The Crystal and Molecular Structure of [π-(2,3-Dimethylbutadiene)$Co(CO)_2]_2$

By P McARDLE and A R MANNING*
(*Department of Chemistry, University College, Belfield, Dublin 4, Ireland*)
and F S STEPHENS
(*Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex*)

Summary An *X*-ray diffraction study has shown that [π-(2,3-dimethylbutadiene)$Co(CO)_2]_2$ has a centrosymmetric carbonyl bridged structure similar to that of [π-$C_5H_5Fe(CO)_2]_2$

IT has been suggested that the i r spectra of [π-(diene)$Co(CO)_2]_2$ complexes are only consistent with a [π-$C_5H_5Fe(CO)_2]_2$ type of structure *cis–trans*-Isomerism is thus possible, and has been observed[1,2] The *trans*-tautomers are favoured by methyl substituents on C(2) and C(3) of the butadiene ligand This behaviour may be explained on the assumption that the butadiene adopts a *cis*-conformation and that it is fixed with respect to the metal so that C(2)–C(3) lies at right angles to the Co–Co axis with C(2) and C(3) closer to the other cobalt atom than C(1) and C(4). Steric interactions between methyl substituents on C(2) and C(3) would then destabilize the *cis*-isomer[2]

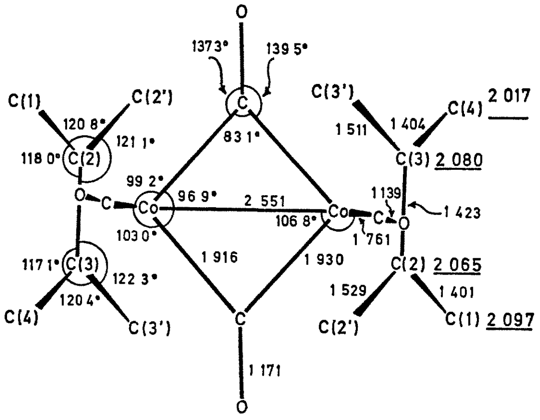

FIGURE *The molecular structure of* [π (2 3 *dimethylbutadiene*) $Co(CO)_2]_2$ *when viewed along an axis perpendicular to the* CoC_2Co *plane The underlined dimensions* (Å) *represent the* Co–C (*butadiene*) *bond lengths, and* C(2′) and C(3′) *are methyl group carbon atoms* [σ Co–Co = 0 002 Co–C = 0 006—0 008, C–O = 0 008—0 011, C–C = 0 011—0 013 Å]

I r spectral evidence indicates that [π-(2,3-dimethylbutadiene)$Co(CO)_2]_2$ exists solely as the *trans*-species both in the solid state,[2] and in solution[1,2] Brown crystals of this compound were grown from hexane solution, and one subjected to an *X*-ray diffraction study [a = 16 163 ± 0 028, b = 8·744 ± 0 014, c = 12 259 ± 0 026 Å, β = 105°40′ ± 5′, U = 1668 3 Å^3, D_m = 1 56 g cm^{-3} (by flotation), M = 394 2, Z = 4, D_c = 1 569 g cm^{-3}, space group C 2/c (C_{2h}^6, No 15)] Data were collected on a Pailred diffractometer with monochromatised Mo-K_α radiation for layers h, k, 0, and h, 0, l—h, 12, l to sin θ/λ = 0 5, 1744 non-zero unique reflections Systematic absences in the *X*-ray spectra indicated that the space group was either *Cc* or *C*2/*c*, the latter being confirmed from the three-dimensional Patterson synthesis The structure was solved by normal heavy-atom methods, and refined by full-matrix least-squares techniques with individual isotropic thermal parameters The present *R* value is 0 082

The molecular structure is illustrated in the Figure The molecule is centrosymmetric (crystallographic requirement) with a planar $Co(CO)_2Co$ bridging system The butadiene ligand is planar, but the two methyl groups, C(2′) and C(3′), lie closer to the Co atom than do C(1), C(2) C(3), and C(4) Co–C and C–C distances are similar to those found in related compounds[3] The metal–metal bond length of 2 551(2) Å is larger than the value of 2 535(2) Å found for the isoelectronic, and isostructural, compound, *trans*-[π-$C_5H_5Fe(CO)_2]_2$[4]

(*Received, January* 21*st*, 1970, *Com* 094)

---

[1] P McArdle and A R Manning, *Chem Comm* 1968, 1020
[2] P McArdle and A R Manning, *J Chem Soc* (*A*), in the press
[3] L Porri, G Vitulli, M Zocchi, and G Allegra, *Chem Comm* , 1969, 276
[4] R F Bryan and P T Greene, personal communication