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THERMOLYSIS OF ACETYLENECOBALT COMPLEXES: A NOVEL ROUTE TO BISCARBYNE COMPLEXES, $(\mu_3\eta^1\text{-}CR^1)(\mu_3\eta^1\text{-}CR^2)[(\eta^5\text{-}C_5H_5)Co]_3$

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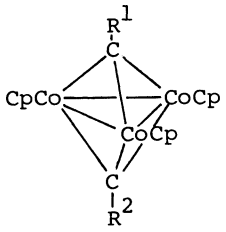
Thermolysis of (η^2-disubstituted acetylene)(η^5-cyclopentadienyl)(triphenylphosphine)cobalt appeared to be a novel route to biscarbyne complexes $(\mu_3\eta^1\text{-}CR^1)(\mu_3\eta^1\text{-}CR^2)[(\eta^5\text{-}C_5H_5)Co]_3$, one of which ($R^1$=Me, R^2=CO_2Me) was crystallographically analyzed. As an exception, thermolysis of dimethyl acetylenedicarboxylate-cobalt complex gave a novel olefin complex, $(\eta^5\text{-}C_5H_5)[\overline{CoP(Ph_2)C_6H_4C(CO_2Me)}{=}CH(CO_2Me)]$.

Recently, Vollhardt et al.[1] have reported the formation of a novel triangle cobalt cluster capped by two triply bridging carbyne ligands (1a) from the reaction of bis(trimethylsilyl)acetylene or bis(trimethylsilyl)butadiyne with η^5-cyclopentadienyldicarbonylcobalt. Now we wish to report here a more general method to obtain such a complex and a crystallographic analysis of the product.



Cp= η^5-C_5H_5

1a: R^1=Me_3Si, R^2=$Me_3SiC{\equiv}C$
1b: R^1,R^2=Ph
1c: R^1=Ph, R^2=CO_2Me
1d: R^1=Ph, R^2=CN
1e: R^1=Me, R^2=CO_2Me

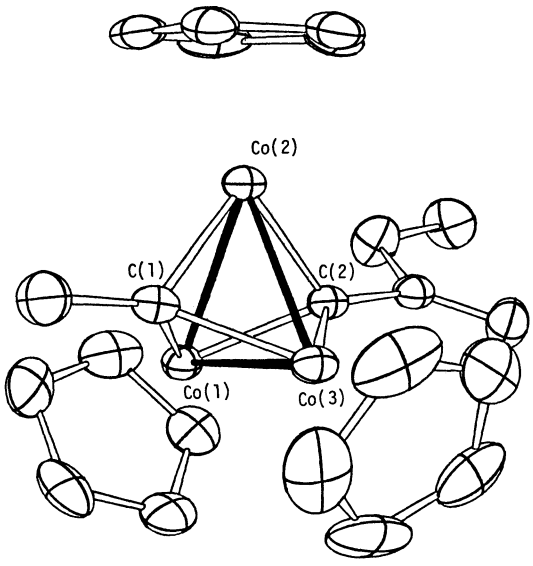
When crystals of (η^2-disubstituted acetylene)(η^5-cyclopentadienyl)(triphenylphosphine)cobalt, $Co(\eta^5\text{-}C_5H_5)(\eta^2\text{-}R^1C{\equiv}CR^2)(PPh_3)$ (2), were heated just above the melting point for a few minutes under a nitrogen atmosphere, a dark-purple crystalline complex (1b∿1e) was obtained together with (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt and/or (η^5cyclopentadienyl)(triphenylphosphine)(cobaltacyclopentadiene) complexes.[2,3] The composition of the purple complexes was $(R^1C_2R^2)(C_5H_5Co)_3$. Since $(CO)_3Fe$ and $(\eta^5\text{-}C_5H_5)Co$ moieties are isoelectronic, we originally assigned the structure analogous to that of $(PhC{\equiv}CPh)Fe_3(CO)_9$[5] to these cobalt complexes.[4]

Table 1. Physical properties of $(\mu_3\eta^1\text{-}CR^1)(\mu_3\eta^1\text{-}CR^2)[(\eta^5\text{-}C_5H_5)Co]_3$

	R^1	R^2	mp °C	NMR (ppm in $CDCl_3$) C_5H_5	CH_3	Mass m/e (%)
1b	Ph	Ph	259-260	4.41		550(65) 370(38) 361(15) 312(24) 311(12) 310(14) 302(10) 247(24) 189(100)
1c	Ph	CO_2Me	189-190	4.48	4.28	532(27) 370(6) 349(12) 247(15) 189(100)
1d	Ph	CN	294-296	4.50		499(62) 247(17) 189(100)
1e	Me	CO_2Me	222-224	4.43	4.28 4.99	470(60) 370(9) 287(14) 247(18) 189(100)

However, the close similarity of color, stability, and mass spectra of 1b~1e (see Table 1) to those of recently reported 1a promoted us to check if the structure must be revised. To clear up this, X-ray crystallographic analysis of 1e was carried out.

