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Preliminary communication

Molecular and crystal structures of *cis*- and *trans*-(π-cyclopentadienyl)-[π-bis(trimethylsilyl)diphenylcyclobutadiene] cobalt

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Although many metal complexes with π-bonded "sandwich" structures have been studied by X-ray crystallography, no detailed investigation has been reported on (π-cyclopentadienyl)(π-cyclobutadiene)cobalt derivatives. We report here the molecular and crystal structures of both (π-cyclopentadienyl)[π-*trans*-bis(trimethylsilyl)diphenylcyclobutadiene] cobalt (I) and the corresponding *cis* isomer (II). These compounds were first prepared as a mixture by Helling, Rennison and Merijan[1], and were separated and characterized recently[2].

Suitable crystals of (I) and (II) were obtained from acetone solutions. The space group of orthorhombic (I), m.p. 161–163°, is *Pbca* with the cell dimensions: $a = 29.522$, $b = 9.949$, and $c = 17.110$ Å. The space group of (II), m.p. 133–134°, is monoclinic, $P2_1/c$ with: $a = 15.306$, $b = 10.500$, $c = 18.001$ Å and $\beta = 106.70°$. The three dimensional intensity data were collected to $2\theta = 55°$ with a Rigaku Denki four-circle automatic diffractometer using $2\theta - \omega$ scan techniques and Mo-$K\alpha$ radiation, yielding 3697 and 4773 independent reflections for (I) and (II) respectively. The structures were both solved by symbolic addition methods and by difference Fourier syntheses. Block-diagonal least-squares refinements were recycled with anisotropic thermal parameters for all non-hydrogen atoms. Although hydrogen atoms except for those in $Si(CH_3)_3$ groups were located by difference Fourier syntheses for reflections within $\sin\theta/\lambda = 0.45$, these parameters were not added to refinements. The final R factors are 0.092 and 0.073 for (I) and (II) respectively.

Figure 1 shows that both five- and four-membered rings are π-bonded to the metal, and in both isomers the skeletons of the molecular structures are of essentially the same geometry. Thus, the cobalt atom is "sandwiched" between the cyclobutadiene and cyclopentadiene groups which are both planar and parallel to each other (within 0.8°). The symmetrical axes of both five- and four-membered rings coincide with each other and the cobalt atom lies on the common axis. Interestingly, the centers of the two rings are

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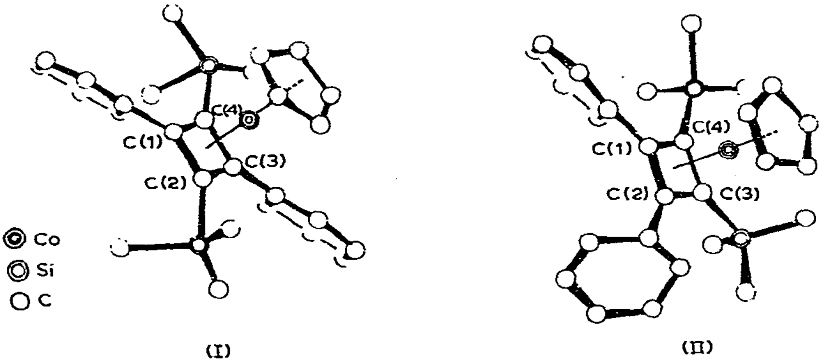

Fig. 1. The structures of (I) and (II) viewed down the *b* axes.

the same distance from the cobalt atom (1.68 Å) and consequently the Co–C distances to the four-membered ring, average value 1.97 Å, are slightly smaller than the Co–C (5-ring) distances, 2.05 Å. The values for the distances between the cobalt atom and the center of the five-membered ring in several π-cyclopentadienylcobalt complexes range from 1.62–1.67 Å[3–5]

The lengths of the C–C bonds in the five-membered rings fluctuate considerably because of a large thermal motion, but the average values for (I) and (II) are both 1.40 Å, being in good agreement with those observed in ferrocene (1.40 Å)[6], ruthenocene (1.43 Å)[7] and other π-cytoclopentadienyl cobalt complexes.

Figure 2 shows the relative positions of the four- and five-membered rings and the dimensions of the four-membered ring. The C–C bond lengths of the four-membered ring in (I) are equal within experimental error, while the length C(3)–C(4) (1.477 Å) is characteristically longer than that of C(1)–C(2) (1.435 Å) in (II). Internal ring bond

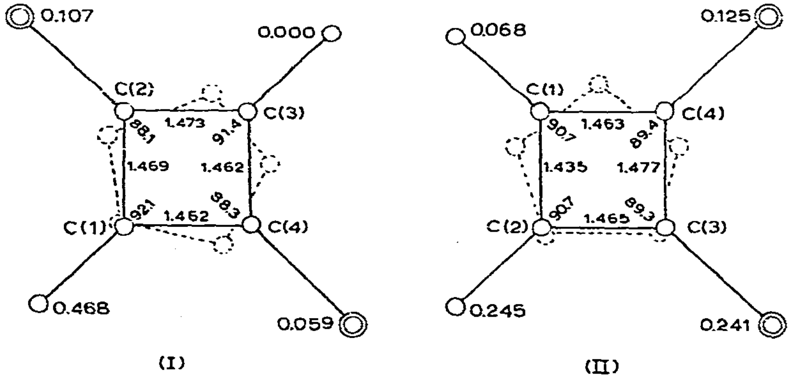

Fig. 2. Internal rotation conformers of (I) and (II) with some dimensions of the four-membered rings. E.s.d.'s in bond lengths and angles are av. 0.011 Å and 0.7°, respectively. Out-of-plane displacement of carbon and silyl atoms are shown in the unit of Å, displaced outward from the plane through the four-membered ring.

angles of (I) and (II) indicate that the cyclobutadiene ring appears to change from an exactly square form to a lozenge-shape for the former and a trapezoid for the latter. Although these deviations are only small, internal ring bond angles for all the C atoms attached to Si atoms are smaller than those to phenyl groups in both (I) and (II). Such distorsions may be due to either or both electronic or steric factors. Owing to the increase in *s*-character of the C—Si bond, which should cause a relative increase in the *p*-character of the other two C—C ring bonds, the innercyclic bond angle and bond lengths would become more acute and longer, respectively[8]. The expansion of the ring size of (I) (av. bond length 1.467 Å), as compared with the case of (π-tetraphenylcyclobutadiene)iron tricarbonyl (av. bond length 1.459 Å)[9] may be reasonably explained on the basis of such consideration.

On the other hand, we can not neglect the steric factor of the bulky trimethylsilyl group. Large out-of-plane displacements are observed for the phenyl and trimethylsilyl groups attached to carbon atoms which eclipse the corners of the five-membered ring; these displacements are due to intramolecular steric forces. Details will be reported later.

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