | 6294(8) | 1792(6) | 35(2) |
| C(7) | 2110(10) | 4414(8) | 3442(7) | 38(2) |
| C(8) | 3018(10) | 10506(8) | 1023(7) | 37(2) |
| C(9) | 994(9) | 11880(8) | 2204(7) | 40(2) |
| C(10) | 5142(9) | 4230(8) | 3626(6) | 35(2) |
| C(11) | 7003(9) | 3173(7) | 2345(8) | 39(2) |
| C(12) | 4697(8) | 4155(8) | 1742(6) | 32(2) |
| C(13) | 3193(8) | 8288(7) | 2847(5) | 26(2) |
| C(14) | 3770(7) | 7469(6) | 2184(5) | 23(1) |
| C(15) | 3910(9) | 9061(7) | 3159(6) | 29(2) |
| C(16) | 3188(9) | 9685(8) | 3954(6) | 30(2) |
| C(17) | 3802(10) | 10522(9) | 4199(7) | 38(2) |
| C(18) | 5119(11) | 10726(9) | 3670(7) | 44(2) |
| C(19) | 5843(10) | 10131(8) | 2892(7) | 36(2) |
| C(20) | 5237(9) | 9323(7) | 2620(6) | 30(2) |
| C(21) | 5224(8) | 6856(6) | 1900(6) | 25(2) |
| C(22) | 6128(9) | 6460(7) | 2611(6) | 30(2) |
| C(23) | 7492(10) | 5715(8) | 2393(8) | 37(2) |
| C(24) | 7949(10) | 5323(8) | 1492(8) | 39(2) |
| C(25) | 7100(9) | 5690(7) | 781(7) | 32(2) |
| C(26) | 5748(8) | 6415(7) | 988(6) | 29(2) |
| H(16) | 240(9) | 951(8) | 440(6) | 25(21) |
| H(17) | 350(11) | 1094(11) | 459(8) | 55(34) |
| H(18) | 588(12) | 1125(11) | 390(9) | 74(36) |
| H(19) | 661(7) | 1032(6) | 243(5) | 0(14) |
| H(20) | 575(8) | 886(8) | 210(6) | 25(20) |
| H(22) | 582(7) | 652(6) | 322(5) | 0(14) |
| H(23) | 796(13) | 564(12) | 271(10) | 74(44) |
| H(24) | 870(11) | 484(10) | 138(8) | 47(29) |
| H(25) | 741(9) | 544(8) | 224(7) | 25(21) |
| H(26) | 513(7) | 656(6) | 470(5) | 1(15) |
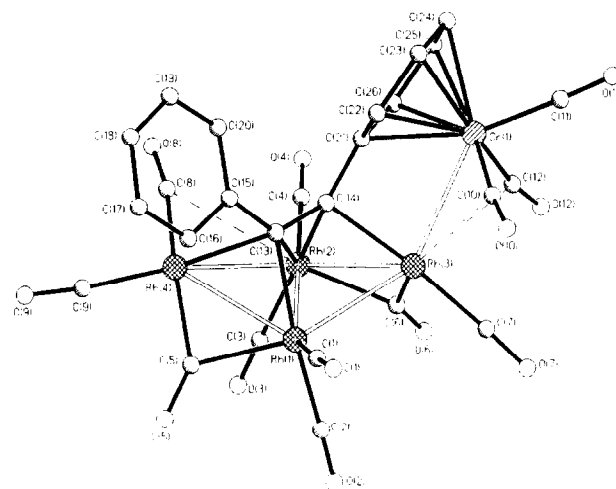


Fig. 1. Molecular structure of IV.

