Pseudorotation in π-Cyclopentadienyltricarbonyltungsten Hydride

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Summary An idealized 3 : 4 co-ordination geometry has been deduced for π-$C_5H_5W(CO)_3H$ and this structure has been shown to undergo a rapid intramolecular rearrangement in which carbonyl and hydride co-ordination positions are interchanged.

ONE may consider π-$C_5H_5W(CO)_3H$ as a formally seven-co-ordinate tungsten complex with three co-ordination positions occupied by the cyclopentadienyl group. Comparison of the crystal structures of the molybdenum ethyl,[1] perfluoropropyl,[2] and dimer[3] analogues suggests that the most probable stable configuration would involve 3 : 4 type co-ordination (*i.e.*, the structure with the hydrogen atom and the carbon atoms of the carbonyls lying at the corners of a square). Nevertheless, the steric requirements of a hydride ligand are less restrictive and the relative stability of other seven-co-ordinate geometries[4] should be considered. Although one might expect i.r. analysis to distinguish the 3 : 4 structure from the more symmetrical 3 : 3 : 1 structure, the distortion of the C_{3v} symmetry of the $M(CO)_3R$ moiety in the 3 : 3 : 1 structure to C_s symmetry in a 3 : 4 structure does not appear to be sufficiently great to provide a reliable delineation of geometry. That is, only two of the three expected carbonyl stretching modes for C_s symmetry are observed for the $M(CO)_3R$ moiety in π-$C_5H_5W(CO)_3CH_3$; hence the only observable effect of perturbing the idealized C_{3v} symmetry to C_s symmetry is a slight broadening of the "*E*-mode" because the *A′* and *A″* components are not resolved. Consequently, the greater half-width of the "*E*-mode" in π-$C_5H_5W(CO)_3H$ (7·0 cm.$^{-1}$) compared with that of a model C_{3v} compound, such as π-$C_5H_5Mn(CO)_3$ (5·3 cm.$^{-1}$) suggests that the structure of the hydride is based upon the 3 : 4 geometry, but is not conclusive.† We have examined the (^{13}CO)–H coupling constants in the ^1H n.m.r. spectrum of π-$C_5H_5W(CO)_3H$ in $CDCl_3$ and have concluded that not only is the 3 : 4 geometry predominant, but that this molecule is fluxional[5] and is undergoing rapid pseudorotation[6] on the n.m.r. time scale[7] at room temperature.

At temperatures below −70° one observes the ^{183}W satellites (14% abundant, $I = 1/2$) and the *cis*-(^{13}CO) satellites (1·1% abundant, $I = 1/2$) on either side of the main hydride resonance at τ 17·3 within experimental error of the expected intensity ratio of 7 : 1 : 83 : 1 : 7. The splittings indicate coupling constants of $|J(^{183}W\text{–}H)| =$ 36·7 Hz. and $|J(^{13}CO_{cis}\text{–}H)| =$ 18·5 Hz. The *trans*-(^{13}CO) coupling constant could not be measured accurately, but the splitting of *ca.* 5·5 Hz. can be observed as shoulders on the main hydride resonance of π-$C_5H_5{}^{184}W(^{12}CO)_3H$. These results are consistent with the idealized 3 : 4 structure being the lowest energy configuration and the "static" structure.

As the temperature is raised, the *cis*- and *trans*-(^{13}CO) satellites begin to broaden and then coalesce to the averaged (^{13}CO) coupling of 14·1 Hz.‡ Above 2° there are five observable resonances, including the ^{183}W satellites, in the expected ratio of 6·9 : 1·4 : 83 : 1·4 : 6·9. Since the (^{13}CO) coupling and the ^{183}W coupling (*J* 36·9) are retained in the averaged spectrum, the process which interchanges *cis*- and *trans*-carbonyls must be intramolecular. We suggest that the most likely mechanism involves a 3 : 3 : 1 transition state or intermediate. There is widespread occurrence of this stereochemically nonrigid[7] process in phosphine, phosphite, arsine, and stibine derivatives of other π-$C_5H_5M(CO)_3R$ (M = Cr, Mo, W; and R = H, alkyl, halide) complexes. Although the detailed quantitative effects of

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† The frequencies (cm.$^{-1}$) of the A_1 and "*E*" carbonyl stretching modes and their widths at half height (in parentheses) are as follows: π-$C_5H_5W(CO)_3H$, 2028 (3·3), 1939 (7·0); π-$C_5H_5W(CO)_3CH_3$, 2022 (3·7), 1932 (6·5); and π-$C_5H_5Mn(CO)_3$, 2030 (3·0) and 1947 (5·2) cm.$^{-1}$.

‡ We do not observe any side-bands from ^{13}C in the cyclopentadienyl ring; this implies that the coupling is less than 4 Hz. The averaging of the ^{13}C coupling to 14·1 Hz. instead of 10·6 Hz. requires that the *cis*- and *trans*-(^{13}CO) coupling constants have the same relative sign. It is interesting to note that the *cis*-coupling is larger than the *trans*-coupling. Similarly we have also noted that coupling to phosphorus-31 is greater for *cis*- than *trans*-phosphite or -phosphine derivatives in these π-cyclopentadienyl complexes.[8]

steric and electronic factors on the energy barrier to this "square pyramidal" pseudorotation will require further study, we have found that it is the bulkiness of the alkyl or hydride ligand which apparently predominates in the determination of the magnitude of the barrier to interconversion of isomers. Furthermore, neither the substitution of a phosphine or phosphite for a carbonyl ligand, nor increasing the size of the phosphorus-containing ligands appear to appreciably increase the barrier. That is, barriers for the hydride complexes lie within the range of 10—13 kcal./mole, whereas those of the methyl complexes lie in the range 17—20 kcal./mole for molybdenum derivatives. Halide derivatives usually exhibit still higher barriers—iodides having $E_{\mathrm{act}} > 22$ kcal./mole.

It is most important to recognise that the barriers for most hydrides are sufficiently low for averaged spectra to be observed in n.m.r. experiments performed at room temperature. This averaging has frequently led to erroneous interpretations of the quantities of *cis* and *trans* isomers of the hydrides.[9]

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