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# Reactions of ($\eta^6$-diphenylacetylene) chromiumtricarbonyl complexes with polynuclear carbonyls

## I. Synthesis of $Cr(CO)_3(\eta^6$-diphenylacetylene) complex and its reaction with $Co_2(CO)_8$. Crystal and molecular structure of $Cr(CO)_3(\eta^6:\eta^2$-diphenylacetylene)$Co_2(CO)_6$

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**Abstract**

The reaction of $Cr(CO)_3(NH_3)_3$ with diphenylacetylene affords as a main product the complex with $Cr(CO)_3$ moiety bound to a phenyl ring of diphenylacetylene; $Cr(CO)_3(\eta^6\text{-}PhC_2Ph)$ (**I**). Complex **I** readily reacts with $Co_2(CO)_8$ yielding the mixed metal complex $Cr(CO)_3(\eta^6:\eta^2\text{-}PhC_2Ph)Co_2(CO)_6$ (**II**). The reaction proceeds with retention of the $Cr(CO)_3(\eta^6$-arene) structural unit, the $Co_2(CO)_6$ fragment being bound to the triple bond of diphenylacetylene in $\mu_2,\eta^2$-mode. The structure of **II** was determined by single crystal X-ray analysis. The complex crystallizes in space group $P2_1/c$ with unit cell parameters $a$ 8.666(3) Å, $b$ 18.046(3) Å, $c$ 15.155(6) Å, $\beta$ 97.57(3)°, $V$ 2349(2) Å$^3$, $Z = 4$, $D_x = 1.70$ g/cm$^3$. The structure was solved by direct methods and refined by full-matrix least-squares technique to $R$ and $R_w$ values of 0.032 and 0.034, respectively, for 3655 observed reflections. The data obtained show that two structural units in **II**, $Cr(CO)_3(\eta^6$-Ph–) and $Co_2(CO)_6(\mu_2,\eta^2\text{-}C{\equiv}C)$, are distorted due to steric repulsion between these metal carbonyl moieties. The $Cr(CO)_3$ fragment is shifted from the centre of the phenyl ring and slightly tilted with respect to the phenyl ring plane. The $Co_2C_2$ tetrahedron in the $Co_2(CO)_6(\mu_2,\eta^2\text{-}C{\equiv}C)$ moiety is distorted in such a way that two of the four $Co_i$–$C_j$ bonds are elongated.

*Key words:* Chromium; Carbonyl; Cobalt; Acetylene; Crystal structure

## 1. Introduction

The synthesis of mixed-metal polynuclear complexes has attracted considerable attention over recent years. The presence of a few metal centres in a molecule can lead to unique reactive properties arising from metal-metal or ligand-polymetallic centre(s) interactions. Such interactions and the resulting unusual reactivity are of interest to preparative organometallic chemistry as well as to the understanding of the nature of the catalytic processes proceeding on heterometallic catalytic centres [1–3]. Different reactive metal centres can be joined in a single molecule either by direct metal–metal bonds (as in homo- and heteronuclear clusters) or by bridging polyfunctional ligands (assembling ligands). The use of bidentate phosphine ligands in the linking of metal carbonyl fragments is an obvious and easy

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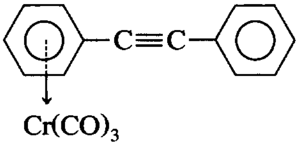
variant of the latter approach [4–6]. However, the diphosphines are not easily accessible substrates and their catalytic or stoichiometric conversion on polymetallic centres are not of principal importance to organic catalytic chemistry. In contrast, the study of the binding of different metal carbonyl fragments by polyfunctional unsaturated hydrocarbons is of fundamental interest owing to wide application of their catalytic reactions in modern chemistry and industry. In this series of papers we are going to report on the reactions of the aryl-alkyne ligand (diphenylacetylene) with $Cr(CO)_3(NH_3)_3$ aimed to anchor the $Cr(CO)_3$ fragment to the aryl function(s) of the ligand and on the subsequent reactions of the complexes obtained with di- and polynuclear carbonyl compounds of cobalt, rhodium, ruthenium, and osmium.