Crystals of 1e belong to the triclinic, space group $P\bar{1}$ (from hexane). Unit cell data are a= 13.246(3), b= 9.171(5), c= 8.942(2) Å, α= 61.52(3), β= 97.97(2), γ= 105.66(3)°, Z= 2, U= 919.3(6)Å^3, Dm= 1.69(1), Dc= 1.698 gcm^{-3}, μ(Mo Kα)= 27.35 cm^{-1}, transmission factor = 0.73-0.89. Current R is 0.048 for 3754 reflections (2θ ≤55°, Fo ≥ 3σ(Fo), Rigaku diffractometer, Mo Kα radiation).



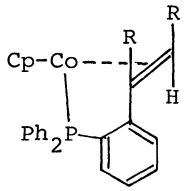
Relevant bond distances:

Co(1)-Co(2)= 2.366(1)Å
Co(2)-Co(3)= 2.366(1)
Co(1)-Co(3)= 2.393(2)
Co(1)-C(1)= 1.873(8)
Co(2)-C(1)= 1.881(7)
Co(3)-C(1)= 1.873(6)
Co(1)-C(2)= 1.867(6)
Co(2)-C(2)= 1.865(5)
Co(3)-C(2)= 1.869(8)

Figure 1. Perspective view of $(\mu_3\eta^1\text{-}CMe)(\mu_3\eta^1\text{-}CCO_2Me)[(\eta^5\text{-}C_5H_5)Co]_3$

The molecular skelton shown in Figure 1 appeared to be mostly identical to that of 1a, consisting of a triangle cobalt cluster capped by two μ_3-bonded carbyne ligands which are derived from alkyne bond cleavage. Dihedral angles of Co_3 triangle and the three η^5-C_5H_5 rings are mostly normal (90.2-90.9°). The C(1) and C(2) are separated by 2.546(9)Å.

Thus, thermolysis of 2 provides a general route to the synthesis of triangle cobalt clusters having two triply bridging carbyne ligands. However, we also observed an exceptional case. Thermolysis of 2 (R^1,R^2=CO_2Me) gave a dark-red crystalline complex which has the same composition with that of starting 2 (22% yield). The ^1H NMR spectrum in $CDCl_3$ showed a doublet centered at δ 2.05(1H), singlets at 3.45(3H), 3.68(3H) and 4.60(5H), and complex phenyl proton bands ranging from 6.5 to 8.5 ppm. The doublet may be assigned to the coordinated olefin proton coupled with ^{31}P nucleus because the coupling constant (J_{PH}=13Hz) is of the similar magnitude to those observed for olefinic protons located cis to phosphorus atom in (η^2-olefin)(η^5-cyclopentadienyl)(triphenylphosphine)cobalt complexes.[6,7] The mass spectrum of this complex showed three strong peaks, a parent peak at m/e 528.080 (17%, Calcd. for $C_{29}H_{26}O_4PCo$: 528.090), fragment ion peak at m/e 373.104 (100%, Calcd. for $C_{23}H_{18}O_3P$: 373.099) and 345.105 (87%, Calcd. for $C_{22}H_{18}O_2P$: 345.104). The latter two strong peaks suggest the bond formation between triphenylphosphine and dimethyl acetylenedicarboxylate. Based on these results we assign structure 3 to this complex.



3 Cp= η^5-C_5H_5
R= CO_2Me

The marked difference of product in thermolysis reaction may be attributed to the difference in stability of the starting complexes. When both of the substituents of the alkyne are strongly electron-withdrawing, alkyne and triphenylphosphine may be coordinated more tightly to the metal than in other complexes and have enough time to permit intramolecular addition of ortho phenyl proton to the alkyne before the alkyne undergoes degradative intermolecular reaction.

References and Notes

1) J.R.Fritch, K.P.C.Vollhardt, M.R.Thompson, and V.W.Day, J.Am.Chem.Soc., 101, 2768 (1979).

2) H.Yamazaki and Y.Wakatsuki, J.Organometal.Chem., 139, 157 (1977); ibid., 149, 377 (1978).

3) In a typical reaction, 2 (R^1, R^2= Ph) (0.8 g) was heated at 150°C for a few minutes in a flask filled with nitrogen. The resulting melted mass was dissolved in a small amount of benzene and chromatographed on alumina. A yellow and a purple zone separated on elution with benzene/hexane mixture (1/3). Work up of the eluates gave yellow crystals of (η^4-tetraphenylcyclobutadiene)(η^5-cyclopentadienyl)cobalt (0.09 g) and dark purple crystals of 1b (0.06 g). Satisfactory elemental analysis were obtained for all new compounds.

4) The complexes 1b and 3 were presented at the 21st Annual Meeting of The Chemical Society of Japan, Suita, Osaka, April 3, 1968 (Preprints III, p.1972).

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