(CO)$_2$ complex, in the course of reaction with Cr(CO)$_3$arene, loses one CO group to form an Rh–Cr bond that is very similar to the stoichiometry of IV. Indeed, reactions of symmetrical alkynes with the iso-electronic analogues of Rh$_4$(CO)$_{12}$ {Co$_4$(CO)$_{12}$ [16], Co$_2$Rh$_2$(CO)$_{12}$ [17], Co$_3$Rh(CO)$_{12}$ [18]}, yield the M$_4$(CO)$_{10}$(RC$_2$R) clusters containing the two $\mu_2$-CO and eight terminal CO groups, two at each metal atom. In the case of complex IV, direct interaction of the Cr(CO)$_3$ fragment with the Rh(3) atom results in the loss of one CO ligand (of the two normally attached to this wing metal atom) and formation of the direct Cr(1)–Rh(3) bond. The arrangement of carbonyl ligands at other rhodium atoms remains nearly the same as that in the M$_4$C$_2$ cobalt subgroup clusters mentioned above. Another resemblance of the structures (C$_5$Me$_5$)Rh(CO) –Cr(CO)$_3$arene and IV is the semibridging nature of the two CO groups bound to Cr atoms. Both in (C$_5$Me$_5$)Rh(CO)–Cr(CO)$_3$arene and in IV two (of there) Cr–C–O fragments are slightly bent (154.4(6) and 173.6(8), 169.8(7)° respectively), and the Rh–C(O) dis-tances in both cases are shorter than the Van der Waals contacts (2.200(7) and 2.85(1), 2.66(1) Å). It is obvious, however, from the above parameters, that the Rh–C(O) interactions in the case of molecule IV are much weaker than that in the pentamethylcyclopentadienyl derivative. The Cr(1)–C(10) and Cr(1)–C(12) distances (1.881(9) and 1.879(8) Å) are slightly but significantly longer than Cr(1)–C(11) (1.857(8) Å), and all these distances are longer than those in "unbound" Cr(CO)$_3$arene compounds (av. 1.838 Å in Co$_2$(CO)$_6$($\mu_3$,$\eta^2$:$\eta^6$-PhC$_2$Ph)Cr(CO)$_3$ [6], 1.824 Å in Cr(CO)$_3$toluene [19], 1.830 Å in Cr(CO)$_3$(1,3,5-triphenylbenzene) [20].

Moreover, the Rh(3)–C(10) and Rh(3)–C(12) inter-action is also manifested in ^{13}C NMR spectra. First, the CO ligands bound to the chromium atom are stereo-chemically rigid not only at 225 K but at room tempera-ture as well, in contrast to the behaviour of other

"non-bound" Cr(CO)₃-containing compounds, which exhibit non-rigidity (unhindered rotation) of the $Cr(CO)_3$ fragment in solution [20,21]. Second, the semibridging nature of the C(10)O(10) and C(12)O(12) ligands is also confirmed by the splitting of both corresponding $^{13}C$ signals (224.72 and 231.84 ppm) into doublets ($^1J$(Rh–C) = 2 Hz), which are resolved upon treatment of the spectrum with a resolution enhancement procedure, Fig. 2, inset.

A very similar behaviour of the $Cr(CO)_3$(arene) fragment was earlier observed for the mixed metal CrPd [12,13] and $CrRu_3$ [14,15] compounds, with the chromium atom directly bound to coordinatively unsaturated Pd and Ru centres. Formation of the donor Cr → Pd

and Cr → Ru bonds results in the formal fulfilment of the 18e requirements for Pd and Ru electrophilic centres. The lengths of Cr–Pd (2.768 Å [13]) and Cr–Ru (2.9704 Å [15]) are similar to that of the Cr–Rh bond (2.891 Å) in the complex IV. It is noteworthy that the essential features of the structures of $CrRu_3$ and IV are very similar, in spite of differences in the nature and number of platinum group metal atoms ($Rh_4$ instead of $Ru_3$) and the type of binding ligand (benzene instead of tolanechromiumtricarbonyl).