## 2. Results and discussion

The reaction of $Cr(CO)_3(NH_3)_3$ with excess of diphenylacetylene affords $Cr(CO)_3(\eta^6\text{-}PhC_2Ph)$ as the

$$Cr(CO)_3(NH_3)_3 + PhC_2Ph \xrightarrow[\text{reflux, 8 h}]{\text{dioxane}} \underset{\substack{(\mathbf{I})\\ 31\%}}{Cr\,CO_3(\eta^6\text{-}PhC_2Ph)} \quad (1)$$

main product where the $Cr(CO)_3$ moiety is bound to a phenyl ring of the ligand. It should be noted that we did not observe the competitive reaction of diphenylacetylene coordination via triple bond that has been reported as the main process for the reactions of $M(CO)_3Py_3$ (M = Mo, W) with the same ligand [7]. Spectral and analytical characteristics of the complex **I** are given in Table 1. The IR spectrum of the complex displays two intense bands in the carbonyl region typical of $Cr(CO)_3$(arene) moieties [8]. The presence of a $Cr(CO)_3$ fragment coordinated to phenyl group in the molecule is attested by the well resolved phenyl group pattern in the range 5.2–5.5 ppm in the $^1H$ NMR spectrum. In addition to this group of signals the multiplet of uncoordinated phenyl group is observed in the range 7.3–7.5 ppm. The data obtained give a good fit to the spectral characteristics of the previously characterized complexes containing the free and the complexed phenyl groups [9] and allow to formulate the structure of the complex I as follows.



The alkyne function of complex **I** remains free and the reaction yields the novel mixed-metal complex **II**

$$Cr(CO)_3(\eta^6\text{-}PhC_2Ph) + Co_2(CO)_8 \longrightarrow \underset{(\mathbf{II})}{Cr(CO)_3\left(\eta^6:\eta^2\text{-}PhC_2Ph\right)Co_2(CO)_6} \quad (2)$$

where arene and alkyne functions of the starting ligand bear the $Cr(CO)_3$ and $Co_2(CO)_6$ fragments respectively. Spectral characteristics of complex **II** are given in Table 1. The $^1H$ NMR spectrum of **II** displays a pattern which is very similar to that of **I** with a slight downfield shift of the both phenyl multiplets. The spectrum shows that the phenyl rings remain unchanged in the molecule **II** as compared to the starting $Cr(CO)_3(\eta^6\text{-}PhC_2Ph)$ complex, and the $Co_2(CO)_6$ fragment in **II** is bound to the triple bond in ($\eta^2$,$\mu_2$) mode as is usual in dicobalt hexacarbonyl-alkyne complexes.

The spectroscopic data obtained are fully consistent

TABLE 1. Analytical and spectroscopic data for the compounds obtained

| Compound | Analysis %C Found (Calc.) | Analysis %H Found (Calc.) | IR spectrum $\nu$(CO), cm$^{-1}$ hexane | $^1H$ NMR, $CDCl_3$, $\delta$, ppm |
|---|---|---|---|---|
| I | 64.59 (64.97) | 3.26 (3.21) | 1986vs<br>1922s | 7.50, m, (2H) Ph<br>7.35, m, (3H) Ph<br>5.52, d, 6 Hz (2H) $Cr(CO)_3Ph$<br>5.35, t, 6 Hz (2H) $Cr(CO)_3Ph$<br>5.25, t, 6 Hz (1H) $Cr(CO)_3Ph$ |
| II | | | 2094m<br>2062vs<br>2036sh<br>2032s<br>2018w<br>1984s<br>1978vs<br>1916m,br | 7.65 m (2H) Ph<br>7.40 m (3H) Ph<br>5.86 d, 6 Hz (2H) $Cr(CO)_3Ph$<br>5.54 t, 6 Hz (1H) $Cr(CO)_3Ph$<br>5.23 t, 6 Hz (2H) $Cr(CO)_3Ph$ |

with the solid state structure of **II** studied by single-crystal X-ray analysis. The atomic coordinates, intramolecular bond distances and angles are summarized in Tables 2–4. An ORTEP drawing of the molecular structure of **II** is shown in Fig. 1. The molecule consists of two structural units, $Cr(CO)_3(\eta^6\text{-Ph-})$ and $Co_2(CO)_6(\mu_2,\eta^2\text{-C}\equiv\text{C})$, certain distortions in the arrangement of these fragments being observed as compared with the unhindered analogues, *e.g.* $Cr(CO)_3$-$PhCH_3$ [10] and $Co_2(CO)_6(\mu_2,\ \eta^2\text{-Ph-C}\equiv\text{C-Ph})$ [11].

