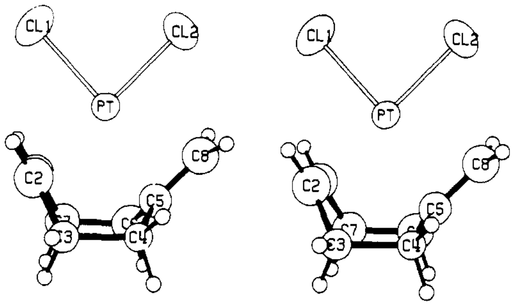

Figure 1. A stereopair drawing of dichloro(5-methylenecycloheptene)-platinum(II). The view is approximately normal to the pseudo-fourfold axis of the square plane and shows only one of the two disordered orientations. The other may be generated by rotation about the pseudo-twofold axis which bisects the ClPtCl angle.

In both cases, the Pt and Cl ligands were given anisotropic temperature factors, and the real and imaginary parts of their anamolous dispersion were considered.[13] *Model 1*: The ligands were treated as individual atoms with each olefinic carbon occupying two positions with an occupancy of one-half and with the four methylene carbons occupying average positions with occupancies of one. *Model 2*: Rigid-body refinement was carried out with one-half occupancy for each of two 5-methylenecycloheptene orientations. The ligand atom coordinates used for the rigid body were derived from molecular mechanics calculations[14] (including hydrogens) on the symmetrical boat conformation indicated by model 1. After energy minimization in the local "boat" minimum, the coordinates of C8 were slightly adjusted so that C5 is nonplanar to the same extent observed by us for other palladium(II)- and platinum(II)-olefin complexes. Therefore, rehybridization at C5 due to metal-olefin interaction was properly included.[15] Model 1 required 76 parameters and converged to a weighted residual (R_w) on the basis of $F = 0.0396$; model 2 required 56 parameters and converged with $R_w = 0.0378$. The models are self-consistent and lead to the same chemical conclusions. Since the accuracy of atom positions from model 1 is predictably poor (±0.04 Å for carbons) and since our concern is with metal-olefin interaction and not with the olefin structure per se, further discussion is based on model 2, which has an unweighted R of 0.0414 and a standard deviation of an observation of unit weight of 0.78.[16] A final difference map computed for this model had four peaks which we consider to be above noise level. They ranged in size between 1.28 and 1.00 e/Å^3, and three were located within 1 Å of the platinum. The fourth was observed ca. 0.3 Å from C4 and C7 of ligand orientations 1 and 2, respectively.

The structure (Figure 1) is monomeric with the exocyclic (C5-C8) double bond in the plane of the PtCl$_2$ unit. The two Pt-olefin bonds differ in length and, hence, presumably in strength, with the normally observed perpendicular bond being 0.1 Å shorter [2.10 (1) vs. 2.21 (1) Å to bond midpoints] than the in-plane bond. Support for the current thesis[2,5,6] that this difference is due to steric rather than to electronic requirements is clear in our observation of the very small ClPtCl angle of 86.6 (2)° compared to the usual 90 ± 1° for a normal Zeise's salt type complex.[17,18] No lengthening of the Pt-Cl bond was observed; indeed, the distance, 2.303 Å, lies at the low end of the 2.302-2.314 Å range found in the literature.[17] Other angles of interest are as follows: Cl2-Pt-C5-C8 bond midpoint, 89.7 (2)°; C1-C2 bond midpoint-Pt-C5-C8 bond midpoint, 91.5 (2)°; Cl1-Pt-C1-C2 bond midpoint, 91.8 (2)°. Related to and most likely the cause of the small ClPtCl angle is an unusually short Cl2-C8 distance of 2.75 (3) Å, which is 0.5 Å shorter than the two equivalent Cl1-C1 and Cl1-C2 distances of 3.24 (3) Å. The observed Cl2-C8 distance is, of course, a disorder-average distance. It is highly likely that the Cl2-C8 distance is greater than 2.75 Å in the "ordered" molecule. We estimate a more probable Cl2-C8 distance for the ordered structure through a (model) "rotation" of the PtCl$_2$ moiety 1.8° away from C8, about an axis through the Pt, and perpendicular to the square plane. The magnitude of the rotation was chosen to bring the C1-C2 bond midpoint-Pt-Cl1 angle to the nominal 90°. Support for the correction can be found in the chlorine thermal ellipsoids (Figure 1) which suggest two site-disordered positions for chlorines in the plane of our rotation. As a result of the 1.8° correction, the Cl2-C8 distance is increased to 2.80 Å, and the Cl1 to C1 and C2 distances decrease to 3.19 Å. Both of these can be compared to the sum of van der Waals radii for Cl and C, which is 3.35-3.7 Å. Since a certain amount of shortening of van der Waals contact is always expected for geminal groups, we suggest that the Cl1-C1-C2 distance of 3.19 Å is a valid reference point. Given that reference, a 0.4 Å shortened Cl2-C8 nonbonded repulsion is indicated, and this undoubtedly represents a great deal of steric repulsion.

