Journal of Organometallic Chemistry, 61 (1973) 311–314

THE NEMATIC-PHASE PROTON NMR SPECTRUM OF π-CYCLOPENTADIENYLTRICARBONYLTUNGSTEN HYDRIDE

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(Received March 20th, 1973)

SUMMARY

A re-evaluation of the nematic-phase NMR spectrum of $(\pi\text{-}C_5H_5)W(CO)_3H$ has shown that *three* orientation parameters are required to specify the orientation of the molecule and not one as was previously reported. Attempts to obtain additional dipolar couplings by ^{13}CO substitution failed to give a W–H bond length because of uncertainties in the structure of the $(\pi\text{-}C_5H_5)W(CO)_3$ part of the molecule, ambiguities in the signs of direct and indirect spin couplings, and difficulties in determining the three orientation parameters.

In a preliminary communication one of us reported[1] the NMR spectrum of $(\pi\text{-}C_5H_5)W(CO)_3H$ (I) in a nematic liquid crystal solvent and concluded that the hydride proton occupies a non-axial position (Fig. 1), undergoing "pseudo-rotation" giving rise to "pseudo-symmetry". There were, however, insufficient dipolar couplings to determine both the W–H bond length and the angle α (Fig. 1). It was suggested[1] that substitution with ^{13}CO might provide the additional dipolar couplings required, and a check on whether one orientation parameter was sufficient to specify the orientation of the molecule. We find that *three* orientation parameters are required to define the mean orientation and report a re-evaluation of the proton NMR spectrum and that, even with ^{13}CO substitution, we were unable to determine the W–H bond length and angle α for a number of reasons which are discussed.

Analysis of the proton NMR spectrum of the partially ^{13}CO substituted complex dissolved in N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA) gave the "best fit" parameters shown in Table 1. Errors in relative signs[1] have been corrected and the couplings redefined according to the more general scheme:

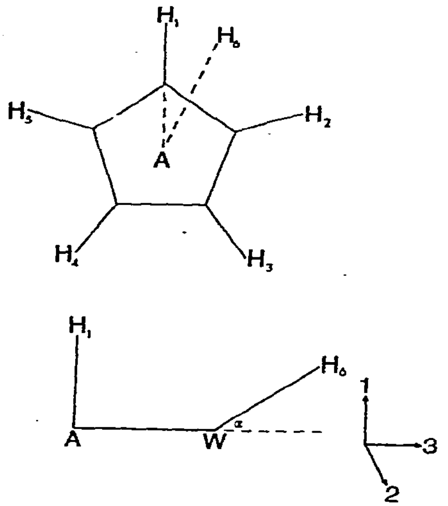

Fig. 1. The numbering of the protons in (I) and the definition of the molecule-fixed axes and angle α.

TABLE 1

NMR PARAMETERS[a] FOR (I) DISSOLVED IN MBBA AT 18°

$D_{12}(=D_A)$ 178.0 ± 0.7 $D_{13}(=D_B)$ 43.1 ± 1.1 $D_{16}(=D_C)$ −71.8 ± 1.4 Hz
$|D(^{13}CH_1)|$ 16.5 ± 3.0
$|2D(^{183}WH_6)+J(^{13}CH_6)|$ 138.0 ± 5.0 Hz $|2D(^{13}CH_6)+J(^{13}CH_6)|$ 69.1 ± 2.0 Hz
$J_{12}(=J_A)$[b] 3.0 $J_{13}(=J_B)$[b] 0.8 $J_{16}(=J_C)$ 0.0 Hz
$J(^{13}CH_1)$ 0.0 $|J(^{13}CH_6)|$[c] 14.1 $|J(^{183}WH_6)|$[c] 36.7 Hz
S_{33} 0.0606 ± 0.0002
r.m.s. error in line fitting 1.0 Hz

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[a] The original paper[1] contained an error in the sign of D_{16} (D_C), and the parameter D_D was the quantity $|J(^{183}WH_6)+2D(^{183}WH_6)|$. Also the parameter $D(^{183}WH_1)$ $(=D_E)$ was an approximate upper limit based on the experimental linewidth. We did not observe this coupling, and have omitted it in the above Table.

[b] Taken from ref. 1.

[c] Taken from ref. 4.

TABLE 2

GEOMETRICAL DATA OBTAINED FROM RELATED COMPOUNDS

r(H–C)[a]	1.093 Å
r[C–C(Cp)][b]	1.45 Å
r(A–W)[b]	2.00 Å
r(W–H)[c]	1.6 Å
r(W–C)[b]	1.96 Å
CO semi-cone angle[b]	56°

[a] Ref. 5. [b] From an X-ray study of $(\pi\text{-}C_6H_5)W(CO)_3AuP(C_6H_5)_3$ Wilford and Powell[6]. [c] The value assumed in ref. 1.

$$D_{ij} = \frac{-\hbar\gamma^i\gamma^j}{2\pi r_{ij}^3}\{S_{33}(\tfrac{3}{2}\cos^2\beta_3^{ij}-\tfrac{1}{2})+\tfrac{1}{2}(S_{11}-S_{22})(\cos^2\beta_1^{ij}-\cos^2\beta_2^{ij})$$
$$+2S_{12}\cos\beta_1^{ij}\cos\beta_2^{ij}+2S_{23}\cos\beta_2^{ij}\cos\beta_3^{ij}+2S_{31}\cos\beta_3^{ij}\cos\beta_1^{ij}\} \quad (1)$$

and β_n^{ij} is the angle between the internuclear vector and the n axis.

