A But-2-enyl–Buta-1,3-diene Complex of Cobalt

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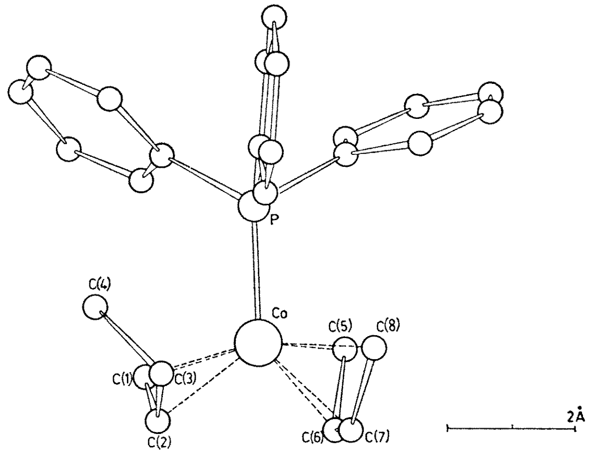
ONLY a few allyl derivatives of cobalt are known.[1] We describe the preparation and properties of two but-2-enyl complexes of Co, which are remarkably stable. Buta-1,3-diene (40 cc) reacts at 0° with (PPh$_3$)$_2$CoCl$_2$ (6 g.) and Zn powder in benzene–ethanol (3 : 1 v/v.) to give (3—4 days) a red solution, from which, after filtration and cooling to −30°, red diamagnetic crystals of formula (PPh$_3$)CoC$_8$H$_{13}$, $\frac{1}{2}$C$_6$H$_6$ (I) are deposited. Recrystallization of (I) from n-pentane gives crystals that do not contain clathrated benzene, (PPh$_3$)CoC$_8$H$_{13}$. With anhydrous HCl (I) gives buta-1,3-diene and a mixture of n-butenes, along with CoCl$_2$,PPh$_3$.

Similarly, a red diamagnetic complex of formula (PPh$_3$)-CoC$_{10}$H$_{17}$ (II) is obtained from isoprene and (PPh$_3$)$_2$CoCl$_2$: it gives isoprene and a mixture of 3-methylbut-1-ene and 2-methylbut-2-ene on reaction with HCl.

Both (I) and (II) are very soluble in aromatic or aliphatic solvents, and in ethanol; they are also soluble in chlorinated solvents, but rapidly decompose with formation of CoCl$_2$. In the crystalline state they remain unaltered in the air for several hr., while they are much less stable in solution. The complexes are recovered unchanged after treatment with either carbon monoxide or cyclo-octa-1,5-diene (boiling benzene).

Both (I) and (II) catalyze the polymerization of allene and acetylene to linear crystalline polymers.

The molecular structure of (I) has been determined by X-ray diffraction methods. The integrated intensities of 3324 reflections from a single crystal were measured with a General Electric XRD6 diffractometer down to $d \simeq 0{\cdot}9$ Å (Mo-K_α). The unit cell parameters are: $a = 9{\cdot}23(1)$; $b = 14{\cdot}94(2)$; $c = 10{\cdot}99(1)$ Å; $\alpha = 101°46'(6')$; $\beta = 124°57'(6')$; $\gamma = 83°35'(6)'$, with $Z = 2$. From the analysis of the interatomic vectors the space group was determined as $P1$. The structure was solved by Fourier methods and refined by least-squares (7 cycles) in the block-diagonal approximation using anisotropic temperature factors. The final reliability index R was 0·125 for the 2450 non-zero reflections. The cobalt atom is co-ordinated by a butadiene molecule, a 1-methylallyl group and a triphenylphosphine molecule (Figure and Table). The mean square distance of the butadiene C atoms from their average plane is 0·009 Å. The C–C bond-lengths suggest[2] that the lowest antibonding orbital of butadiene contributes significantly to the bonding in this molecule; this probably involves a significant amount of back-donation from the cobalt atom. In the but-2-enyl



FIGURE

Bonds	Distances (Å)	Bonds	Distances (Å)
Co–P	2·191(4)	C(1)–C(2)	1·425(23)
Co–C(1)	2·129(18)	C(2)–C(3)	1·431(21)
Co–C(2)	2·006(17)	C(3)–C(4)	1·528(24)
Co–C(3)	2·149(15)	C(5)–C(6)	1·467(31)
Co–C(4)	3·182(19)	C(6)–C(7)	1·405(24)
Co–C(5)	2·115(23)	C(7)–C(8)	1·462(27)
Co–C(6)	2·031(18)		
Co–C(7)	2·052(17)		
Co–C(8)	2·128(14)		

Angles		Angles	
C(1)–C(2)–C(3)	120·1°	C(1)–C(6)–C(7)	117·2°
C(2)–C(3)–C(4)	122·4°	C(6)–C(7)–C(8)	117·1°

The estimated standard deviations of the bond distances, (× 10^3), are given in parentheses: for the bond angle, $\sigma = 1°$.

group the angle C(2)–C(3)–C(4) is 122·4° and the dihedral angle defined by the planes C(1)–C(2)–C(3) and C(2)–C(3)–C(4) is 47° (σ 2°). This implies that the p orbital of C(3), not involved in the sp^2 hybridization, points in a direction rather close to the Co–C(3) axis.

The benzene molecule plays no role in the cobalt coordination and its centre coincides with the centre of symmetry at $\frac{1}{2}$, $\frac{1}{2}$, 0.

The chemical evidence indicates that complex (II) has a structure essentially analogous to that of complex (I).

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