Hoffmann and co-workers[2] calculated that the cis chlorines in PtCl$_3$(C$_2$H$_4$)$^-$ would be bent ca. 7° away from the "in-plane" ethylene carbons at the total energy minimum representing that olefin orientation. This prediction is borne out by the distortions extant in this structure.

In summary, we find clear evidence that steric factors play an important role in olefin coordination geometry.

Acknowledgments. We thank the National Science Foundation for support of this work through Grant CHE-78-22691 and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for assistance under Grant PRF 11375-AC3,4. G.R.W. acknowledges support from the Research Corporation Cottrell Grants program.

Supplementary Material Available: Fractional coordinates and thermal parameters (Table I), distances (Table II), and structure factors (Table III) (20 pages). Ordering information is given on any current masthead page.

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Received January 11, 1980

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(15) C8 was moved 0.15 Å away from Pt; C5 is therefore ~sp$^{2.2}$ hybridized. The position of C8 is the same in model 1 and model 2, within standard error limits.

(16) Model 2 is better at the 99.9% confidence level: W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

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(18) The structure of dipentene·PtCl$_2$ reported by N. C. Baenziger, R. C. Medrud, and J. R. Doyle, *Acta Crystallogr.*, **18**, 237 (1965), provides another example of a very small Cl-Pt-Cl angle, 86.2 (8)°, and an olefinic bond twisted 62° from the coordination plane.

A New Series of Alkyldimolybdenum($M\equiv M$) Compounds: Direct Observation of Rotation About the Triple Bond and Alkyl Ligand Transfer

Sir:

We report the synthesis of a new series of triple-bonded ethanelike transition-metal complexes of general formula Mo$_2$X$_2$(CH$_2$SiMe$_3$)$_4$.[1] ^{1}H NMR studies of these compounds provide the first direct observation of facile rotation about the triple bond.

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(1) (a) For recent reviews of the chemistry associated with triple-bonded compounds of dimolybdenum, see: M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, **11**, 356 (1978). (b) The detailed electronic structures are reviewed: F. A. Cotton, *ibid.*, **11**, 225 (1978).

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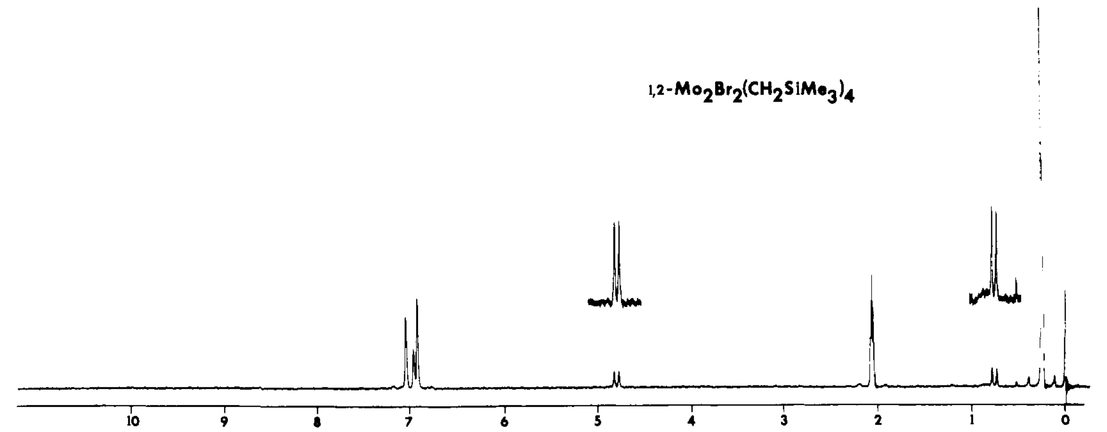


Figure 1. ^1H NMR spectrum of $Mo_2Br_2(CH_2SiMe_3)_4$ recorded at 220 MHz, 16 °C in toluene-d_8. The methyne protons form an AX spectrum are shown in the insets at higher magnification.

