

Preliminary communication

The structure of $[\text{Co}_2(\text{CO})_5(\mu_2, \eta^4\text{-CPhCHCHCPh})]$ a cobalt analogue of the 'ferroles'

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Abstract

$[\text{Co}_2(\text{CO})_5(\mu_2, \eta^4\text{-CPhCHCHCPh})]$, a new cobaltacyclopentadiene dinuclear compound, was isolated and characterized by spectroscopic techniques. The X-ray structure of this compound has been determined.

Keywords: Cobalt; Carbonyl; Metallacycle; Alkyne; π -bonding; Cluster

Compounds of the type $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')] \mathbf{1}$ have been prepared by the reaction of a great variety of alkynes with octacarbonyldicobalt [1]. These compounds, including phosphine-substituted derivatives, have been extensively studied as stoichiometric and catalytic reagents in organic synthesis [2,3]. Complexes of the type $\mathbf{1}$ are very reactive towards alkynes, leading to 'fly-over bridge' compounds $[\text{Co}_2(\text{CO})_4(\text{RC}_2\text{R}')_3] \mathbf{3}$, which are the precursors to hindered aromatic compounds formed by ring closure [2]. The mechanism of the formation of the 'fly-over bridge' is not known, but it is thought that $\mathbf{1}$ reacts with one mole of alkyne to give a cobaltacyclopentadiene intermediate $[\text{Co}_2(\text{CO})_5(\text{RC}_2\text{R}')_2] \mathbf{2}$, which leads to $\mathbf{3}$ by coupling with a third alkyne [2] (see Scheme 1).

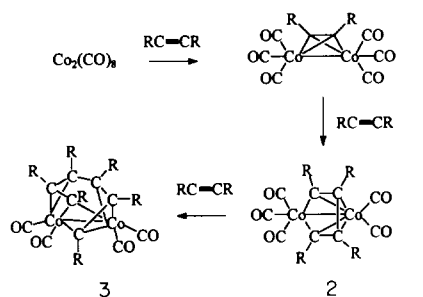
Although compounds of the type $\mathbf{2}$ have been proposed as intermediates, to our knowledge they have been structurally characterized only for two singular alkynes: cyclooctyne [4] and tetramethyldipropargyl-*N*-methylamine [5]. In both cases it has been established that the compounds of type $\mathbf{2}$ react with alkynes to give a cyclotrimerisation, supporting the proposal of their role as intermediates.

Given that isoelectronic ferracyclopentadiene compounds $[\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R}')_2]$ are common [6], it is surprising that the cobaltacyclopentadienes $[\text{Co}_2(\text{CO})_5(\text{RC}_2\text{R}')_2] \mathbf{2}$ are so rare.

Notwithstanding, some mononuclear cobaltacyclopentadienes are known and they have been used as a source of homo- and hetero-dinuclear metallacyclopentadiene complexes. This is the case of the complex $[\text{Co}(\text{C}_5\text{H}_5)(\sigma, \eta^2\text{-C}_4\text{R}_4)(\text{PPh}_3)]$ which reacts with $[\text{Co}_2(\text{CO})_8]$ in refluxing benzene giving the phosphine-substituted cobaltacyclopentadiene dinuclear compound $[\text{Co}_2(\text{C}_4\text{R}_4)(\text{CO})_4(\text{PPh}_3)]$ [7].

