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Preliminary communication

PENTACARBONYLTUNGSTEN COMPLEXES OF *cis*- AND *trans*-AZOISOPROPANE. AZO LIGAND GEOMETRY EFFECTS ON THE FORMATION AND PROPERTIES OF ORGANOMETALLIC COMPLEXES

M.N. ACKERMANN*, D.B. SHEWITZ and C.R. BARTON
Department of Chemistry, Oberlin College, Oberlin, Ohio 44074 (U.S.A.)
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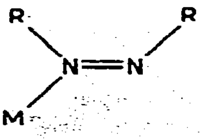
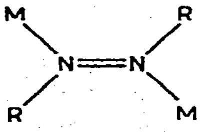
Summary

A pair of azo ligand complexes $W(CO)_5L$ (L = *cis*- or *trans*-azoisopropane) are reported in which ligand geometry is the only structural difference. The properties and particularly the difference in dynamical behavior of the complexes is discussed.

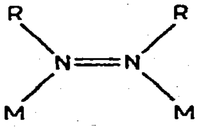
The coordination chemistry of the azo linkage ($-\ddot{N}=\ddot{N}-$) has been a fertile area of recent research [1,2]. Although a variety of coordination modes for the azo group have been found [3], the relative importance of a *cis* or *trans* geometry of the free ligand azo linkage in promoting effective coordination has received little attention. Ideally an investigation of the role of ligand geometry should involve comparison of complexes in which the only difference is in geometry of the azo group of the ligand. Until recently the only free ligands available in both *cis* and *trans* forms have been azobenzene (azb) and its substituted analogs; Herberhold [4] has observed a difference in the coordination behavior of the isomers of azobenzene. The complex (*cis*-azb)$Cr(CO)_5$ (I: M = $Cr(CO)_5$, R = C_6H_5) was obtained from the reaction of $Cr(CO)_5(THF)$ with the free ligand. The same procedure did not yield an analogous *trans*-azobenzene complex with that ligand but instead a bridging complex $[(CO)_5Cr]_2$(*trans*-azb) (II: M = $Cr(CO)_5$, R = C_6H_5) was isolated.



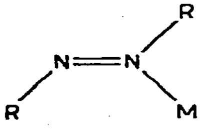
(I)



(II)



(III)



(IV)

In a different approach Sellmann has reported the synthesis of the bridging diazene complex $[Cr(CO)_5]_2N_2H_2$ by an in situ ligand synthesis [5]. Based on infrared spectroscopic data he argues for both *cis* and *trans* forms (II and III, R = H, M = $Cr(CO)_5$) with the *trans* form more stable in tetrahydrofuran solution. Despite these reports the extreme instability of free diazene and the facile thermal and photochemical conversion of *cis*-azobenzene to the *trans* form do not make these two ligand systems very promising candidates for exploring ligand geometry effects on azo ligand coordination. Consequently we have begun to examine this question using the ligand pair *cis*- and *trans*-azoisopropane (*c*-AIP and *t*-AIP) which are the earliest examples of isomeric acyclic, non-aromatic azo compounds in which the *cis* form is both reasonably stable and available in amounts suitable for synthetic studies [6,7]. Our work has enabled us to isolate a pair of complexes in which ligand geometry is unambiguously the only structural difference and which show interesting property differences.

The two isomeric complexes are obtained from addition of the free ligand to a tetrahydrofuran (THF) solution of photochemically prepared $W(CO)_5(THF)$. Removal of the solvent followed by chromatography on Florisil or alumina with petroleum ether/dichloromethane eluant gives a major yellow band of the product contaminated with varying amounts of $W(CO)_6$. Pure yellow $W(CO)_5$(*t*-AIP) (IV: M = $W(CO)_5$; R = $CH(CH_3)_2$), m.p. 81—83°C, is obtained in ~10% yield after repeated chromatography on alumina to remove $W(CO)_6$ followed by sublimation (40°C/10^{-2} torr). Yellow-orange $W(CO)_5$(*c*-AIP) (I: M = $W(CO)_5$, R = $CH(CH_3)_2$), m.p. 32—34°C, is obtained in ~35% yield by low temperature crystallization of the oil obtained from a single chromatography on Florisil.