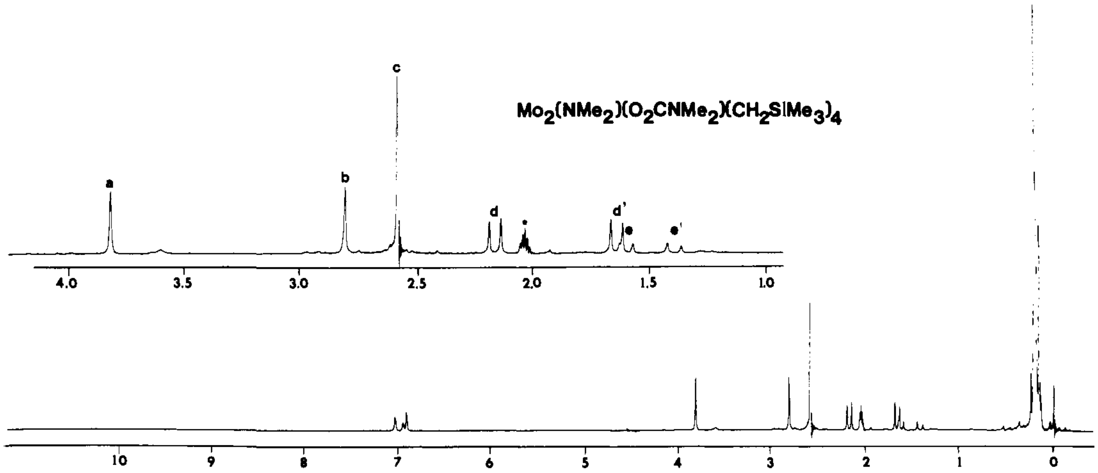
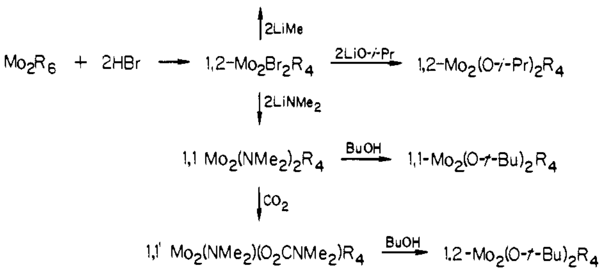


Figure 2. ^1H NMR spectrum of $Mo_2(NMe_2)(O_2CNMe_2(CH_2SiMe_3)_4$ recorded at 220 MHz, 16 °C in toluene-d_8. The inset is shown at scale expansion, ×2.5, and shows the proximal (a) and distal (b) Mo–NMe$_2$ signals, the O_2CNMe_2 signal (c), and the methylene proton resonances which form two slightly overlapping AB quartets in the integral ratio 3:1 (d, d' and e, e', respectively). The toluene-d_8 methyl proton impurity is indicated by an asterisk.

Careful addition of anhydrous HBr (2 equiv) to a saturated solution of $Mo_2(CH_2SiMe_3)_6$[2] in hexane at ca. −78 °C leads to the formation of $Mo_2Br_2(CH_2SiMe_3)_4$ as an orange crystalline compound which can be isolated in greater than 60% yield on the basis of molybdenum. The purification of $Mo_2Br_2(CH_2SiMe_3)_4$ is by toluene extraction of the solids formed upon addition of HBr, followed by low-temperature crystallization from hexane. $Mo_2Br_2(CH_2SiMe_3)_4$ is slightly soluble in toluene but essentially insoluble in hexane at low temperatures. The preparation of $Mo_2Br_2(CH_2SiMe_2)_4$ affords an entry into a new area of dimolybdenum chemistry since the Mo–Br groups are labile to a number of metathetic reactions as shown in Scheme I.[3]

1,2- and 1,1-substituted compounds are readily distinguished by ^1H NMR studies. The 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ compounds show only a single methyl resonance and an AX or AB spectrum for the methylene protons of the (trimethylsilyl)methyl ligands.[4] The ^1H NMR spectrum of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ is shown in Figure 1. The 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ compounds, where X = CH_3, O-*i*-Pr and O-*t*-Bu, show in addition only one type of X group in the temperature range −60 to +60 °C. These observations are consistent with the presence of either the pure anti rotamer or a mixture of anti and gauche rotamers which are rapidly equilibrating on the NMR time scale.