All examples given above clearly show the ability of the $Cr(CO)_3$(arene) fragments to acts as a two electron donor on exposure to closely disposed unsaturated electrophilic centres. It is this kind of $Cr(CO)_3(PhC_2Ph)$

Table 2
Selected bond lengths (Å) and angles (deg) for IV

| | | | |
|---|---|---|---|
| Rh(1)–C(1) | 1.894(8) | Cr(1)–C(10) | 1.881(9) |
| Rh(1)–C(2) | 1.931(9) | Cr(1)–C(22) | 2.202(8) |
| Rh(1)–C(13) | 2.089(7) | Cr(1)–C(26) | 2.211(8) |
| Rh(1)–C(5) | 2.106(8) | Cr(1)–C(24) | 2.214(9) |
| Rh(1)–Rh(2) | 2.6673(11) | Cr(1)–C(23) | 2.219(9) |
| Rh(1)–Rh(3) | 2.8076(10) | Cr(1)–C(25) | 2.230(9) |
| Rh(1)–Rh(4) | 2.8131(10) | Cr(1)–C(21) | 2.254(7) |
| Rh(2)–C(4) | 1.920(8) | O(1)–C(1) | 1.141(10) |
| Rh(2)–C(3) | 1.926(9) | O(2)–C(2) | 1.131(11) |
| Rh(2)–C(8) | 2.978(9) | O(3)–C(3) | 1.134(11) |
| Rh(2)–C(14) | 2.102(7) | O(4)–C(4) | 1.122(10) |
| Rh(2)–C(6) | 2.106(8) | O(5)–C(5) | 1.176(10) |
| Rh(2)–C(13) | 2.563(7) | O(6)–C(6) | 1.145(10) |
| Rh(2)–Rh(3) | 2.7761(9) | O(7)–C(7) | 1.128(11) |
| Rh(2)–Rh(4) | 2.8907(10) | O(8)–C(8) | 1.132(10) |
| Rh(3)–C(7) | 1.908(9) | O(9)–C(9) | 1.143(10) |
| Rh(3)–C(6) | 1.943(8) | O(10)–C(10) | 1.148(10) |
| Rh(3)–C(10) | 2.853(9) | O(11)–C(11) | 1.133(10) |
| Rh(3)–C(12) | 2.659(9) | O(12)–C(12) | 1.155(9) |
| Rh(3)–C(14) | 2.107(7) | C(13)–C(14) | 1.406(10) |
| Rh(3)–Cr(1) | 2.891(2) | C(13)–C(15) | 1.471(10) |
| Rh(4)–Cr(9) | 1.882(9) | C(14)–C(21) | 1.448(10) |
| Rh(4)–C(8) | 1.932(9) | C(15)–C(20) | 1.405(12) |
| Rh(4)–C(5) | 2.017(8) | C(15)–C(16) | 1.420(11) |
| Rh(4)–C(13) | 2.261(7) | C(16)–C(17) | 1.405(12) |
| Rh(4)–C(15) | 2.487(7) | C(17)–C(18) | 1.375(14) |
| Cr(1)–C(11) | 1.857(8) | C(18)–C(19) | 1.382(13) |
| Cr(1)–C(12) | 1.879(8) | C(19)–C(20) | 1.393(11) |
| | | | |
| Rh(2)–Rh(1)–Rh(3) | 60.87(2) | O(5)–C(5)–Rh(4) | 144.7(7) |
| Rh(2)–Rh(1)–Rh(4) | 63.60(2) | O(5)–C(5)–Rh(1) | 129.1(6) |
| Rh(3)–Rh(1)–Rh(4) | 113.44(3) | Rh(4)–C(5)–Rh(1) | 86.0(3) |
| Rh(1)–Rh(2)–Rh(3) | 62.06(2) | O(6)–C(6)–Rh(3) | 141.3(7) |
| Rh(1)–Rh(2)–Rh(4) | 60.66(2) | O(6)–C(6)–Rh(2) | 131.7(7) |
| Rh(3)–Rh(2)–Rh(4) | 112.02(3) | Rh(3)–C(6)–Rh(2) | 86.5(3) |
| Rh(2)–Rh(3)–Rh(1) | 57.07(3) | O(7)–C(7)–Rh(3) | 176.0(9) |
| Rh(2)–Rh(3)–Cr(1) | 116.30(3) | Rh(2)–C(8)–Rh(4) | 68.4(4) |
| Rh(1)–Rh(3)–Cr(1) | 138.14(3) | O(8)–C(8)–Rh(4) | 169.6(8) |
| Rh(1)–Rh(4)–Rh(2) | 55.74(3) | O(9)–C(9)–Rh(4) | 174.1(8) |
| C(10)–Cr(1)–Rh(3) | 69.8(3) | Rh(3)–C(10)–Cr(1) | 72.0(5) |
| C(12)–Cr(1)–Rh(3) | 63.7(2) | O(10)–C(10)–Cr(1) | 173.6(8) |
| O(1)–C(1)–Rh(1) | 176.8(8) | O(11)–C(11)–Cr(1) | 177.6(8) |
| O(2)–C(2)–Rh(1) | 178.2(10) | Rh(3)–C(12)–Cr(1) | 77.0(5) |
| O(3)–C(3)–Rh(2) | 178.8(9) | O(12)–C(12)–Cr(1) | 169.8(7) |
| O(4)–C(4)–Rh(2) | 177.8(8) | | |

