however, was not given. In the hydrogenation of phenanthrene, $Co_2(CO)_8$[7] and **1** behave similarly in that phenanthrene is hydrogenated very slowly in comparison to anthracene. However, **1** gave predominantly 1,2,3,4-tetrahydrophenanthrene in contrast to $Co_2(CO)_8$ which yields mainly 9,10-dihydrophenanthrene.

The $Co_2(CO)_8$-catalyzed hydrogenation of polynuclear aromatics has been postulated by Feder and Halpern to proceed via a free-radical mechanism.[8] The various features of the $Co_2(CO)_8$ system which implied the presence of radical intermediates are not seen in the hydrogenation of polynuclear aromatics with the ruthenium complex **1**. In fact, the product selectivities for the hydrogenation of anthracene and phenanthrene with **1**, as well as the relative hydrogenation rates for naphthalene and 2-methylnaphthalene, are in direct contrast to those observed for the cobalt catalyst (cf. Table I and ref 8).

The catalytic activity of **1** toward organic substrates containing polarized multiple bonds was attributed to its anionic hydride character.[1] For example, the rate of hydrogenation of acetone with **1** is sensitive to the polarity of the solvent medium, and particularly to the addition of potassium-complexing crown ethers. However, the rate of hydrogenation of naphthalene with **1** does not show such a dependence and thus appears to be unrelated to the anionic character of the catalyst. The hydrogenation of polynuclear aromatics with **1** most likely proceeds via a conventional π-coordination mechanism.

Acknowledgments. We thank Jeff Corsi and Richard Crissey for assistance in the preparation of **1**.

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[8] Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186-7188.

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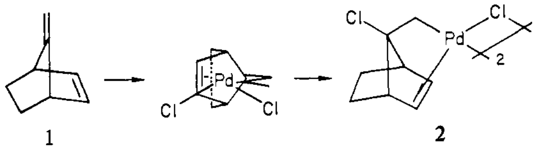
Molecular Structure of Dichloro(5-methylenecycloheptene)platinum(II). "In-Plane" Coordination of the Exocyclic Olefin

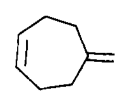
Sir:

The geometric requirements of olefins coordinated to Pt(II) have been of considerable recent interest. In two publications in this journal, Hoffmann and co-workers have utilized extended Hückel theory, first to model olefin insertion into Pt–H bonds,[1] and second to model olefin rotation about the Pt–olefin bond axis.[2] Thorn and Hoffmann[1] concluded that the olefin "insertion" process in *cis*-$L_2Pt(H)$(olefin) proceeds with the lowest activation barrier when the olefinic carbons, Pt, and ligated hydrogen all lie in the square plane of coordination. It was noted that such a coordination geometry has not been observed to date in stable d^8 square-planar olefin complexes.[3] In the second paper, Hoffmann and co-workers concluded that the olefin prefers to bind perpendicular to the coordination plane, primarily as a result of unfavorable steric interactions with the cis ligands in the "in-plane" orientation.[4] This view was presented earlier by Lewis and co-workers,[5] as well as by Ziegler and Rauk.[6]

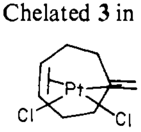
We have been interested in the synthesis of stable "in-plane" coordinated olefins for many years. We have reported[7] our results with 7-methylenenorbornene (**1**), which was expected to bind $PdCl_2$ as a diene, as shown in eq 1. The coordinated diene was not observed but was postulated to be an intermediate in the formation of the chloropalladated σ,π-chelate **2**. In unpublished work done even earlier,[8] we found that 5-methylenecycloheptene (**3**) reacted in a complex manner with $PdCl_2(PhCN)_2$ in aprotic, nondonor solvents. Concurrent with our studies of **3** and Pd(II), Anderson and Michalowski reported[9a] the synthesis and spectral characteristics of the complex $PtCl_2$·**3**, to which they assigned the monomeric structure **4**. Chelated **3** in the Pt(II) complex would seemingly require an "in-plane" or near "in-plane" geometry for the exocyclic olefin.



1 **2** (1)



3



4

In the Hoffmann paper on olefin binding and rotational barriers, doubt was raised concerning the actual (monomeric?)[9b] structure of the adduct of **3** with $PtCl_2$. Since this complex is likely to be prototypal of the "in-plane" geometry for the coordinated olefin, we decided to synthesize the complex and determine the molecular structure by X-ray diffraction.