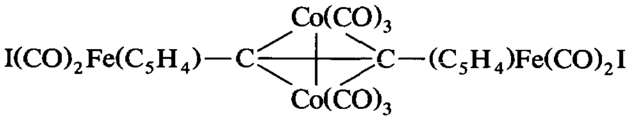
TABLE 2. Positional parameters and $B_{eq}$ for $Cr(CO)_3(\eta^6:\eta^2$-$PhC_2Ph)Co_2(CO)_6$.

| Atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.19816(5) | 0.12367(2) | 0.97098(3) | 2.98(2) |
| Co2 | 0.07945(5) | 0.17538(2) | 1.09671(3) | 2.96(2) |
| Cr | 0.26287(6) | 0.41409(3) | 1.01830(3) | 3.08(2) |
| O1 | 0.5414(3) | 0.4279(2) | 1.1570(2) | 6.7(1) |
| O2 | 0.2370(3) | 0.5794(1) | 1.0198(2) | 5.4(1) |
| O3 | 0.0705(4) | 0.4165(2) | 1.1677(2) | 8.3(2) |
| O4 | −0.0884(3) | 0.1377(2) | 0.8437(2) | 5.8(1) |
| O5 | 0.2403(4) | −0.0341(1) | 1.0167(2) | 6.5(1) |
| O6 | 0.4398(4) | 0.1342(2) | 0.8541(2) | 8.5(2) |
| O7 | −0.2355(3) | 0.2211(2) | 1.0161(2) | 6.7(2) |
| O8 | 0.0312(4) | 0.0318(1) | 1.1800(2) | 6.0(1) |
| O9 | 0.1380(4) | 0.2619(2) | 1.2599(2) | 7.3(2) |
| C1 | 0.2277(3) | 0.2942(2) | 0.9766(2) | 2.7(1) |
| C2 | 0.3734(4) | 0.3203(2) | 0.9563(2) | 3.2(1) |
| C3 | 0.3847(4) | 0.3828(2) | 0.9029(2) | 3.9(1) |
| C4 | 0.2509(4) | 0.4231(2) | 0.8721(2) | 3.9(1) |
| C5 | 0.1051(4) | 0.4000(2) | 0.8929(2) | 3.6(1) |
| C6 | 0.0942(3) | 0.3371(2) | 0.9448(2) | 3.1(1) |
| C7 | 0.2161(3) | 0.2246(2) | 1.0236(2) | 2.8(1) |
| C8 | 0.3004(3) | 0.1748(2) | 1.0749(2) | 2.9(1) |
| C9 | 0.4437(3) | 0.1683(2) | 1.1381(2) | 3.3(1) |
| C10 | 0.5090(4) | 0.2313(2) | 1.1791(2) | 4.6(2) |
| C11 | 0.6430(5) | 0.2269(3) | 1.2410(3) | 6.0(2) |
| C12 | 0.7119(5) | 0.1594(3) | 1.2600(3) | 6.1(2) |
| C13 | 0.6487(5) | 0.0972(3) | 1.2206(3) | 5.8(2) |
| C14 | 0.5141(4) | 0.1002(2) | 1.1594(2) | 4.5(2) |
| C15 | 0.4355(4) | 0.4222(2) | 1.1024(2) | 4.2(2) |
| C16 | 0.2471(4) | 0.5158(2) | 1.0192(2) | 3.9(1) |
| C17 | 0.1442(5) | 0.4133(2) | 1.1099(3) | 4.9(2) |
| C18 | 0.0229(4) | 0.1305(2) | 0.8905(2) | 3.8(1) |
| C19 | 0.2207(4) | 0.0263(2) | 0.9987(2) | 4.0(1) |
| C20 | 0.3458(5) | 0.1299(2) | 0.8982(2) | 4.8(2) |
| C21 | −0.1166(4) | 0.2031(2) | 1.0472(2) | 4.2(2) |
| C22 | 0.0483(4) | 0.0874(2) | 1.1481(2) | 3.8(1) |
| C23 | 0.1095(4) | 0.2297(2) | 1.1964(2) | 4.3(2) |
| H1 | 0.462(4) | 0.295(2) | 0.979(2) | 3.6(7) |
| H2 | 0.480(4) | 0.396(2) | 0.889(2) | 5.2(9) |
| H3 | 0.252(4) | 0.463(2) | 0.840(2) | 4.8(9) |
| H4 | 0.021(3) | 0.427(2) | 0.873(2) | 3.0(7) |
| H5 | −0.000(4) | 0.325(2) | 0.963(2) | 3.9(7) |
| H6 | 0.464(4) | 0.275(2) | 1.168(2) | 4.5(8) |
| H7 | 0.687(5) | 0.271(2) | 1.262(3) | 7(1) |
| H8 | 0.799(5) | 0.157(2) | 1.305(3) | 7(1) |
| H9 | 0.690(4) | 0.052(2) | 1.233(2) | 6(1) |
| H10 | 0.466(4) | 0.054(2) | 1.130(2) | 6(1) |