The $W(CO)_5$(*t*-AIP) product has carbonyl bands at 2072m, 1968vw, 1940vs, 1933s(sh) and 1890vw cm^{-1} in hexane as expected of a pentacarbonyl system. The NMR (acetone-d_6; TMS internal standard) shows two inequivalent isopropyl groups with two septets at τ4.71 and 5.91 ppm* and two doublets at τ8.65 and 8.78 ppm as expected for σ-coordination of only one nitrogen atom. Both septets are shifted substantially downfield from the free ligand value of τ6.47 ppm but the methyl protons at τ8.86 ppm in the ligand are only slightly shifted. For the *cis* product all five ν(CO) bands at 2072m, 1982m, 1938vs, 1933s(sh), and 1915s cm^{-1} are unusually strong for an $LW(CO)_5$ system and indicate significant deviation from an ideal C_{4v} symmetry. At probe temperature (~35°C) the NMR reveals only one type of isopropyl group with the septet and doublet at τ5.49 and 8.62 ppm, respectively. These are only slightly downfield shifted from the corresponding free ligand signals at τ5.86 and 8.80 ppm. Upon lowering the temperature the NMR signals of $W(CO)_5$(*c*-AIP) broaden and at 6°C the methyl protons begin to show four peaks. A limiting spectrum is reached by −30°C with two sharp methyl doublets at τ8.63 and 8.57 ppm. For the weaker CH signals a high resolution spectrum reveals two closely overlapped septets with centers at τ5.49 and 5.38 ppm. Clearly the *cis* ligand complex is undergoing rapid exchange between the two

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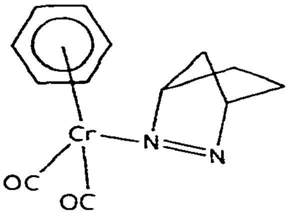
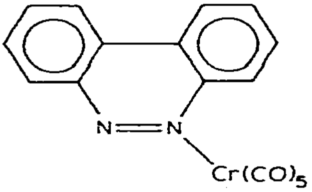
*The coupling constant for the two types of protons in the isopropyl group is about 6.5 Hz in both the free ligands and complexes.

equivalent nitrogen lone pair coordination sites at room temperature. This contrasts sharply with the *trans* ligand complex, which shows no such exchange and demonstrates one striking effect of ligand geometry on the properties of azo complexes. Dynamical behavior has been observed previously for the cyclic *cis* azo ligand complexes $ArCr(CO)_2(C_5H_8N_2)$ (V) (Ar = benzene or substituted benzene) [8] and $Cr(CO)_5(C_{12}H_8N_2)$ (VI) [3] but no comparable *trans* ligand complexes were available for comparative purposes.



(V)



(VI)

The stereochemical non-rigidity observed in $W(CO)_5$(*c*-AIP) may involve either a dissociative process via formation of $W(CO)_5$ and free c-AIP, or an intramolecular process. Competitive exchange experiments between $W(CO)_5$(*c*-AIP) and *t*-AIP or triphenylphosphine (PPh_3) show no evidence of ligand exchange. These results indicate that either a dissociative process is not operative or that $W(CO)_5$(*c*-AIP) is thermodynamically much more stable than $W(CO)_5$(*t*-AIP) and $W(CO)_5(PPh_3)$. While $W(CO)_5$(*c*-AIP) may well be thermodynamically more stable than $W(CO)_5$(*t*-AIP), it seems unlikely to be more stable than $W(CO)_5(PPh_3)$. Hence we favor an intramolecular dynamic process. The difference in behavior of $W(CO)_5$(*c*-AIP) and $W(CO)_5$(*t*-AIP) follows readily from such a proposal. In the *cis* azo group the nitrogen lone pairs are on the same side of the molecule, and the activation energy for coordination site exchange by the metal atom can be relatively low since the original metal—nitrogen bond need not be entirely broken before the new one is formed. In the *trans* case the nitrogen lone pairs are diametrically opposed and the metal—nitrogen bond must be completely severed to permit coordination site exchange. It would be desirable to test for coordination site exchange in a *trans* azo ligand complex. Unfortunately $W(CO)_5$(*t*-AIP) decomposes at an appreciable rate at NMR probe temperature and is not amenable to a high temperature study.

Finally, the higher yield and superior solution stability of $W(CO)_5$(*c*-AIP) compared to $W(CO)_5$(*t*-AIP) suggest that the *cis* ligand is more effective than the *trans* ligand at complex formation. Further work with other metal systems is needed to test the range and generality of these results with tungsten.

Acknowledgements

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