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AN INTERDEPENDENT SITE EXCHANGE PROCESS OF SOME 16-ELECTRON BIS-ACETYLENE-MOLYBDENUM COMPLEXES

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Summary

The propeller-like rotations of each of the coordinated acetylenes in the 16-electron complex $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CMe)_2Cl$ are not independent and the barrier to rotation of one of the acetylenes is influenced by the orientation of the other. The barrier for the propeller-like rotation of the coordinated acetylenes in the similar cationic bis-acetylene complex, $[(\eta^5\text{-}C_5H_5)Mo(HOH_2CC{\equiv}CCH_2OH)_2CO]Cl$ is >5 kcal/mol higher than in the neutral bis-acetylene $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CCH_3)_2Cl$.

We wish to report the synthesis and characterization of two new 16-electron bis-acetylene-molybdenum complexes: $(\eta^5\text{-}C_5H_5)Mo(ClH_2CC{\equiv}CCH_2Cl)_2Cl$ and the cation $[(\eta^5\text{-}C_5H_5)Mo(HOH_2CC{\equiv}CCH_2OH)_2CO]Cl$. These complexes are easily synthesized in relatively high yield (47—80%) by refluxing $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ and the free ligand. The best yields of the neutral 1,4-dichloride are obtained by refluxing in hexanes in a 1/5 mol ratio and the 1,4-diol in methylene chloride in a 1/1 mol ratio of acetylene to molybdenum complex.

The complex $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CMe)_2Cl$ [1] has three rotamers, I, II, and

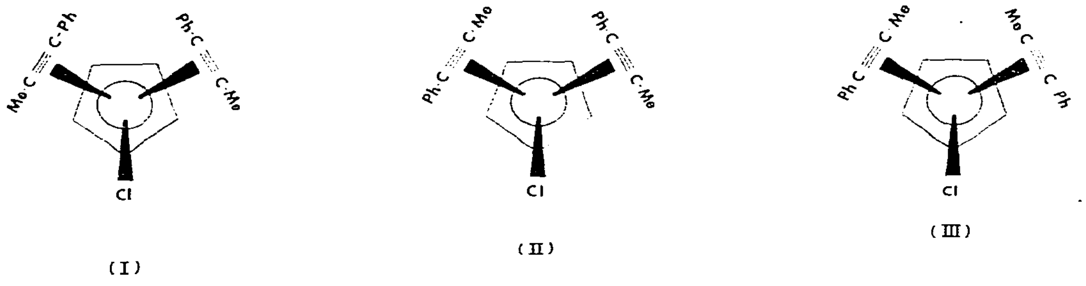

Fig. 1. The rotamers of $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CMe)_2Cl$.

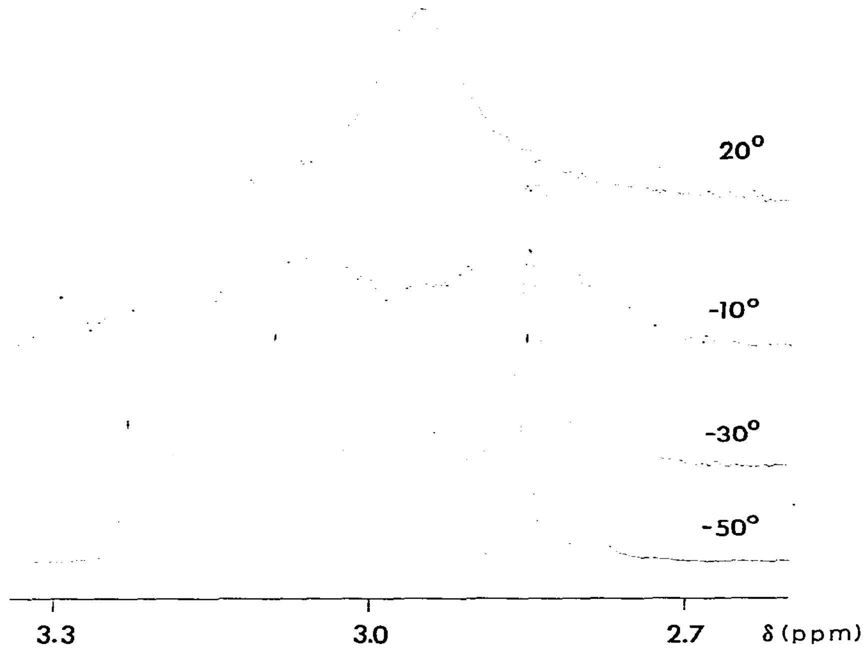

Fig. 2. The averaging of the methyl proton resonances of $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CMe)_2Cl$ at 270 MHz in CD_2Cl_2. Broadening of the δ 2.79 ppm *cis* resonance is already apparent in the —50°C spectrum; whereas the δ 3.23 ppm *cis'* resonance is still sharp. At —30°C the *trans* resonances at δ 3.08 and 2.85 ppm are broadened appreciably by exchange with the *cis* resonance; however, only slight broadening of *cis'* is observed.