Scheme I. Reactions Leading to and Interconverting Compounds of the Form $Mo_2X_2R_4$, where R = CH_2SiMe_3



Rather interestingly, the reaction between 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ and $LiNMe_2$ (2 equiv) in hexane yields the 1,1-bis(dimethylamino) compound $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ which, upon addition of CO_2, reacts to give $(Me_3SiCH_2)(Me_2N)(Me_2NCO_2)Mo{\equiv}Mo(CH_2SiMe_3)_3$. The ^1H NMR spectrum of the latter compound is shown in Figure 2. Note the methylene protons appear as two AB quartets in the integral ratio 3:1, which implies rapid rotation about the Mo–Mo triple bond. Rotation about the Mo–N bond is, however, slow at this temperature, leading to well defined proximal and distal methyl resonances.[5]

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(2) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc. D*, 1071 (1971).

(3) Satisfactory analytical data have been obtained for these compounds. All synthetic and spectroscopic procedures require the use of dry and oxygen-free atmospheres and solvents.

(4) ^1H NMR data for the compounds 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ recorded in toluene-d_8 at 220 MHz and 16 °C. (a) X = Br: δ (Mo–CH_2) 4.76 (d), 0.73 (d, J = 11.1 Hz); δ ($SiMe_3$) 0.22. (b) X = CH_3: δ (Mo–CH_3) 1.49 (s); δ (Mo–CH_2) 1.11 (d), 2.69 (d, J = 11.8 Hz); δ ($SiMe_3$) 0.20 (s). (c) X = O-*i*-Pr: δ (OCH) 5.36; δ ($OCHMe_2$) 1.45 (d, J = 6.5 Hz); δ (Mo–CH_2) 3.63 (d), 0.01 (d, J = 12.0 Hz); δ ($SiMe_3$) 0.21 (s). (d) X = O-*t*-Bu: δ ($OCMe_3$) 1.54 (s); δ (Mo–CH_2) 3.55 (d), 0.03 (d, J = 12.0 Hz); δ ($SiMe_3$) 0.20 (s).

(5) For a discussion of rotations about Mo–NR_2 bonds in these types of molecules and magnetic anisotropy associated with Mo–Mo triple bonds, see: M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.* **98**, 4469 (1976).

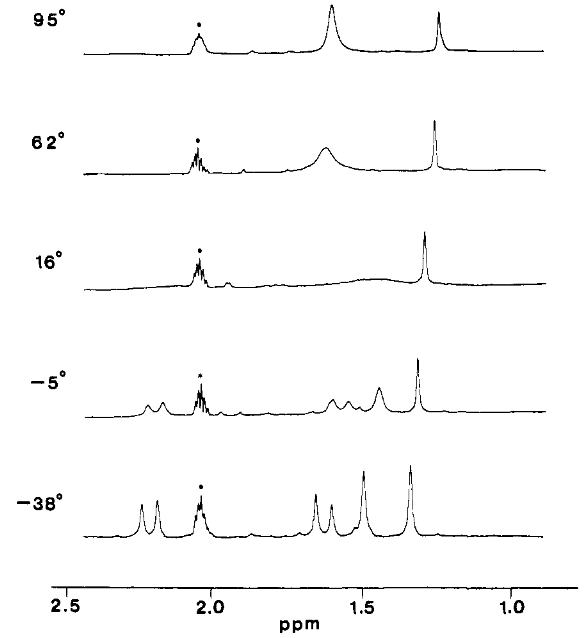
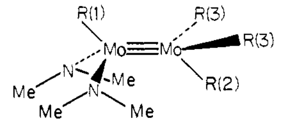


Figure 3. The methylene proton signals of a solution of $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ in toluene-d_8 recorded at various temperatures in the range −38 to +95 °C and at 220 MHz. The signals arising from toluene-d_8 methyl proton impurities are denoted by an asterisk and reveal a slight loss of resolution in both the high and low temperature limiting spectra shown in this figure. Also to be noted is the slight shift to a higher field of the methylene resonances with increasing temperature.