Recently our group reported new methods for the synthesis of homo- and hetero-dinuclear alkenyl compounds from mixtures of metal hydride, alkyne, and $[\text{Fe}_2(\text{CO})_9]$ in which the alkenyl group seemed to be formed by alkyne activation of the iron carbonyl [8,9]. As an extension of that study we allowed $[\text{Fe}_2(\text{CO})_9]$ plus phenylacetylene in THF to react with a $[\text{Co}(\text{CO})_4]^-$ /trifluoroacetic acid mixture at low temperature. Upon allowing the solution to warm to room temperature after 12 h of stirring, we obtained a mixture of products which was chromatographed in a silica column. The first compound isolated was $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{H})]$, and the second band contained a mixture of $[\text{Fe}_3(\text{CO})_{12}]$ and a new red compound $[\text{Co}_2(\text{CO})_5(\text{PhC}_2\text{H})_2] \mathbf{1}$, which crystallized from hexane (10% yield). Compound $\mathbf{1}$ was fully identified by spectroscopy [10]. Its ^1H NMR spectrum showed signals at 6.25 (s, 1H) and 7.48 (br, 5H) ppm. The absence of iron in $\mathbf{1}$ was confirmed by the mass spectrum which displayed the parent ion at $m/z = 462$ with the subsequent loss of five CO ligands. The most intense ion

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detected was $[\text{Co}_2(\text{PhC}_2\text{H}_2)]^+$, and other fragments observed included $[\text{PhC}_2\text{H}_2]^+$ and $[\text{Co}_2]^+$. The possibility that compound **1** might be a key intermediate prompted us to study its X-ray structure [11]. The structure and some important bond lengths and angles of **1** are given in Fig. 1. The structure of **1** consists of $[\text{Co}_2(\text{CO})_5(\text{PhC}_2\text{H}_2)_2]$ units and it can be described as a cobaltacyclopentadiene fragment η^4 -coordinated to another cobalt atom. The two cobalt atoms are coordinated by three and two CO, respectively. The Co(2) forms a cobaltacyclopentadiene ring (with Co(2)–C(12): 1.982(1), Co(2)–C(15): 1.972(1), C(12)–C(13): 1.417(1), C(13)–C(14): 1.399(1) and C(14)–C(15): 1.414(1) Å) which is asymmetrically π -bonded to Co(1) (with Co(1)–C(12): 2.019(1), Co(1)–C(13): 2.107(1), Co(1)–C(14): 2.100(1) and Co(1)–C(15): 2.027(1) Å). The C–C bonds of the cobaltacyclopentadiene show small differences from related structures [4,5], in particular the C(13)–C(14) bond, which is shorter. The hydrocarbon bridge was formed by a head-to-head coupling of two phenylacetylenes, resulting in a 1,4-diphenylbutadiene-

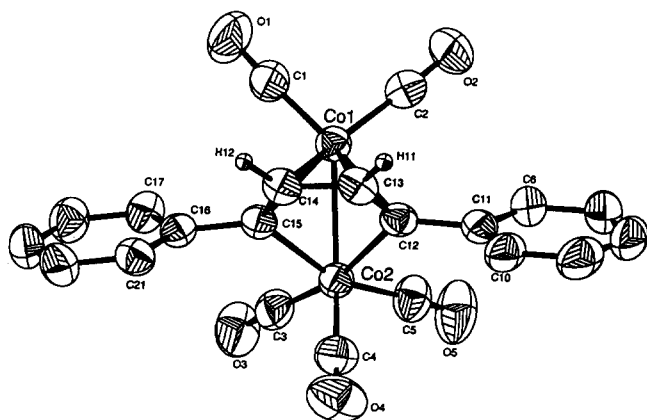


Fig. 1. Structure of the compound $[\text{Co}_2(\text{CO})_5(\mu_2, \eta^4\text{-CPhCHCHCPh})]$ **1**. Selected bond distances (Å) and angles ($^\circ$): Co(1)–Co(2) 2.503(1), Co(1)–C(12) 2.019(3), Co(1)–C(13) 2.107(3), Co(1)–C(14) 2.100(3), Co(1)–C(15) 2.027(3), Co(2)–C(12) 1.982(3), Co(2)–C(15) 1.972(3), C(12)–C(13) 1.417(4), C(13)–C(14) 1.399(5), C(14)–C(15) 1.414(5), C(12)–Co(2)–C(15) 80.8(1), Co(2)–C(12)–C(13) 113.2(2), C(12)–C(13)–C(14) 114.34(3), C(13)–C(14)–C(15) 114.2(3), C(14)–C(15)–Co(2) 113.9(3), Co(1)–C(15)–Co(2) 77.5(1), Co(1)–C(12)–Co(2) 77.5(1).