These distortions are presumably caused by steric hindrances between two metal carbonyl moieties (*e.g.* short nonbonding contact O3–O9; 3.141(5) Å). The $Cr(CO)_3$ fragment in the molecule studied is of approximate $C_{3V}$ local symmetry, but it is shifted from the centre of the phenyl ring (see Fig. 2) to minimize its nonbonding interaction with the $Co_2(CO)_6$ fragment. Moreover, this interaction causes the slight tilt of the $Cr(CO)_3$ fragment with respect to phenyl ring and corresponding dihedral angle between the oxygen atoms of the three CO groups and the phenyl ring plane equals 2.6°. This distortion of the $Cr(CO)_3$phenyl moiety leads to a significant inequivalency in the $Cr-C_{phenyl}$ distances ranging within 2.205–2.263 Å.

The typical elongation of the C–C bonds in the complexed phenyl ring is observed (mean C–C distance 1.405 Å) as compared with the bonds in the noncomplexed one (mean C–C distance 1.380 Å). In the solid state the molecules of **II** are packed so that the phenyl ring planes form a dihedral angle of 9°.

The solid state structure of the $Co_2(CO)_6(\mu_2,\eta^2$-alkyne) molecules has been characterized earlier for the series of symmetric [11,12] and asymmetric [13,14] alkynes, including those with organometal fragments in the alkyne side chains [12–14]. In the molecule **II** the alkyne C–C vector lies perpendicular to the Co–Co vector and this is typical of $Co_2C_2$ pseudotetrahedral units in the other structurally related molecules mentioned above. The Co–Co and $C-C_{alkyne}$ bond distances (2.465 Å and 1.341 Å respectively) fall in the ranges 2.45–2.49 Å and 1.32–1.37 Å observed for the compounds of this class. However, the $Co_2C_2$ tetrahedron in the molecule studied is substantially distorted as compared with the analogous $Co_2(CO)_6(\mu_2,\eta^2$-$PhC_2Ph)$ complex and the others with symmetrical alkynes [11]. In the complex **II** the opposite Co1–C7 (1.987 Å) and Co2–C8 (1.986 Å) bonds of the $Co_2C_2$ tetrahedron are elongated as compared with two others Co2–C7 (1.947 Å) and Co1–C8 (1.937 Å). It is worthy of note that a similar but slighter distortion was observed [12] in the structurally related complex:




In contrast, the complexes of diynes with coordinated $Co_2(CO)_6$ fragments [13,14] exhibit another type of distortion where the $Co_2C_2$ tetrahedron is tilted in such a way that two Co–C bonds between different cobalt atoms and a given carbon atom are elongated relative to two other Co–C bonds.

The carbonyl environment of each cobalt atom in **II** has two CO groups in the *cis* position with respect to

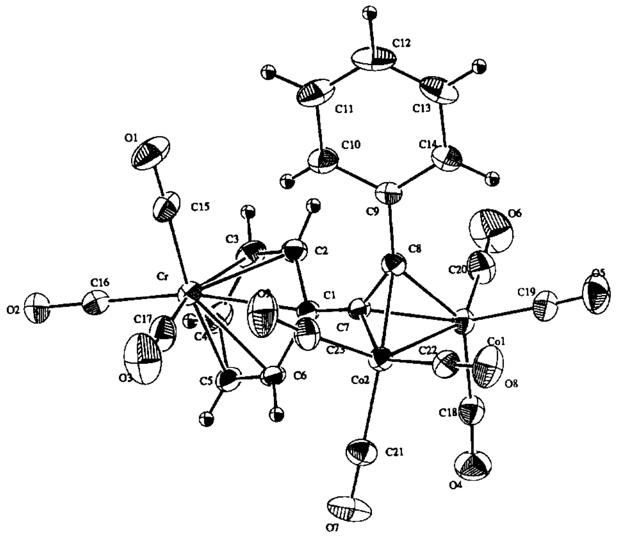


Fig. 1. ORTEP view of the molecular structure of **II**. Ellipsoids represent 50% probability.