The variable temperature ^1H NMR spectra of $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ are particularly fascinating (Figure 3). At 220 MHz and −38 °C, the spectrum is consistent with the adoption of the frozen-out structure shown below. There are three types



of (trimethylsilyl)methyl groups, R(1), R(2), and R(3); the methylene protons associated with R(3) are diastereotopic and appear as an AB quartet while those associated with R(1) and R(2) appear as single resonances in accord with the existence of the molecular plane of symmetry which contains the anti-C–Mo–Mo–C atoms. There are proximal and distal *N*-methyl resonances. When the temperature is raised, the proximal and distal *N*-methyls coalesce to a sharp singlet as rotation about the Mo–N bonds becomes rapid and the AB quartet collapses and coalesces with one of the methylene proton singlets, leading to a simple 3:1 pattern for both the methylene and methyl groups of the (trimethylsilyl)methyl ligands above 60 °C. This is the first direct observation of rotation about a triple bond which, being cylindrical in nature, should have only a sterically imposed rotational barrier.[6]

This work also provides a direct observation of alkyl transfer between the molybdenum atoms in the dimers. This is evidently a slower process than rotation about the Mo–Mo triple bond, as seen for 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, and it remains to be determined whether alkyl transfer occurs by an inter- or intramolecular exchange process. The isolation of 1,1- and 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ from differing reactions (see Scheme I) implies the existence of a fairly sizable energy barrier to alkyl transfer in the pure ethanelike compounds. Moreover, when $Mo_2(CH_2SiMe_3)_6$ and 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ are dissolved together in hydrocarbon solvents, no $Mo_2Br(CH_2SiMe_3)_5$ is formed despite the fact that a ca. 1:2:1 distribution of the hexa-, penta-, and tetraalkyldimolybdenum compounds is formed (a) upon addition of HBr (1 equiv) to a hydrocarbon solution of $Mo_2(CH_2SiMe_3)_6$ and (b) upon addition of $LiCH_2SiMe_3$ (1 equiv) to a hydrocarbon solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_6$.[7]

Further work is in progress.[8]

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[6] Previously we have monitored anti ⇌ gauche isomerization in $Mo_2X_2(NR_2)_4$ compounds, but it has not been possible to establish that this is the effect of a "simple" rotation about the M–M triple bond. See ref 1a and references therein. An estimate for $\Delta G^\ddagger$ for rotation about the Mo≡Mo bond in 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ is 14 ± 2 kcal mol^{-1}.

[7] We have been unable to isolate pure $Mo_2Br(CH_2SiMe_3)_5$ because it is extremely soluble in hydrocarbon solvents and is thus not readily separable from $Mo_2(CH_2SiMe_3)_6$. ^1H NMR data for $Mo_2Br(CH_2SiMe_3)_5$ obtained at 220 MHz, 16 °C in toluene-d_8: $(Me_3SiCH_2)_2BrMo$, δ (CH_2) 4.56 (d), 0.66 (d, J = 11.5 Hz); δ ($SiMe_3$) 0.31 (s); $Mo(CH_2SiMe_3)_3$, δ (CH_2) 2.00 (s); δ ($SiMe_3$) 0.26 (s).

[8] We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the taxpayers of the state of Indiana for financial support of this work.

[9] Camille and Henry Dreyfus Teacher-Scholar, 1979–1984.

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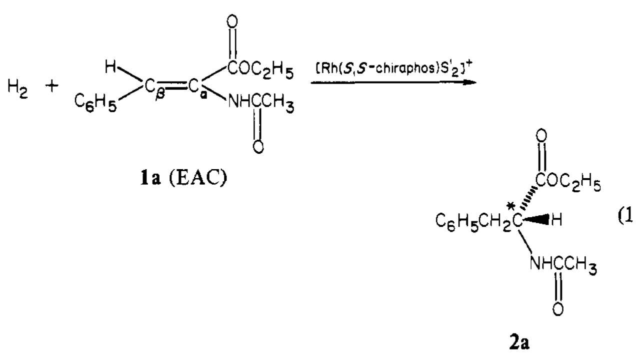
Received January 29, 1980

Identification of the Enantioselective Step in the Asymmetric Catalytic Hydrogenation of a Prochiral Olefin

Sir:

The use of chiral catalysts to effect the asymmetric hydrogenation of prochiral olefinic substrates with high optical yields represents one of the most impressive achievements to date in catalytic selectivity.[1-3] Especially high optical yields, approaching 100% enantiomeric excess, have been achieved in the hydrogenation of prochiral enamides to the corresponding amides, using homogeneous cationic rhodium catalysts containing chiral phosphine [especially chelating bis(tertiaryphosphine)] ligands (eq 1).[1-5] While various studies have documented the empirical dependence of the rates and stereoselectivities of such reactions on structural features of the catalysts and substrates, an understanding of the origin of these remarkable stereoselectivities and rational approaches to the design of such stereoselective catalysts must rest ultimately upon a mechanistic understanding which



1a (EAC)

2a

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