Reliable structural information for $(\pi\text{-}C_5H_5)W(CO)_3H$ does not exist, since the complex was affected by the X-ray beam, causing the crystallographic determination to be rather imprecise[2]. In attempting to calculate the significance of the dipolar couplings, we used structural data from related compounds given in Table 2.

An axially symmetric structure, which requires only one orientation parameter S_{33} to specify the orientation of the molecule in the liquid crystal, was eliminated[1] because the experimental value of D_{16}/D_{12} was always greater than the predicted value for all reasonable structures. The hydride proton must, therefore, occupy a non-axial position similar to the C_2H_5 group in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$[3]. The isotropic NMR spectrum shows that at room temperature (I) is undergoing rapid intramolecular rearrangement in which the CO and H coordination positions interchange[4]. This may be considered as "pseudo-rotation"[4] giving rise to "pseudo-symmetry"[1] which could reduce the number of independent orientation parameters if the rearrangement were rapid compared to the orientation time. The absence of a marked variation of D_{16}/D_{12} with temperature or concentration was taken[1] to suggest strongly that, "notwithstanding its apparently low symmetry, the molecular orientation is determined, to a good approximation, by a single orientation parameter S_{33}". On this basis the half-cone angle α (Fig. 1) was computed as $53 \pm 3°$, using 3-point averaging and assuming a W–H bond length of 1.6 Å. If, however, this cone angle is used to calculate $D(^{183}WH_6)$ we find that it has a value of -3.2 Hz. This is very different from values obtained from Table 1 and indicates that the assumption that the orientation of (I) may be described by a single orientation parameter is false.

The rapid rotation of the $\pi\text{-}C_5H_5$ group reduces the number of independent orientation parameters. In an attempt to obtain additional dipolar couplings to solve unambiguously for the position of the hydride proton we prepared a sample enriched with ^{13}CO by thermal exchange in n-hexane solution. An infrared spectrum showed that approximately 40% of the molecules were $(\pi\text{-}C_5H_5)W(^{12}CO)_2(^{13}CO)H$. Nematic-phase spectra were obtained showing $^{13}C\text{–}H_1$ and $^{13}C\text{–}H_6$ couplings. The observed splittings give $|2D_{ij}+J_{ij}|$, in which both D_{ij} and J_{ij} can have positive or negative signs. If the sign of J_{ij} is unknown, as for $J(^{183}WH_6)$, there are four possible values for D_{ij}. It is possible in theory to overcome the ambiguity in the sign of D_{ij} by using well-determined structural parameters from another technique to compute trial values of D_{ij} which could be refined by iteration. For (I) the X-ray data[2] are not good enough to allow this to be done and suitable distances had to be taken from related compounds (Table 2). It was hoped that $D(^{13}CH_1)$ and D_{16} would give S_{11} and S_{31} since S_{33} was already known from D_{12} and D_{13}, which do not depend on S_{11} and S_{31}. By means of a numerical-integration program, we found that $D(^{13}CH_1)$ and D_{16} have a very similar dependence on S_{31} and are insensitive to variations in both S_{31} and S_{11}, while $D(^{183}WH_6)$ and $D(^{13}CH_6)$ do vary with S_{31} and S_{11}. The insensitivity of $D(^{13}CH_1)$ and D_{16} to variations in S_{31} and S_{11} accounts for the observation[1] that D_{16}/D_{12} remains constant over a range of temperature; a more serious consequence is that $D(^{13}CH_1)$ cannot be used to obtain S_{11} or S_{31}. The combination of the ambiguity of signs and the unfortunate coincidences which prevent the determination of S_{11} and S_{31} from proton magnetic resonance studies, make it impossible for us to deduce a W–H bond length and the angle α. ^{13}C NMR observations might help in the determination of S_{11} and S_{31}.

ACKNOWLEDGEMENTS

We thank Miss F. A. Shipway for her preliminary analysis of this problem, the S.R.C. for a Studentship to D.B., the Royal Society for a Pickering Research Fellowship to A.J.R. and I.C.I. Limited for the use of their 220 MHz spectrometer at Runcorn.

REFERENCES

1 M. C. McIvor, *J. Organometal. Chem.*, 27 (1971) C59.
2 P. L. Johnson, *Diss. Abstr.*, 29 (1968) B1626.
3 M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, (1963) 273.
4 J. W. Faller, A. S. Anderson and C.-C. Chen., *J. Chem. Soc. D*, (1969) 719.
5 L. E. Sutton (Ed.), *Supplement to Tables of Interatomic distances*, Spec. Publ. Chem. Soc. 18, London, 1965.
6 J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, (1969) 8.