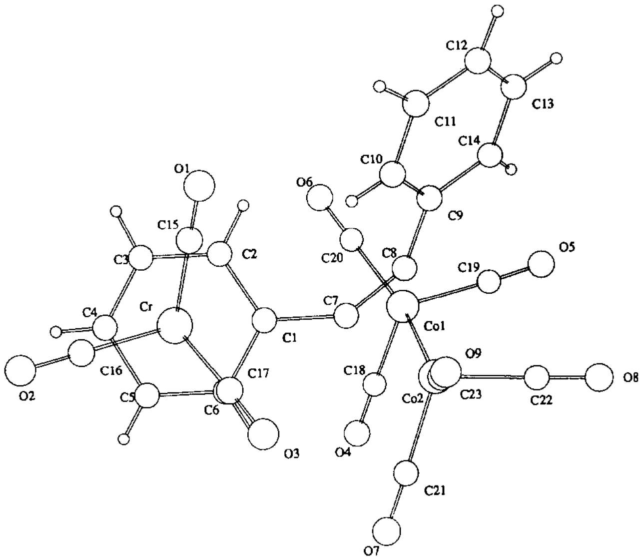



Fig. 2. Projection of **II** on the C1–C6 phenyl ring plane.

Co–Co bond and one CO group which is nearly *trans*. The $Co_i$–$Co_j$–$C_n$(O) angles for *cis* groups {*i*, *j*, *n* = 1, 2, 21; 1, 2, 22; 2, 1, 18; 2, 1, 19} are 104.2°, 95.9°, 95.5° and 103.4° respectively. The corresponding values of the angles for *trans* groups are much greater (*i*, *j*, *n* = 1, 2, 23; 2, 1, 20) at 146.1° and 148.5 respectively. It

TABLE 3. Selected bond distances (Å) for $Cr(CO)_3(\eta^6:\eta^2\text{-}PhC_2Ph)Co_2(CO)_6$

| | | | | | |
|---|---|---|---|---|---|
| Col–Co2 | 2.4651(9) | Col–C18 | 1.823(4) | Col–C19 | 1.812(3) |
| Col–C20 | 1.799(4) | C18–O4 | 1.127(4) | C19–O5 | 1.131(4) |
| C20–O6 | 1.122(4) | Co2–C21 | 1.834(4) | Co2–C22 | 1.804(4) |
| Co2–C23 | 1.791(4) | C21–O7 | 1.123(4) | C22–O8 | 1.131(4) |
| C23–O9 | 1.123(4) | C1–C2 | 1.418(4) | C2–C3 | 1.399(5) |
| C3–C4 | 1.396(5) | C4–C5 | 1.405(5) | C5–C6 | 1.393(4) |
| C6–C1 | 1.422(4) | C1–C7 | 1.454(4) | C7–C8 | 1.341(4) |
| C8–C9 | 1.469(4) | C9–C10 | 1.380(4) | C10–C11 | 1.396(5) |
| C11–C12 | 1.370(6) | C12–C13 | 1.353(6) | C13–C14 | 1.392(5) |
| C14–C9 | 1.390(5) | C7–Co2 | 1.941(3) | C7–Col | 1.987(3) |
| C8–Co2 | 1.986(3) | C8–Col | 1.937(3) | Cr–C15 | 1.839(4) |
| Cr–C16 | 1.841(4) | Cr–C17 | 1.834(4) | C15–O1 | 1.156(4) |
| C16–O2 | 1.151(4) | C17–O3 | 1.152(4) | Cr–C1 | 2.263(3) |
| Cr–C2 | 2.214(3) | Cr–C3 | 2.231(3) | Cr–C4 | 2.210(3) |
| Cr–C5 | 2.205(3) | Cr–C6 | 2.209(3) | | |