behaviour that we observe in the structure of **IV** and rationalization of the electron counting for this cluster can be done on the basis of a conventional [4,5] EAN scheme, taking into account additional 2e donation of the alkyne–chromiumtricarbonyl moiety. Indeed, insertion of the triple bond into the $Rh_4$ framework (6e donor if the alkyne fragment is considered as part of the cluster skeleton), and donation of two electrons from the chromium centre, gives rise to a 62e cluster that corresponds to a *closo* octahedron containing the alkyne fragment [5]. This structure can also be considered as a butterfly cluster of class B or C [4] (EAN 60, because it is more natural to treat alkyne in this case as a four electron external ligand). However, the structural parameters of the rhodium butterfly framework display some peculiarities compared with $M_4C_2$ clusters (class B). These peculiarities are evidently connected with the Cr–Rh interaction and consequently unusual disposition of the alkyne fragment inserted into the tetrarhodium core. The Rh(1)–Rh(2) distance between the hinge atoms is slightly shorter (2.667(1) Å) than those between hinge and wing atoms ($d_{av}$ 2.822 Å), in contrast to the homonuclear $Co_4C_2$ and $Ru_4C_2$ clusters [16,22,23], where, the inverse situation is observed. Normally, the $M_4C_2$ clusters contain the alkyne fragment, which is approximately parallel to the hinge metal–metal bond (the angle between M–M and C–C vectors is close to 0), each carbon atom being bound to three (two wing and one hinge) metal atoms. The interaction of the Cr(1) and Rh(3) atoms causes the rotation of the alkyne moiety with respect to the hinge Rh–Rh bond, the angle between the Rh(1)–Rh(2) and C(13)–C(14) vectors in **IV** being equal to 44.1°. Such a mode of alkyne coordination results in an increase of

