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Preliminary communication

REARRANGEMENT OF ETHYLENE TO HYDRIDO AND ETHYLIDYNE LIGANDS AND FORMALDEHYDE DECARBONYLATION IN THE SYNTHESIS OF $[(\eta^5\text{-}C_5H_5)_4Co_4]$ DERIVATIVES. CRYSTAL STRUCTURE OF $[(\eta^5\text{-}C_5H_5)_4Co_4(\mu_3\text{-}CO)_2]$ *

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Summary

Rearrangement of ethylene to hydrido and ethylidyne ligands bonded to two faces of the tetrahedral $[Cp_4Co_4]$ skeleton ($Cp = \eta^5\text{-}C_5H_5$) in $[Cp_4Co_4(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)]$ was observed upon heating a hexane solution of $[CpCo(C_2H_4)_2]$; treatment of $[CpCo(C_2H_4)_2]$ with formaldehyde gave $[Cp_4Co_4(\mu_3\text{-}CO)_2]$, the X-ray structure of which is reported.

Convenient sources of the fourteen electron species [CpCo] or $[Cp^1Co]$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^1 = \eta^5\text{-}C_5Me_5$) are the recently reported $[CpCo(C_2H_4)_2]$ [1] and its pentamethyl derivative $[(\eta^5\text{-}C_5Me_5)\,Co(C_2H_4)_2]$ [2]. The latter complexes are of considerable interest in respect of their interaction with small molecules and organic functional groups, and as sources of the [CpCo] and $[Cp^1Co]$ fragments in cluster synthesis [3]. Coordination of a small molecule and formation of a polynuclear structure can represent different steps in molecular activation processes. Unanswered questions at present are (a) which step of the activation of a small molecule occurs at a single reaction site when cluster formation is occurring, and (b) what is the role of the polynuclear structure in generating or bonding molecular fragments? The generation of the cluster structure could in-

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*Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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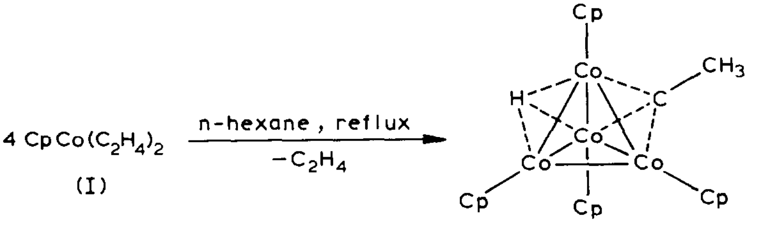
volve, for example, the reaction of a highly reactive metallic fragment with a metal-bonded species.

We deal below with the transformation of C_2H_4 and CH_2O by complex $[CpCo(C_2H_4)_2]$ [1] which is at the same time being transformed into $[Cp_4Co_4]$ derivatives.

A solution of complex I in dry n-hexane was refluxed for 4 hours. The solution changed from deep orange to brown, and standing overnight at −5°C gave black crystals of complex II (ca. 40%)*.



(I) (II) (1)

The gas present at the end of the reaction was C_2H_4 along with traces of H_2. A related rearrangement to ethylidyne was observed in the thermal decomposition of $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ [4], but that reaction differs significantly from reaction 1, in that the final compound $(\eta^5\text{-}C_5Me_5)_3Co_3(\mu_3\text{-}CCH_3)_2$ does not contain any hydrogen atom derived from the rearrangement of C_2H_4 and the organic products (ethane, butenes, hexenes, octenes, decenes) reveal a much more complex ethylene rearrangement. The structure proposed for II is confirmed by preliminary results of an X-ray study. Conversion of ethylene into H and CCH_3 fragments has been suggested to occur on metal surfaces [5], and the reaction has been related to that observed in the presence of polynuclear compounds. The latter complexes, however, are usually hydrido derivatives [6], and the mechanism by which the conversion of ethylene in ethylidyne ligand occurs is rather obscure. Reaction of cobalt-bonded ethylene with [CpCo] generated from I by the thermal reaction can be the source of complex II.