TABLE 4. Selected bond angles (deg) for $Cr(CO)_3(\eta^6:\eta^2\text{-}PhC_2Ph)Co_2(CO)_6$

| | | | | | |
|---|---|---|---|---|---|
| Col–Co2–C21 | 104.2(1) | Col–Co2–C22 | 95.9(1) | Col–Co2–C23 | 146.1(1) |
| Col–C18–O4 | 176.1(4) | Col–C19–O5 | 177.5(3) | Col–C20–O6 | 178.8(4) |
| Col–C7–C8 | 68.0(2) | Col–C7–Co2 | 77.7(1) | Col–C8–Co2 | 77.9(1) |
| Col–C8–C7 | 72.0(2) | Co2–Col–C18 | 95.5(1) | Co2–Col–C19 | 103.4(1) |
| Co2–Col–C20 | 148.5(1) | Co2–C21–O7 | 178.7(3) | Co2–C22–O8 | 178.8(3) |
| Co2–C23–O9 | 175.4(4) | C1–C2–C3 | 121.7(3) | C2–C3–C4 | 119.7(3) |
| C3–C4–C5 | 120.1(3) | C4–C5–C6 | 119.9(3) | C5–C6–C1 | 121.5(3) |
| C6–C1–C2 | 117.0(3) | C6–C1–C7 | 122.0(3) | C2–C1–C7 | 120.9(3) |
| C1–C7–C8 | 142.8(3) | C7–C8–C9 | 141.3(3) | C8–C9–C10 | 119.3(3) |
| C9–C10–C11 | 120.7(4) | C10–C11–C12 | 119.5(4) | C11–C12–C13 | 120.3(4) |
| C12–C13–C14 | 121.1(4) | C13–C14–C9 | 119.5(4) | C14–C9–C10 | 118.8(3) |
| C14–C9–C8 | 121.9(3) | C15–Cr–C16 | 88.3(1) | C15–Cr–C17 | 87.8(2) |
| C16–Cr–C17 | 87.3(2) | | | | |

is interesting that *trans* groups have shorter Co–C(O) distances (mean value 1.795 Å) as compared with those for *cis* groups (mean value 1.818 Å). Angular characteristics of each $Co(CO)_3$ group show some distortions in the fragment structure presumably caused by interaction with $Cr(CO)_3$. The corresponding angles range within the following limits: (O)C–Co–C(O) angle 97.5–106.0°; Co–C–O angle 175.4–178.8°. The $Co(CO)_3$ fragments are disposed in approximately eclipsed configuration with respect to their Co–C(O) bonds.

At present time two other products of the $Cr(CO)_3$-($\eta^6$-$PhC_2Ph$) reactions with $H_2Os_3(CO)_{10}$ and $Rh_4$-$(CO)_{12}$ have been obtained and their structural characterization is now in progress.

## 3. Experimental section

The IR spectra were recorded on a Specord M-80 spectrophotometer. The NMR spectra were recorded on a Bruker AM 500 instrument. $Cr(CO)_6$ and $Co_2(CO)_8$ were commercial grade reagents and were used without purification. $Cr(CO)_3(NH_3)_3$ was prepared according to the published procedure [15]. Dioxane and diethyl ether were purified by distillation from sodium benzophenone ketyl immediately prior to use. Hexane was dried by distillation over sodium. All solutions were degassed by Ar purging.

### *3.1. Reaction of $Cr(CO)_3(NH_3)_3$ with diphenylacetylene*

Freshly prepared $Cr(CO)_3(NH_3)_3$ (700 mg, 3.74 mmol) was added to a solution of diphenylacetylene (10.0 g, 56.2 mmol) in dioxane (100 ml). The mixture was refluxed in a flow of Ar for 8 h. The solvent was then removed under reduced pressure, the residue extracted with hexane and the extract transferred to a chromatographic column (Silpearl, 1.5 × 10 cm). Elution with hexane gave the wide colourless band of diphenylacetylene, the bright-yellow band of $Cr(CO)_3$-($\eta^6$-$PhC_2Ph$) (**I**), and a yellow-green band containing a trace of an unidentified compound. The major product **I** (366 mg) was obtained from the second band in 31.1% yield after removal of the solvent under reduced pressure. Spectral and analytical characteristics of the complex are given in Table 1.

