Crystal Structure of (π-Cyclopentadienyl)-[π-*trans*-diphenylbis(trimethylsilyl)cyclobutadiene]cobalt

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Summary In the title compound the perpendicular distances from the cobalt atom to the planes of the four- and the five-membered rings are 1·69 and 1·67 Å, respectively, the angle between the normals to these planes is 1·6° and the C–C distances associated with the π-cyclobutadienyl ring have an average value of 1·467 (3) Å.

In 1967, Rausch and Genetti reported[1] that the reaction of dicarbonyl-π-cyclopentadienylcobalt and diphenylacetylene in refluxing xylene produced, among other products, two organo-cobalt complexes, (π-cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt and (π-cyclopentadienyl)(tetraphenyl cyclobutadienone)cobalt. This preliminary report was followed by an extensive exploration of the versatility of this reaction by both Rausch and co-workers[2] and by others.[3,4] We were particularly interested in two aspects of these reports (a) the stereochemistry of the four-membered ring (b) providing confirmation to the report by Rausch[3,5] that mass spectral data could accurately distinguish between the *cis*- and *trans*-isomers that result in the course of the syntheses when asymmetric acetylenes are used. Below, we report the details of the first structural analysis of a (π-cyclobutadienyl)cobalt derivative and confirm Rausch's mass spectral prediction that the sample we received was the *trans*-isomer.

Crystal data: orthorhombic, $a = 29{\cdot}622(7)$, $b = 9{\cdot}967(2)$, $c = 17{\cdot}140(3)$ Å, $D_m = 1{\cdot}23(2)$, $D_c = 1{\cdot}24\ \mathrm{g\,cm^{-3}}$ for $Z = 8$, space group *Pbca*. The intensities of 6331 independent reflections were measured and the 3173 reflections for which $F_{\mathrm{obs}} \leqslant 3\sigma\,(F_{\mathrm{obs}})$ were used in refinement of the structure. The structure was solved by heavy-atom techniques and the refinement converged at values of $R_1 = 0{\cdot}038$ and $R_2 = 0{\cdot}044$.

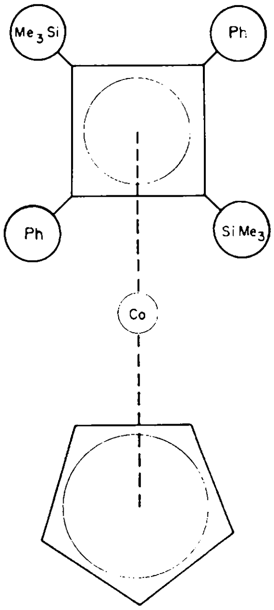

Figure. *A sketch of the molecular configuration of the title compound. As predicted from mass spectral data* (*Ref.* 5) *the crystals submitted for* X-*ray analysis were of the* trans-*diphenylbutadiene derivative.*

The molecular configuration of $(\pi\text{-}C_5H_5)[\pi\text{-}Ph_2(Me_3Si)_2\text{-}C_4]Co$ is shown in the Figure. The $\pi\text{-}C_5H_5$ group is quite normal with C–C distances which range from 1·373(6) to 1·408(6) Å to give a mean value of 1·389(17) Å. The Co–C distances range from 2·042(3) to 2·057(4) Å with a mean value of 2·049(7) Å. The Co-ring centroid distance is 1·67 Å. This compares well with such compounds as $(\pi\text{-}C_5H_5)Co(PhC_5H_5)$[6] and $(\pi\text{-}C_5H_5)Co[(CF_3)_4\ C_5O]$[7] in which the mean Co–C distances were 2·08 and 2·075 Å, respectively, and the Co-ring centroid distances were 1·67 and 1·68 Å, respectively.

The geometry and bonding in the $Ph_2(Me_3Si)_2C_4$ portion of the molecule is of great interest since one could readily visualize a variety of bonding modes between the metal and the olefin. The C–C distances associated with the four-membered ring range from 1·463(4) to 1·471(4) Å. The Co–C distances range from 1·968(3) to 2·002(3) Å with an average value of 1·982(15) Å. The Co-ring centroid distances is 1·69 Å. These results are similar to those obtained from $(\pi\text{-}PhC_4)Fe(CO)_3$[8] and $(\pi\text{-}Me_4C_4)NiCl_2,0{\cdot}5\text{-}C_6H_6$[9] in which the average C–C distances associated with the π-cyclobutadiene ring were 1·459 and 1·431 Å, respectively. The phenyl rings have an average C–C bond length of 1·382(9) Å and the average Si–C bond length is 1·864(11) Å.

The $\pi\text{-}C_5H_5$ ring is planar and the largest deviation of an atom out of the plane is 0·006 Å. The atoms of the C_4 ring are also planar within ±0·003 Å. The first carbon atoms of the phenyl rings and the Si atoms bend out of the plane of the π-cyclobutadiene ring and away from the Co atoms. The carbon atoms are 0·10 Å out of the plane while the Si atoms are 0·036 and 0·434 Å out of the plane. The plane of $\pi\text{-}C_5H_5$ ring and the cyclobutadiene ring are almost parallel, the angle between normals being 1·6°.

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