diyl fragment. In contrast to the ‘ferroles’, which have a semibridging CO, complex **1** has only terminal carbonyls [12]. The Co(2) atom is coordinated by three carbonyl with cobalt–carbon distances averaging 1.80 Å, whereas Co(1) is bonded to two carbonyls with cobalt–carbon bond lengths of ca. 1.74 Å. The Co(1)–Co(2) distance is 2.503(1) Å, slightly longer than in related compounds and in complexes $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{-R}^\prime)]$. This difference could arise from steric effects of the phenyl groups that are linked to C(12) and C(15), respectively, which are bonded to both cobalt atoms. The formation of compound **1** is unprecedented and, to our knowledge, this is the only case of the formation of a cobalt carbonyl compound with a ‘ferrole’ type structure, with a simple alkyne. This shows that the formation of **1** is possible only in unusual circumstances (reaction conditions or particular alkynes). The phenylacetylene dimerisation may arise from the activation of the $\text{C}\equiv\text{C}$ bond by the iron carbonyl and a subsequent coordination to cobalt carbonyl fragments. We can not rule out previous formation of a ferracyclopentadiene compound which may have transferred the organic ligand to a cobalt carbonyl fragment, although this has not been confirmed experimentally by us. The origin of **1** is under study.

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References and notes

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- [10] Preparation of **1**: 0.22 cm³ (2 mmol) of phenylacetylene were added to a 25 cm³ of a solution of 0.5 g (1.4 mmol) of $[\text{Fe}_2(\text{CO})_9]$ dissolved in dry THF at -77°C . The mixture was allowed to warm to room temperature and stirred for 12 h. Evaporation to dryness in vacuo gave a residue which was extracted with hexane and chromatographed on a column of silica using hexane as eluant. The first fraction contained brown $[\text{Co}_2(\text{CO})_6(\text{PhCCH})]$

(70% yield). The second green fraction contained a mixture of $[\text{Fe}_3(\text{CO})_{12}]$ and **1**. The dicobalt compound $[\text{Co}_2(\text{CO})_5(\text{PhC}_2\text{H}_5)_2]$ **1** was separated by crystallisation in hexane (10% yield).

The new complex **1** was characterized by elemental analyses and spectroscopic techniques; $\nu(\text{CO})/\text{cm}^{-1}$ (hexane) 2082m, 2025vs and 1968m; ^1H NMR (CDCl_3) δ 7.48 (m, 5H) and 6.25 (s, 1H); $[\text{M}]^+ m/z = 462$.

[11] Crystals of **1** were obtained from hexane solution. Crystal data for **1**: $\text{C}_{21}\text{H}_{12}\text{Co}_2\text{O}_5$, $M = 462.17$; monoclinic, space group $P2_1/c$ (no. 14), $a = 10.562(3)$, $b = 10.4518(9)$, $c = 17.372(1)$ Å, $\beta = 95.06(1)^\circ$; $V = 1910.3(6)$ Å³, $Z = 4$; $D_c = 1.607$ g cm⁻³; $\mu =$

17.65 cm⁻¹. Measurements: Enraf-Nonius CAD4; radiation, graphite monochromated Mo-K α ($\lambda = 0.71069$ Å), $T = 293$ K, data collection range $2 < 2\theta < 50^\circ$, ω - 2θ scan, absorption correction based on psi-scan measurements; solution, SHELXS-86 program, refinement on F^2 for all reflections, SHELXL-93 program, 3355 unique reflections, 2323 observed [$I > 2\sigma(I)$], number of variables: 254, hydrogen atoms with an overall isotropic temperature factor. $R(F) = 0.0284$, $R_w(F^2) = 0.0619$ for the observed reflections. Full lists of structural parameters have been deposited at the Cambridge Crystallographic Data Centre.

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