the dihedral angle between butterfly wings of up to 141.7°, considerably larger compared with the angles in $M_4C_2$ clusters having the usual alkyne coordination (112–118° [4]). The butterfly wing angle found in **IV** is closer to the corresponding parameters for the class C butterfly clusters, where insertion of an *XY* diatomic fragment into the $M_4$ core is highly asymmetrical. The bonding mode of the C=C moiety to the $Rh_4$ framework is asymmetrical as well. The C(14) carbon atom is bound to two Rh atoms (bond lengths 2.102(7) [Rh(2)–C(14)] and 2.107(7) [Rh(3)–C(14)] Å respectively), whereas C(13) forms three bonds to Rh atoms (bond lengths 2.089(7) [Rh(1)–C(13)], 2.261(7) [Rh(4)–C(13)], and 2.563(7) [Rh(2)–C(13)] Å respectively). The latter bond distance is significantly longer than the other Rh–C bonds in **IV**, and could be regarded as a non-bonding contact. However, the signals of C(13) and C(14) carbons appear in the ^{13}C NMR spectra (Fig. 2, inset) as ddd ($^1J$(Rh–C) = 5.0, 7.5, 13.5 Hz) and dd ($^1J$(Rh–C) = 7.2, 15.2 Hz), suggesting that the C(13) and C(14) atoms are indeed bound to three and two rhodium atoms respectively. This position of the alkyne triple bond in the cluster skeleton closely matches that of the nitrile group in the $Fe_4(CO)_{12}(NCPh)$ cluster [24], where the nitrogen atom is bound to three (two hinge and one wing) metals and the nitrile carbon to only two (one hinge and one wing) metals on the $Fe_4$ skeleton. The dihedral angle in this cluster framework (135°) is very close to that in **IV** as well. The solid state structure of **IV** reveals a very short contact (2.487(8) Å) between the *ipso*-C(15) atom of the phenyl ring and Rh(4). The presence of chemical bonding between carbon and rhodium atoms is normally reflected in the ^{13}C NMR spectra by Rh–C splitting of the corresponding carbon
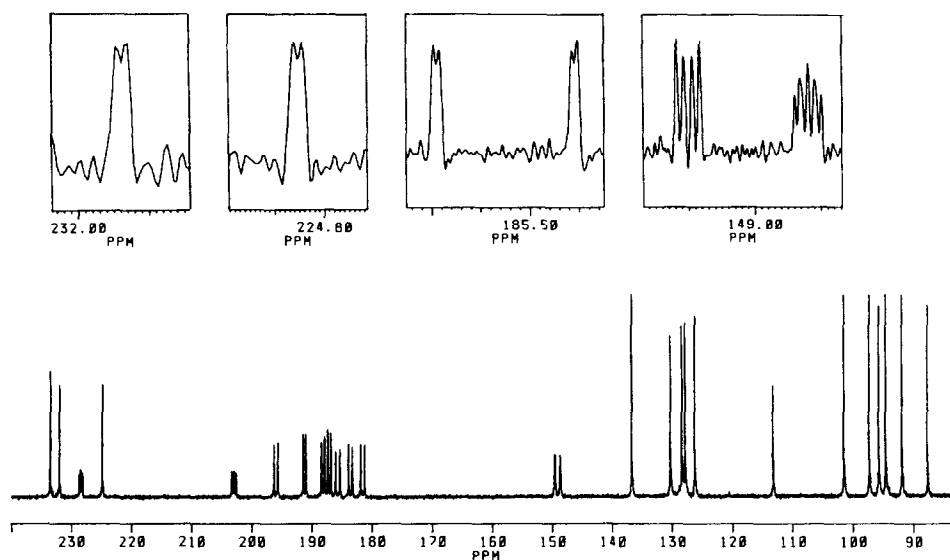


Fig. 2. ^{13}C NMR spectrum of $Rh_4(CO)_9(\mu_5,\eta^2:\eta^6\text{-PhC}_2Ph)Cr(CO)_3$, $CDCl_3$, 215 K, the signals shown in insets were obtained using a resolution enhancement procedure (LB $-6.0$, GB 0.35).

signal, and the NMR probe can be considered as a reliable test for direct Rh–C interaction. NMR confirmation of Rh–C bonding was found in the low temperature ^{13}C spectrum of **IV** (Fig. 2, Table 3) for all bonds revealed in the solid state structure, except the Rh(4)–C(15) contact. The resonance of the C(15) carbon (113.1 ppm) was unambiguously assigned using the DEPT-90 technique, but we failed to detect any splitting of the signal even after treatment of the spectrum with various resolution enhancement procedures. This makes us believe that the short Rh(4)–C(15) distance is just a result of general molecular overcrowding and does not correspond to any attractive interaction.

