

The Crystal Structure of [(Prop-*cis*-2-enylphenyl)diphenylphosphine]tetracarbonylmolybdenum(0)

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THE catalytic isomerisation of 2-allylphenyldiphenylphosphine ($\text{Ph}_2\text{PC}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$) to (prop-2-enylphenyl)diphenylphosphine ($\text{Ph}_2\text{PC}_6\text{H}_4\cdot\text{CH}=\text{CH}\cdot\text{CH}_3$), pp, has been shown^{1,2} to occur on formation of a complex with certain metals, Pt, Cr, Mo, and W. For M = Cr, Mo, and W, the intermediate complexes, $\text{M}(\text{CO})_4\text{pp}$ were isolated;

investigation by n.m.r. and i.r. spectroscopy indicated that they were isostructural, with the strongest M-C bonding in the tungsten compound. It appeared that the isomerisation had taken place during the formation of the metal complex to give an olefin which was π -bonded to the metal.

We have determined the crystal structure of the

complex $\text{Mo}(\text{CO})_4$ *cis*-pp from three-dimensional X-ray diffraction measurements at 150–155°K. In a triclinic unit cell having $a = 10.53$, $b = 13.26$, $c = 9.36$ Å, $\alpha = 100.3^\circ$, $\beta = 91.0^\circ$, $\gamma = 118.2^\circ$ and space group $P\bar{1}$ there are two molecules. The molybdenum and phosphorus atoms were located by Patterson syntheses and the light atoms, excluding hydrogen, from electron density difference syntheses. At present $R = 0.15$ for 3512 observations and refinement is being continued.

The stereochemistry is shown in the Figure. It establishes that deduced^{1,2} from i.r. and n.m.r. spectra. In particular the *cis* configuration of the olefinic bond in the catalytic intermediate is

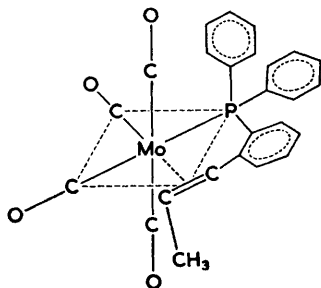


FIGURE. One molecule of [(*prop-cis-2-enylphenyl*)-*diphenylphosphine*]tetracarbonylmolybdenum(0). The drawing is somewhat idealised; in a projection with the other atoms resolved, as shown, the two unsubstituted phenyl groups overlap one another.

confirmed. The preferential formation of the *cis*-isomer which has a higher energy than the *trans*-isomer is remarkable because the stable complex $\text{Mo}(\text{CO})_4$ -*trans*-pp can be made directly from the *trans*-ligand, and experiments with models show that it could have a structure differing from that in the Figure merely by the C-CH₃ bending "upwards" instead of "downwards."

Detailed discussion of bond lengths will be deferred until refinement is complete but some features of interest are unlikely to change significantly. If the mid-point of the olefinic bond is considered as one ligand, all the angles subtended at the molybdenum atom are 90° or 180° (within 3°). Both olefinic carbon atoms lie in the plane (A) defined by the molybdenum and phosphorus atoms and two carbonyl groups. The bond length in the olefin is 1.40 ± 0.02 Å, significantly longer than a C=C double bond, while the C-C=C angles are 126° and 124°, consistent with sp^2 hybridisation without additional p character. The molybdenum to mid-point direction, shown by a broken line in the Figure, is not normal to the C(methyl)-C=C-C(phenyl) plane, the substituents are bent away from the molybdenum so that the normal to this plane makes an angle of 107° with the normal to the plane (A). This may be merely a steric effect but it is consistent with distortion arising from the presence of electrons in the antibonding π^* -orbital of the co-ordinated olefin.

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