### *3.2. Reaction of I with $Co_2(CO)_8$*

A solution of $Co_2(CO)_8$ (115 mg, 0.40 mmol) in hexane (10 ml) was added to a solution of **I** (35 mg, 0.11 mmol) in 30 ml of hexane. The mixture was stirred for 15 min and its colour turned to grey-blue. The volume of the mixture was reduced under vacuum to ca. 10 ml and it was transferred to a chromatographic column (Silpearl, 1.5 × 8 cm). Elution with hexane/ether = 6/1 mixture gave the following bands in the order of elution: the brown band of unreacted $Co_2(CO)_8$, trace amounts of **I**, and grey-blue band of $Cr(CO)_3(\eta^6,\eta^2$-$PhC_2Ph)Co_2(CO)_6$ (**II**). The solvent was removed from the third band under reduced pressure and the product **II** was obtained in 49.5% yield (33.0 mg).

### *3.3. Structure determination*

Dark brown prismatic single crystals of **II** suitable for X-ray analysis were grown from hexane at −10°C. The substance crystallizes in the monoclinic space group $P\,2_1/c$ with unit cell parameters $a$ 8.666(3) Å, $b$ 18.046(3) Å, $c$ 15.155(6) Å, $\beta$ 97.57(3)°, $V$ 2349(2) Å$^3$, $D_x$ 1.70 g/cm$^3$, and $Z = 4$.

A crystal 0.10 × 0.15 × 0.25 mm was used for X-ray measurements on a Rigaku AFCSR diffractometer with graphite monochromated Mo K$\alpha$ radiation. The data were collected at 296 K using the $\omega$-$2\theta$ scan technique to a maximum $2\theta$ value of 55.0° for 5406 unique reflections. The structure was solved by direct methods using the programs MITHRIL [16] and DIRDIF [17] and non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and their parameters refined by the use of isotropic temperature factor. The final agreement factor of full-matrix least-squares refinement based on 3655 observed reflections ($I > 3\sigma I$) was 0.032 ($R_w = 0.034$). The refinement calculations were performed using the TEXSAN crystallographic package [18]. The positional atomic parameters are given in Table 2.

## References


1 W.L. Gladfelter and G.L. Geoffroy, *Adv. Organomet. Chem., 18* (1980) 207.
2 E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem., Rev., 65* (1985) 219.
3 Polyhedron Symposia-in-Print Number 8: *The Chemistry of Heteronuclear Clusters and Multimetallic Catalysts*, Proc. Semin. Konigstein, 7–11 Sept., 1987, *Polyhedron, 7* (1988) No. 22–23.
4 E. Sappa, *J. Organomet. Chem., 352* (1988) 327, and ref. therein.
5 B.F.G. Johnson, J. Lewis, A.D. Massey, P.R. Raithby and W.T. Wong, *J. Organomet. Chem., 397* (1990) C28.
6 S.P. Tunik, M.V. Osipov and A.B. Nikol'skii, *J. Organomet. Chem., 426* (1992) 105.
7 A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, *J. Organomet. Chem., 102* (1975) 185.
8 G. Wilkinson and G.L. Geoffroy (Eds.), *Comprehensive Organometallic Chemistry, Vol. 3*, 1982, p. 1052.
9 B. Mailvbaganam, B.E. McCarry, B.G. Sayer, R.E. Perrier, R. Faggiani and M.J. McGlinchey, *J. Organomet. Chem., 335* (1987) 213.
10 F. van Meurs and H. van Koningsveld, *J. Organomet. Chem., 131* (1977) 423.
11 D. Gregson and J.A.K. Howard, *Acta Cryst., C39* (1983) 1024.
12 C.L. Sterzo, M.M. Miller and J.K. Stille, *Organometallics, 8* (1989) 2331.
13 B.F.G. Johnson, J. Lewis, P.R. Raithby and D.A. Wilkinson, *J. Organomet. Chem., 408* (1991) C9.

14 D. Seyferth, R.J. Spohn, M.R. Churchill, K. Gold and F.S. Scholer, *J. Organomet. Chem.*, *23* (1970) 237.
15 M.D. Rausch, G.A. Moser, E.J. Zaiko, Jr. and A.L. Lipman, *J. Organomet. Chem.*, *23* (1970) 185
16 C.J. Gilmor, *J. Appl. Crystallogr.*, *17* (1984) 42
17 P.T. Beurskens, Technical Report 1984/1; Crystallography Laboratory, Toernooiveld, 6525 Ed., Nijmegen, Netherlands.
18 TEXRAY *Structure Analysis Package*, Molecular Structure Corporation, Woodlands, TX, USA, 1985.