According to the structural parameters found for **IV**, the carbonyl ligands bound to the $Rh_4$ core can be subdivided into six terminal ligands, one semibridging C(8)O(8), and two bridging C(5)O(5) and C(6)O(6) ones. A low temperature ^{13}C NMR spectrum shows that

this structure remains unchanged in solution as well. The resonances of the terminal CO ligands are split into doublets, with substantial variations in $^1J$(Rh–C) ranging from 57 to 81 Hz. These variations, as well as those in the Rh–C bond lengths (from 1.882(9) to 1.931(9) Å), reflect the differences in the corresponding bond strength. The signal of the semibridging C(8)O(8) group (Rh(4)–C(8) 1.932(9); Rh(2)–C(8) 2.978(9) Å) appears in the spectrum as a doublet of doublets ($^1J$(Rh–C) 88 and 4 Hz). The carbonyl ligands bridging the Rh(2)–Rh(3) and Rh(1)–Rh(4) bonds are only slightly asymmetrical, the Rh–C(O) distances to the wing rhodium atoms being shorter (Rh(3)–C(6) 1.943(8) and Rh(4)–C(5) 2.017(8) Å) than those to hinge rhodiums (Rh(2)–C(6) 2.106(8) and Rh(1)–C(5) 2.106(8) Å). This asymmetry is manifested in the ^{13}C NMR spectrum where the corresponding signals appear as doublets of doublets, Table 3. It should be noted that the pairs of

Table 3
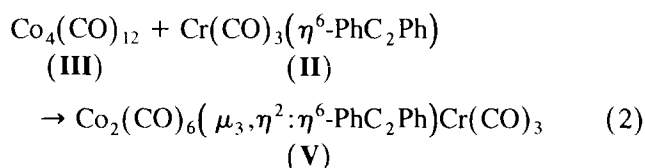Spectroscopic data for the $Rh_4(CO)_9(\mu_5, \eta^2 : \eta^6\text{-PhC}_2\text{Ph})Cr(CO)_3$ cluster

| IR ($\nu_{CO}$, cm$^{-1}$) CH$_2$Cl$_2$ | ^{1}H NMR ($\delta$, ppm) CD$_3$COCD$_3$, 297 K | Assignment |
|---|---|---|
| 2086s | 7.75–7.40, m (4H) | Ph |
| 2060vs | 6.70, t, 6.5 Hz (1H) | |
| 2024s,br | 6.63, t, 7 Hz (1H) | |
| 1972m | 6.00, t, 7Hz (1H) | |
| 1920sh | 5.72, t, 7 Hz (1H) | PhCr(CO)$_3$ |
| 1902m,br | 4.60, d, 7 Hz (1H) | |
| 1846m,br | 4.15, d, 7 Hz (1H) | |

