The Structure of $[\pi\text{-(Diolefin)Co(CO)}_2]_2$ Complexes in Solution

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As both dicobalt octacarbonyl $Co_2(CO)_8$,[1] and π-cyclopentadienylirondicarbonyl dimer $[\pi\text{-}C_5H_5\text{-}Fe(CO)_2]_2$,[2] exist as mixtures of isomers in solution, it might be anticipated that the related $[\pi\text{-(diolefin)}Co(CO)_2]_2$ complexes[3] would also exhibit tautomerism. Our studies of the derivatives of 2,3-dimethylbuta-1,3-diene (I), cyclohexa-1,3-diene (II), and norbornadiene (III) (Table) shows that this is so.

The i.r. spectra, proton n.m.r. spectra,[3] and molecular weights[3] of (I) and (III) indicate that in solution they exist as diamagnetic dimers with terminal and bridging carbonyl groups. The i.r. spectrum of (I) (Table) is consistent only with a centrosymmetric species having a planar $Co(CO)_2Co$ unit and a molecular geometry similar to that of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ rather than the bridged form of $CO_2(CO)_8$. There is no evidence for other isomers, and so we would suggest that only *trans*-$[\pi\text{-}C_6H_{10}Co(CO)_2]_2$ is present in solution. On the other hand, (III) probably exists solely as *cis*-$[\pi\text{-}C_7H_8Co(CO)_2]_2$ in solution as no other species appear to be present. The symmetric C–O stretching vibration of the bridging carbonyl groups of this molecule, though i.r. allowed, may only gain intensity by mixing with other modes of the same symmetry. As this is probably limited, a weak absorption band, B, results. This effect is characteristic of the spectra of non-centrosymmetric molecules such as $(\pi\text{-}C_5H_5)_2FeNi(CO)_3$,[4] which possess a planar $M(CO)_2M'$ unit.

Although n.m.r. studies show that (II) is diamagnetic and, presumably, dimeric in n-heptane solution, the i.r. spectrum indicates that more than one species is present. Comparison of this spectrum with those of (I) and (III) suggests that both *cis*- and *trans*-$[\pi\text{-}C_6H_8Co(CO)_2]_2$ are present. The former is the dominant isomer and gives rise to absorption bands A, B, D, and E, whilst C and an absorption band accidentally coincident with A may be assigned to the *trans*-complex. Furthermore, the i.r. spectrum of (II) is solvent-dependent. The intensity of A relative to that of E decreases markedly in donor solvents. This is consistent with the observations by Fröhlich that this compound is monomeric in benzene solution.[5]

We have also prepared the derivative of 1,2,3,4-tetramethylbuta-1,3-diene. This exhibits another form of isomerism in that it exists as the *trans*-form in solution, but the absorption band C is split into three components. This may be attributed to the fact that there are two configurations of the

The i.r. spectra of $[\pi\text{-(diolefin)Co(CO)}_2]_2$ *complexes in the* 1700—2100 *cm.*$^{-1}$ *region.* (*n-heptane solution*). *Peak positions are given in cm.*$^{-1}$*, and relative peak intensities are enclosed in parentheses.*

	A	B	C	D	E
(I)	1811(10)		1997(18·3)		
(II)	1815(10)	1824(sh)	1966 (2·7)	2002(2·8)	2026 (7·3)
(III)	1804(10)	1816(sh)		1995(4·7)	2019(16·8)

cis-1,2,3,4-tetramethylbuta-1,3-diene ligand,† and so three isomers of *trans*-$[\pi\text{-C}_8\text{H}_{14}\text{Co(CO)}_2]_2$ are possible.

From these observations, it can be seen that the structure of diolefin–cobalt carbonyl complexes in solution is dependent upon the diolefin. In an effort to clarify the nature and extent of this dependence we are extending our investigations to related compounds including the monosubstituted π-(diolefin)$\text{Co}_2\text{(CO)}_6$ derivatives.

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† Although three configurations of this ligand are theoretically possible, one may be eliminated on steric grounds.

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