III, distinguished by the relative orientation of the complexed acetylene substituents to the chloride ligand. Complexes I and III are *cis* isomers and II is *trans* isomer (see Fig. 1).

In the slow exchange limit (<—75°C) three proton resonances in the $\eta^5\text{-}C_5H_5$ region (δ —5 ppm) are observed, one resonance for each rotamer. In the methyl region (δ —2.8 ppm) of the ^1H NMR spectrum the *cis* rotamers give rise to one resonance each, the *trans* rotamer gives rise to two resonances of equal intensity. The relative populations in the slow exchange limit are *trans/cis'/cis* of 8.5/2.1/1 *. As the temperature is increased the methyl resonances of all of the rotamers are seen to broaden and coalesce into a single resonance. Careful examination of the line shapes of the proton spectra as a function of temperature (see Fig. 2) indicates that the *trans—cis* exchange is faster than the *trans—cis'* exchange. The high field *cis* resonance broadens into the baseline and extensive broadening of the *trans* resonances occurs before significant broadening of the low field *cis'* resonance. A pathway consistent with these observations is given in Scheme 1.

NMR line shape analysis of the proton spectra in the region of slow exchange indicates that the rate constants for *trans* → *cis* exchange differ by an order of magnitude depending upon which *cis* isomer is involved. This is reflected in a difference of 1.2 kcal mol^{-1} between II → I and II → III for $\Delta G^{\neq}$. Precisely

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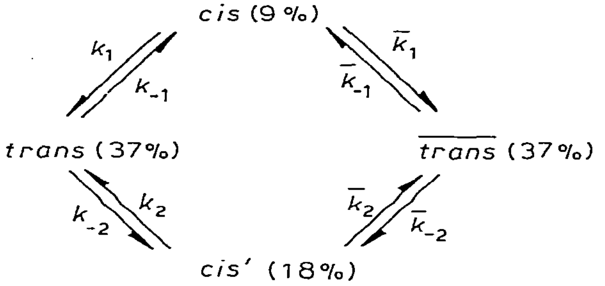
* The assignment of I or III to *cis* and *cis'* is uncertain.

SCHEME 1



$k_1 = \bar{k}_1 = 29\ \mathrm{sec}^{-1}$

$k_2 = \bar{k}_2 = 2.4\ \mathrm{sec}^{-1}$

$k_{-1} = \bar{k}_{-2} = 6.8\ \mathrm{sec}^{-1}$

$k_{-2} = \bar{k}_{-2} = 1.2\ \mathrm{sec}^{-1}$

which *cis* isomer is more stable has not been determined. These observations indicate that the barriers and rate constants for rotation of one of the complexed acetylenes of the *trans* isomer is governed by the relative orientation of the other complexed acetylene. Thus, it is clear that the acetylene ligands in this bis-acetylene-molybdenum complex do not rotate independently.

Rotation about different Mo(—C≡C—) axes results in isomer interconversion, see Fig. 3. If the rotation of 180° about axis 1 occurs then the *trans* isomer is converted to I. If a 180° rotation about axis 2 occurs then the *trans* rotamer is converted to III. The interconversion process was shown to be intramolecular by addition of free ligand and the absence of additional broadening of the averaged methyl resonance.

The chloroalkyne complex $(\eta^5\text{-}C_5H_5)Mo(ClH_2CC{\equiv}CCH_2Cl)_2Cl$ shows a dynamic process with a barrier very similar to the corresponding process in $(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CMe)_2Cl$, ($\Delta G^{\ddagger}_{68°} = 10.3$ kcal/mol). Since the 1,4-dichloro-2-butyne ligand is symmetrical only one isomer of $(\eta^5\text{-}C_5H_5)Mo(ClH_2CC{\equiv}CCH_2Cl)_2Cl$ is observed. In the slow exchange limit the CH_2Cl groups of the complexed acetylenes give rise to two AB quartets each with an integrated area of four protons relative to the $\eta^5\text{-}C_5H_5$ ring [3]. At +40°C, one AB quartet is observed with an integrated area of eight protons relative to the $\eta^5\text{-}C_5H_5$ ring.