^{13}C{^{1}H} NMR, CDCl$_3$

| Assignment | 225 K | | | 297 K | | |
|---|---|---|---|---|---|---|
| | $\delta$(ppm) | Multiplicity | $^1J$(Rh–C) (Hz) | $\delta$(ppm) | Multiplicity | $^1J$(Rh–C) (Hz) |
| C(11)O(Cr) | 233.4 | s | | 233.3 | s | |
| C(12)O(Cr) | 231.8 | d | 2 | 231.6 | d | 2 |
| $\mu_2$-CO(Rh) | 228.3 | dd | 37,25 | ca. 225 | broad | |
| C(10)O(Cr) | 224.7 | d | 2 | 225.2 | d | 2 |
| $\mu_2$-CO(Rh) | 202.8 | dd | 58,35 | ca. 202 | broad | |
| CO(Rh) | 195.8 | d | 81 | 195.7 | d | 79 |
| CO(Rh) | 191.0 | d | 57 | 191.1 | d | 58 |
| CO(Rh) | 188.0 | d | 62 | 188.1 | d | 62 |
| CO(Rh) | 186.9 | d | 65 | ca. 186 | broad | |
| C(8)O(Rh) | 185.5 | dd | 88, 4 | ca. 185 | broad | |
| CO(Rh) | 183.4 | d | 77 | 183.9 | d | 79 |
| CO(Rh) | 181.4 | d | 79 | 181.8 | d | 75 |
| C(13) | 149.4 | dd | 15, 7 | 150.3 | m | |
| C(14) | 148.5 | ddd | 14, 8, 5 | 148.3 | m | |
| C$_{Ph}$ | 136.5 | s | | 136.5 | s | |
| C$_{Ph}$ | 130.1 | s | | 130.0 | s | |
| C$_{Ph}$ | 128.2 | s | | 128.2 | s | |
| C$_{Ph}$ | 127.7 | s | | 128.2 | s | |
| C$_{Ph}$ | 126.1 | s | | 126.4 | s | |
| C(15)$_{Ph,ipso}$ | 113.1 | s | | 115.9 | s | |
| C$_{Ph}$(Cr) | 101.3 | s | | 101.2 | s | |
| C$_{Ph}$(Cr) | 97.1 | s | | 96.8 | s | |
| C$_{Ph}$(Cr) | 95.5 | s | | 95.3 | s | |
| C$_{Ph}$(Cr) | 94.4 | s | | 94.1 | s | |
| C$_{Ph}$(Cr) | 91.7 | s | | 92.1 | s | |
| C(21)$_{Ph,ipso}$ (Cr) | 87.5 | s | | 87.7 | s | |

spin–spin coupling constants recorded for these resonances ($^1J$(Rh–C): 37 and 25 Hz for the signal at 228.28 ppm, 58 and 35 Hz for that at 202.79 ppm) are closer to each other than to that for semibridging C(8)O(8), and values of small constants in each pair are larger than those for the semibridging carbonyls spanning the Cr–Rh bond. Thus, high a resolution $^{13}$C NMR spectrum of **IV** reflects most of the structural details found in the solid state, including variations in bond length and bonding mode for certain carbon atoms. At room temperature the bridging carbonyls take part in an exchange with adjacent terminal and semibridging carbonyls (see Table 3), this type of carbonyl environment non-rigidity was earlier observed for the $Co_2Rh_2C_2$ clusters [17].

The reaction between $Co_4(CO)_{12}$ and $Cr(CO)_3(\eta^6$-$PhC_2Ph$):

$$Co_4(CO)_{12} + Cr(CO)_3(\eta^6\text{-}PhC_2Ph)$$
$$(\mathbf{III}) \qquad\qquad (\mathbf{II})$$

$$\rightarrow Co_2(CO)_6(\mu_3,\eta^2{:}\eta^6\text{-}PhC_2Ph)Cr(CO)_3 \qquad (2)$$
$$(\mathbf{V})$$

results in the formation of the dicobalt–chromium cluster previously obtained in the reaction of **II** with $Co_2(CO)_8$ [6]. The partial destruction of the starting $Co_4$ core in the course of the reaction is evidently due to the following reasons. The initial insertion of the functionalized alkynes **II** into the $Co_4$ framework is likely to yield a structure with considerable steric hindrance between the $Co_4(CO)_x$ and $Cr(CO)_3$ carbonyl fragments bound to the alkyne. This structure could probably be retained in a manner similar to that found in **IV**, but the lower strength of the Co–Co bonds results in degradation of the cluster core and formation of the less hindered compound **V**. It should be noted as well that a similar degradation of the $Co_4$ framework was observed in the reaction of $Co_4(CO)_{12}$ with non-functionalized alkynes [25,26], and is not unusual for this type of reaction.

## Acknowledgements

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