Complex I was treated with paraformaldehyde in toluene at 60°C (reaction a in Scheme 1), heating being stopped when gas evolution ceased. The gases were found to be C_2H_4, C_2H_6, H_2, and CO was absent. The solution was filtered from the excess of solid paraformaldehyde, concentrated, and kept at 0°C overnight. Black crystals of $[Cp_4Co_4(\mu_3\text{-}CO)_2]$ (III)** were obtained. Complex III was previously observed as a by-product from photochemical and thermal decomposition of $CpCo(CO)_2$ [7a] and from thermal decomposition of $[CpCo(CO)(R)]_2$

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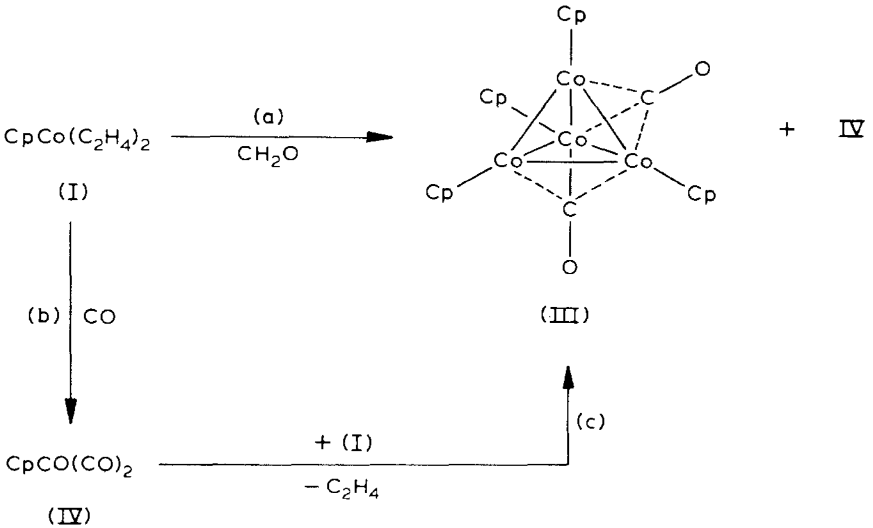
*Anal. Found: C, 50.1; H, 4.85. $C_{22}H_{24}Co_4$ calcd.: C, 50.36; H, 4.58%. The parent peak for $[Cp_4Co_4(H)(CCH_3)]^+$ was observed in the mass spectrum at *m/e* 524; ^1H NMR spectrum in C_6D_6 has peaks at δ 4.96 (s, 3 H, Me); 4.85 (s, 5 H, Cp); 4.61 (15 H, s, Cp); −19.8 (H, broad band) ppm.

**Anal. Found: C, 47.5; H, 3.82. $C_{22}H_{20}Co_4O_2$ calcd.: C, 47.85; H, 3.62%. Complex III showed the parent peak at *m/e* 552 in the mass spectrum; the ^1H NMR spectrum (C_6D_6) at 25°C has two singlets of the same intensity for the Cp ligand at δ 4.68 and 4.74 ppm; C—O stretching frequencies (Nujol mull) for the triply bridging CO fall at 1680 and 1665 cm^{-1}.



SCHEME 1

(R = Me, Et) [7b]. The solution from reaction a in Scheme 1 contained as main products III and $CpCo(CO)_2$ (IV), the latter being the only product observed upon the carbonylation of I with CO [1] (reaction b in Scheme 1).

Formation of III from formaldehyde probably involves initial formation of IV, which subsequently reacts with I. In a separate experiment we found that heating a toluene solution of IV and I gave complex III (reaction c in Scheme 1), through intermediates which are under investigation. Decarbonylation of formaldehyde via formation of hydridoformyl complexes [8] is in line with the well known metal-promoted decarbonylation of aldehydes [9]. The structure of III was determined by X-ray diffraction.