The results are interpreted as the exchange of two diastereotopic protons of the complexed acetylene. A propeller-like rotation along the molybdenum—acetylene bond is postulated as the mechanism for exchange as in the bis(phenylmethylacetylene) complex. The non-equivalence requires that the process be

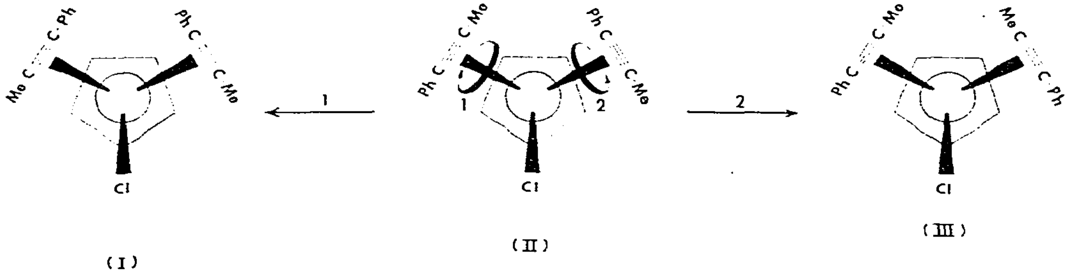


Fig. 3. The effect of rotation about different Mo—(C≡C) axes.

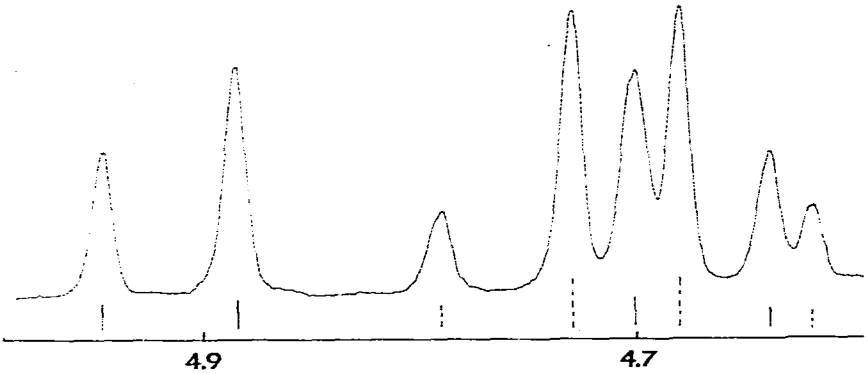


Fig. 4. The 270 MHz methylene proton region of $[\eta^5\text{-}C_5H_5)Mo(HOH_2CC{\equiv}CCH_2OH)_2CO]Cl$ in D_2O.

intramolecular and that the acetylene ligands do not exchange places.

The cationic complex $[(\eta^5\text{-}C_5H_5)Mo(HOH_2CC{\equiv}CCH_2OH)_2(CO)]Cl$ is similar to $(\eta^5\text{-}C_5H_5)Mo(ClH_2CC{\equiv}CCH_2Cl)_2Cl$ and two AB quartets (see Fig. 4) are observed in the slow exchange NMR for each complex. There is only one $\eta^5\text{-}C_5H_5$ resonance for the cation in the slow exchange limit because there is only one isomer. Slow exchange spectra are observed at room temperature, in contrast to the neutral complex. The NMR spectra show no exchange broadening up to 85° C. This implies a barrier to rotation >5 kcal/mol higher in the cation than in the neutral complexes *.

Experimental

Materials

The $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ was synthesized by a standard procedure [4]. All of the acetylene ligands were obtained from Aldrich Chemical Co. and were used without further purification, except for the 1,4-diol which was sublimed before use. All solvents were purged with nitrogen before use in either synthesis or chromatography. Melting points are uncorrected. All IR spectra were obtained on a Perkin—Elmer model 237B grating spectrometer. The NMR spectra were obtained on a Bruker HX 270 or Varian HA-100 Spectrometer. The Bruker HX 270 provides a spectrum displayed over 8000 (8192) points, which allows high accuracy in determining relative chemical shift positions. The conductivity measurements were made with a Beckman model RC16B2 bridge with an immersion electrode. A 0.01 *M* KCl solution was used as a standard in the conductance measurements [5].

$[(\eta^5\text{-}C_5H_5)Mo(HOH_2CC{\equiv}CCH_2OH)_2CO]Cl$

This cation was prepared in 48% yield by combining $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (9.40 g, 1.4 mmol) and $HOH_2CC{\equiv}CCH_2OH$ (0.165 g, 1.9 mmol) in 100 ml of methylene chloride. The reaction mixture was refluxed for 20 h. The small yellow crystals of the insoluble cation were filtered from the mixture and

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[*] A similar increase in barrier upon conversion has been noted previously in allyl rotations and oscillations [2,3].

washed with methylene chloride. These crystals, melting sharply at 124—125° C, could not be recrystallized without decomposition or hydration. Conductivity measurements in water gave a Λ_m 101.8 l Ω^{-1} mol^{-1} cm^{-1}, indicating a 1/1 electrolyte. A single carbonyl band was observed in the IR at 2073 cm^{-1} (Nujol).

