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Preliminary communication

X-RAY CRYSTAL STRUCTURE OF TRICARBONYL (1-KETO-π-2,3,4-TRIPHENYLCYCLOBUTENYL)COBALT

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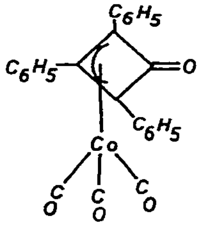
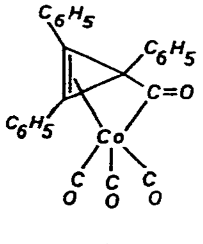
Summary

Tricarbonyl (1-keto-π-2,3,4-triphenylcyclobutenyl)cobalt provides the first example of a complex containing a keto-π-cyclobutenyl ligand.

In 1962, Coffey [1] reported the formation of $(C_6H_5)_3C_3COCo(CO)_3$ and suggested two plausible structures, I and II, for this complex. Evidence supporting structure II came [1] from oxidation of the related iron complex $(C_6H_5)_3C_3COFe(CO)_2NO$ with 1,3-diphenylallyl chloride which gave $[(C_6H_5)_3C_3^+]FeCl_4^-$. More recently, King and Efraty [2] prepared the methyl analogue $(CH_3)_3C_3COCo(CO)_3$; they found a structure of type I in good agreement with PMR and mass spectral data. Here, we report the molecular structure of $(C_6H_5)_3C_3COCo(CO)_3$.



(I)



(II)

The compound was prepared by the method of Coffey and recrystallized from hexane. The crystals are monoclinic: *a* 18.336, *b* 11.537, *c* 21.243Å, β 111.68°, *U* 4175Å^3, *Z* = 8, D_m 1.401(2), D_c 1.395 g/cm^3, space group $P2_1/a$. Since the unit cell contains eight molecules, there are two molecules per asymmetric unit. Three-dimensional X-ray data were collected with an Enraf-Nonius CAD-3 diffractometer using Mo-K_α radiation. Data were collected to

$\theta = 30°$ and 2016 independent reflections ($F^2 \geqslant 2.5\ \sigma$) from a total of 5775 were used in the refinement. Cobalt coordinates could not be located easily from a Patterson map and the structure was solved by reiterative application of Sayre's equation. Because of the large number of parameters, each molecule was refined independently and anisotropic temperature factors were used only for cobalt. Currently, $R = 0.099$.

Both molecules have the same structure I and are equivalent in their gross features. Each cobalt atom (see Fig. 1) is bonded to three terminal carbonyl groups and to a keto-π-cyclobutenyl ligand. The carbonyl groups exhibit typical interatomic distances [av. Co—CO distance, 1.83 Å; av. CoC—O distance, 1.12 Å] and angles [av. Co—C—O angle, 176°]. The cyclobutenyl rings are symmetrically coordinated to cobalt via allyl carbon atoms C(2)—C(4) as indicated by the Co—C distances in the figure legend. Terminal allyl carbon atoms are nearly equidistant and significantly further from cobalt than the central atom C(3). All C—C distances and C—C—C angles in the cyclobutenyl rings are equivalent to within experimental error. However, the rings are puckered slightly [dihedral angle C(1)—C(2)—C(4)/C(2)—C(3)—C(4), 10.7(11.4)°]*. Atoms C(1) and O(1) are displaced from the allyl plane by 0.20(0.21) and 0.49(0.50)Å respectively and are *exo* with respect to cobalt. The *exo* configuration and the rather long Co· · ·C(1) distances [2.440(2.370)Å] suggest very little, if any, bonding interaction between these atoms, in accord with a previous suggestion [2] based on spectroscopic evidence. Dihedral angles between the phenyl and allyl planes vary from 10 to 87° while phenyl carbon atoms bonded to the allyl groups deviate from the allyl planes by 0.08 to 0.40 Å and are also *exo* to cobalt.

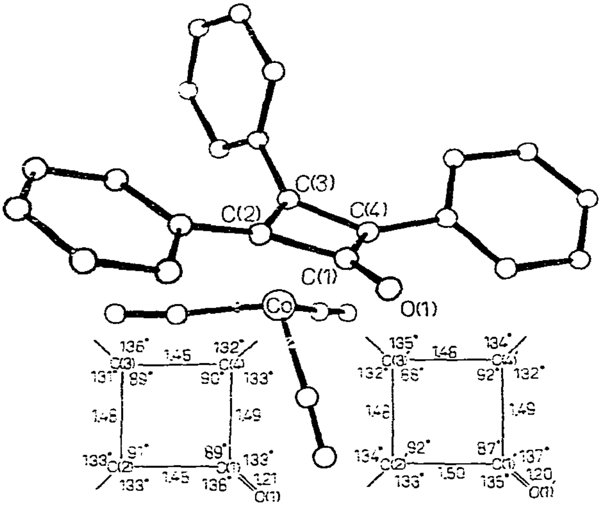


Fig. 1. Top. View of molecule II. Co—C distances are: Co—C(1), 2.440(2.370); Co—C(2), 2.121(2.113); Co—C(3), 2.017(1.981); Co—C(4), 2.135(2.074)Å. Bottom. Structural details of the cyclobutenyl rings. Average esd's for bond lengths and angles are: Co—C, 0.017; C—O, 0.024; C—C, 0.026Å; angles, 1.8°.

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* Values in parentheses refer to the second molecule in the asymmetric unit.

The present structure provides the first example of a cyclobutenyl ligand with each C_4 ring atom nominally sp^2 hybridized. Other structures known to contain cyclobutenyl ligands are $[(CH_3)_4C_4C_5H_5]NiC_5H_5$ (III) [3], $[(C_6H_5)_4C_4$-*exo*-$OC_2H_5]_2Pd_2Cl_2$ (IV) [4] and $[(C_6H_5)_4C_4$-*endo*-$OC_2H_5]_2$-Pd_2Cl_2 (V) [4]; in each of these, the non-allylic ring carbon atom is sp^3 hybridized and is effectively non-bonding with respect to the metal atom. Although internal ring angles and allylic C—C distances in III-V closely resemble those in I, a decrease from 1.56 to 1.48 Å is observed for the average C(allyl) — C(non-allyl) distance, reflecting the difference in hybridization. Lastly, the C_4 rings in I are more nearly coplanar than those in III-V; less ring deformation in I might be expected because of conjugation of the allyl and ring carbonyl moieties.

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