Crystal data for complex III: $C_{22}H_{20}Co_4O_2$, monoclinic, space group $P2_1/c$, a 9.147(2), b 15.304(3), c 14.165(3) Å, β 95.67(2)°, V 1973.2(7) Å^3, $Z = 4$, D_c 1.86 g cm^{-3}, $F(000) = 1104$, λ(Mo-K_α) radiation 0.71069 Å, μ(Mo-K_α) 33.2 cm^{-1}. The structure was solved by the heavy atom method and refined by full-matrix least-squares. For 2362 unique observed structure amplitudes $[I>3\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractometer in the range $5<2\theta<53°$, the current R is 0.042*.

The structure of complex IV (Fig. 1) consists of a slightly distorted tetrahedron of cobalt atoms, each coordinated to a planar η^5-bonded cyclopentadienyl ring. Two of the four faces of the Co_4-cluster are symmetrically bridged by the two carbonyl groups. The molecule possesses a local *Cm* symmetry with a mirror plane running through Co(2)—Co(3). The values of the Co—Co bonds conform with this symmetry, the Co(2)—Co(3) distance (2.455(2) Å) being significantly longer than the others, which fall in a rather narrow range (2.381(2)—2.409(2) Å). The shortest Co—Co and Co—CO bond distances belong

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*A list of fractional atomic coordinates may be obtained from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, England. The full literature citation for this Communication should accompany any request.

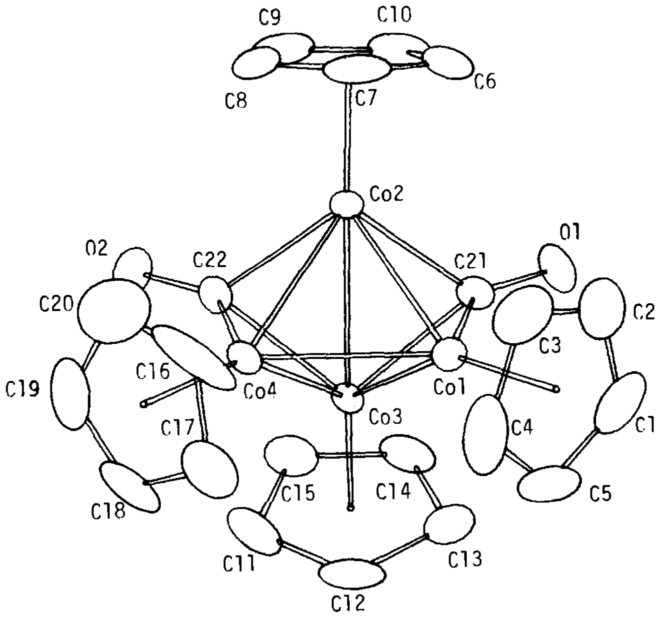

Fig. 1. Molecular structure of complex III, $[Cp_4Co_4(\mu_3\text{-}CO)_2]$. Bond distances (Å): Co(1)—Co(2), 2.381(2); Co(1)—Co(3), 2.397(2); Co(1)—Co(4), 2.395(2); Co(2)—Co(3), 2.455(2); Co(2)—Co(4), 2.409(2); Co(3)—Co(4), 2.399(2); Co(1)—C(21), 1.890(8); Co(2)—C(21), 1.946(8); Co(2)—C(22), 1.970(8); Co(3)—C(21), 1.952(8); Co(3)—C(22), 1.987(8); Co(4)—C(22), 1.890(8); Co(1)—Cp(1), 1.73(2); Co(2)—Cp(2), 1.72(1); Co(3)—Cp(3), 1.73(1); Co(4)—Cp(4), 1.73(2); C(21)—O(1), 1.21(1); C(22)—O(2), 1.20(1).

to the cobalt atoms doubly bridged by CO, Co(1)—C(21) and Co(4)—C(22), the values being 1.890(8) Å, with all the other Co—C bond distances significantly longer (1.952(8)—1.987(8) Å). Bond distances within the $[Cp_4Co_4]$ skeleton [10] and for the Co—C and C—O bonds [11] agree with those in the literature for analogous species.

The formation of $[Cp_4Co_4]$ derivatives seems to occur because the fragment [CpCo] from complex I reacts with cobalt-bonded ethylene and carbon monoxide in complexes I and IV, respectively. This process leads to coordination of molecular fragments to a polymetallic skeleton.

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