Anal. Found: C, 41.32; H, 4.64. $MoC_{14}H_{17}O_5Cl \cdot \frac{1}{2}H_2O$ calcd.: C, 41.45; H, 4.47%.

The ^{1}H NMR spectrum (D_2O, ambient temperature, relative to 2,2-dimethyl-2-sila-5-pentane-sodium sulphalene (DSS)) showed a cyclopentadienyl resonance at δ 6.098 ppm; one AB methylene pattern with a coupling of 17.4 Hz at δ 4.92 and 4.67 ppm; and a second AB methylene pattern with a coupling of 16.7 Hz at δ 4.75 and 4.66 ppm (see Fig. 3). The ^{13}C-{^{1}H} NMR spectrum (D_2O, ambient temperature, DSS external standard) showed resonances at: δ 215.96 ppm for the terminal carbonyl; δ 170.65 and 150.41 ppm for the alkyne carbons; δ 101.25 ppm for the cyclopentadienyl carbons; and δ 64.86 and 62.56 ppm for the methylene carbons. The assignments were confirmed by off resonance decoupling experiments which showed triplets for the methylene carbons and a doublet of multiplets for the ring carbons.

$(\eta^5\text{-}C_5H_5)Mo(ClH_2C\text{-}C{\equiv}CH_2Cl)_2Cl$

The neutral complex was prepared by combining $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (0.40 g, 1.4 mmol) and 1.00 g (8.1 mmol) of the dichlorobutyne in 100 ml of hexane and heating to 70° C for 5 h. Upon cooling to —5° C crystals formed, were filtered from the mixture and recrystallized from a methylene chloride/hexane solvent mixture. These yellow crystals, which were formed in 82% yield (0.52 g), melted with decomposition at 99—100° C. The complex was nonionic as indicated by an observed molar conductivity of 2.13 l Ω^{-1} mol^{-1} cm^{-1} (acetonitrile).

Anal. Found: C, 35.44; H, 3.15. $MoC_{13}H_{13}Cl_5$ calcd.: C, 35,27; H, 2.95%. The ^{1}H NMR in acetone-d_6 at 54° C showed averaged resonance at: δ 5.76 ppm for the C_5H_5 ring and an AB methylene pattern with a 16.3 Hz coupling at δ 5.18 and 5.08 ppm. At —80° C the spectrum showed the cyclopentadienyl resonance at δ 5.98 ppm and two AB patterns at: δ 5.80, and 5.65 and 5.11, 5.10 ppm with splittings of 16.3 and 16.4 Hz respectively. In both fast and slow exchange each line showed small splittings (<1 Hz) from coupling between methylenes in the same acetylene, which complicates the analysis of couplings. Thus, the coupling in the high temperature AA'BB' system is less accurate and has an uncertainty of ±0.2 Hz.

$(\eta^5\text{-}C_5H_5)Mo(PhC{\equiv}CCH_3)_2Cl$

This complex was prepared following the procedure of Stone et al. [1]. At —80° C the NMR spectrum showed methyl resonances at δ 3.23, 3.08, 2.85, and 2.79 ppm in a ratio of 2.1/4.3/4.3/1. Cyclopentadienyl resonances were observed at δ 5.709, 5.674, and 5.653 ppm in ratio of 8.5/2.1/1. At 25° C the resonances averaged to yield a single methyl resonance at δ 2.92 ppm and a single cyclopentadienyl resonance at δ 5.64 ppm.

Rates

Site exchange rates were measured using computer-simulated spectra [6] generated via the Kubo—Sack matrix method [7]. In the $PhC{\equiv}CCH_3$ complex the rate for leaving the *cis* site was 5.5 sec^{-1} at —50°C ($\Delta G^{\neq}_{-50°}$ 12.2 kcal/mol) and the *cis'* site was 4.8 sec^{-1} at —30°C ($\Delta G^{\neq}_{-30°}$ 13.4 kcal/mol). The population ratios showed no significant variation between —75 and —50°C; hence population changes as a function of temperature were not included in the calculations. The barrier difference of 1.2 kcal/mol assumes that $\Delta S = 0$, as expected for an intramolecular process.

The barrier for rotation in the $ClCH_2C{\equiv}CCH_2Cl$ complex was determined from ^{13}C data because of the difficulty involved in calculating rates for exchange between two AB systems, as observed in the proton spectrum. At —68°C, the rate constant of 47 sec^{-1} implies a $\Delta G^{\neq}$ of 10.3 kcal/mol.

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