The title compound was prepared by direct reaction of sodium tetrachloroplatinate(II) with 5-methylenecycloheptene[10] in 1-propanol. The crystalline product was filtered after standing for 24 h and was recrystallized from $HCCl_3$, yielding clear yellow needles. An orthorhombic prism, 0.25 × 0.21 × 0.15 mm, was selected for X-ray analysis. Cone-axis and zero-level precession photographs clearly gave the space group $P2_12_12_1$, and least-squares refinement of 12 carefully centered reflections with $2\theta \geq 40°$ [$\lambda_{\mathrm{Mo}\,K\alpha_1} = 0.70926$ Å] results in cell dimensions of $a_0 = 11.881$ (3), $b_0 = 7.094$ (2), and $c_0 = 11.344$ (3) Å.[11] One octant of data collected to a 2θ limit of 60° on an automated Picker FACS I diffractometer with the θ–2θ scan method (scan = 1.8 + 0.692 tan θ) yielded 1386 intensities greater than 2σ. An empirical absorption correction was made for the data on the basis of the intensity variation observed during rotation about the diffraction vector of five 00*l* reflections.[12] The maximum to minimum absorbance ratio was 4.1:1.

Due to disorder about a pseudo-twofold axis bisecting the ClPtCl angle, great care was taken in selection of refinement models. Two such models are relevant to the following discussion.

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[1] D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2079 (1978).

[2] T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, **101**, 3801 (1979).

[3] S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976); see also ref 2, citation 23.

[4] Typical barriers to olefin rotation lie in the range 10–20 kcal/mol (ref 2).

[5] C. E. Halloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

[6] T. Ziegler and A. Rauk, *Inorg. Chem.*, **18**, 1558 (1979).

[7] G. Wiger, G. Albelo, and M. F. Rettig, *J. Chem. Soc., Dalton Trans.*, 2242 (1974).

[8] Reported in the Ph.D. Thesis of George R. Wiger, Chemistry Department, University of California, 1975.

[9] (a) C. B. Anderson and J. T. Michalowski, *J. Chem. Soc., Chem. Commun.*, 459 (1972). (b) Note that this ligand need not chelate to a metal. Indeed, the lowest energy conformation of 5-methylenecycloheptene is probably a chair form which is incapable of chelation and which would have a strain energy on the order of 4–5 kcal/mol less than the boat or twist-boat conformations required for chelation. It is not unusual, in our experience, for dimer or polymer formation to occur via bridging diolefin under the circumstances.

[10] 5-Methylenecycloheptene was prepared in four steps, starting from cycloheptene-5-carboxylic acid (see ref 8).

[11] A careful search for evidence indicating the need to double the unit cell was made at the suggestion of referee II. No such evidence was found after long-exposure cone-axis and oscillation photographs were examined.

[12] A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **A24**, 351 (1968).

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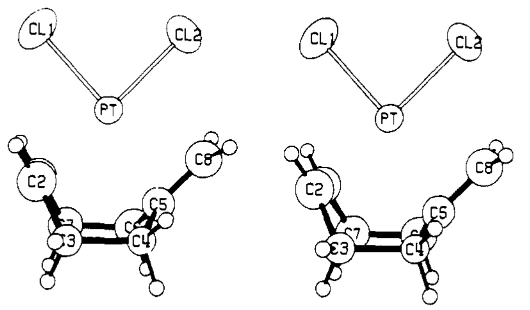

Figure 1. A stereopair drawing of dichloro(5-methylenecycloheptene)platinum(II). The view is approximately normal to the pseudo-fourfold axis of the square plane and shows only one of the two disordered orientations. The other may be generated by rotation about the pseudotwofold axis which bisects the 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 $PtCl_3(C_2H_4)^-$ 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.

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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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(13) International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.

(14) (a) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968). (b) A modified Allinger force field was used: L. J. DeHayes, Ph.D. Dissertation, Ohio State University, Columbus, Ohio (1973).

(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).

(17) (a) R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews, and R. Bau, *Inorg. Chem.*, **14**, 2653 (1975); (b) R. Mason and G. B. Robertson, *J. Chem. Soc. A*, 492 (1969); (c) J. Hubert, A. L. Beauchamp, and T. Theophanides, *Can. J. Chem.*, **51**, 604 (1973).

(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 $Mo_2X_2(CH_2SiMe_3)_4$.[1] ^1H 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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