distances themselves fully describe the geometry of the planar M_2S_2 ring.

The series of structures at hand represent a very favorable situation where we can follow the structural rearrangements in a system with constant primary geometry but varying total electron count. Hopefully this system may also offer an understanding of the electronic requirements for the transition-metal-assisted coupling or cleavage of two sulfur atoms, I.

I

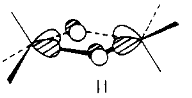
A formal counting of electrons in the complexes can be done by considering that the total charge of the S_2 grouping varies between 4– and 2–. These limits correspond either to no interaction between the sulfido anions or to a single bond between the sulfur species. Although a S–S distance of ca. 2.6 Å does not exclude some interaction between the sulfur atoms,[7] compounds **2** and **3** are near the former limit. Conversely, the short S–S distance in **1** suggests approach to the latter limit. Accordingly, the metals may be regarded as having formal oxidation state II/III (d^7/d^6) in **2**, II (d^7/d^7) in **3**, and I/II (d^9/d^8) in **1**. Therefore, the reactions leading to **1** and **2** are only stoichiometrically analogous since, in the

$$\mathrm{M(H_2O)_6{}^{2+} + triphos \xrightarrow{H_2S} [(triphos)SM]_2{}^{+}} \qquad \begin{array}{l} \mathbf{1}, \mathrm{M = Ni} \\ \mathbf{2}, \mathrm{M = Co} \end{array}$$

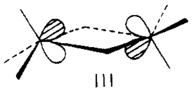
former case, a reduction of the nickel ions occurs with the formation of S–S bonding. That is to say that the formation of **1** may also be regarded as the first step toward reductive elimination of an S_2 unit from two sulfido ligands.

The bonding capabilities of the S_2 grouping are dramatically changed within the series. If the 18-electron rule is used for qualitative evaluation, $S_2{}^{4-}$ must be taken as a 10-electron donor in the cobalt complexes, while $S_2{}^{2-}$ serves as a 6-electron donor in the nickel compound. In a loose manner, total counts of 17.5 and 18 electrons can be formally calculated at each metal center in **1**, **2**, and **3** respectively.

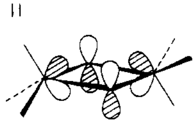
The above considerations find some support from a preliminary analysis[8] of the orbital interactions of $L_6M_2{}^{4b}$ and S_2 fragments. Frontier MOs of increasing energy are schematically shown in II–IV. III is a metal-centered MO since no combination of sulfur p orbitals can overlap positively with it. A different population of III (HOMO in **2** and **3**) cannot affect the S–S distance. The LUMO (in **2** and **3**) is IV, a metal–sulfur $\pi_{\perp}{}^*$ orbital. Its low-lying bonding counterpart, V, can be regarded as a donation of an S_2 π lone pair into appropriate metal orbitals. Besides, the other four σ lone pairs are donated to the metals, VI. II is a delocalized description of one of those, that involving the $p_{\sigma}\cdot$ combination of two sulfido anions. When IV becomes populated, as is the case in **1**, most of the sulfur to metal π donation is obviously lost; at the same time, the S–S π-bonding nature of IV may trigger a shortening of the S–S distance. The fact itself is not sufficient to fully rationalize the observed S–S coupling. On the other hand, a shortening of the S–S distance rapidly destabilizes the S_2 σ^* orbital that participates in the formation of II. Thus, on account of the progressively larger energy gap between the interacting fragment orbitals, the S_2 contribution almost disappears in II where the populating electrons acquire more and more metallic character. At a S–S distance of 2.2 Å, the empty S_2 σ^* combination lies unmixed at high energy. Accordingly, the following points may be rationalized: (i) a formal reduction of the metals, (ii) the formation of an S–S bond order, and (iii) the diminishing of the donor capabilities of the S_2 unit. The EPR data are supportive of the assignment of the HOMO (IV) in **1**. This and other points will be described in detail in a forthcoming paper.



II



III



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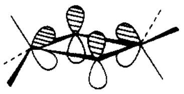
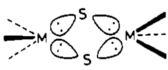


V



VI

Acknowledgment. Thanks are due to Professor Roald Hoffmann for stimulating discussions and encouragement.

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Supplementary Material Available: Listings of positional and thermal parameters for **1** (3 pages). Ordering information is given on any current masthead page.

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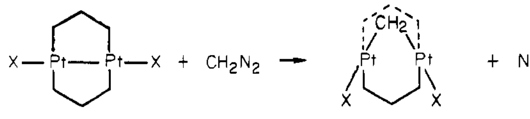
Mechanism of "Molecular A-Frame" Formation by Methylene Insertion into a Platinum–Platinum Bond

Sir:

The literature contains no reports of the rates and mechanisms of μ-methylene complex formation by insertion reactions of diazomethane. We thus undertook studies of this general reaction type, utilizing the dinuclear haloplatinum(I) complexes $X_2Pt_2(\mu\text{-dppm})_2$, where dppm = bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$. The reaction in which a μ-methylene group is inserted into the Pt–Pt bond of the parent complex, shown in eq 1, yields the well-characterized "molecular A-frame" product.[1]



(1)

$X_2Pt_2(\mu\text{-dppm})_2$ $\qquad$ $X_2Pt_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2$

Binuclear and polynuclear metal complexes may serve as models for intermediates formed during reactions catalyzed by metal surfaces.[2-5] Relatively new groups of such complexes

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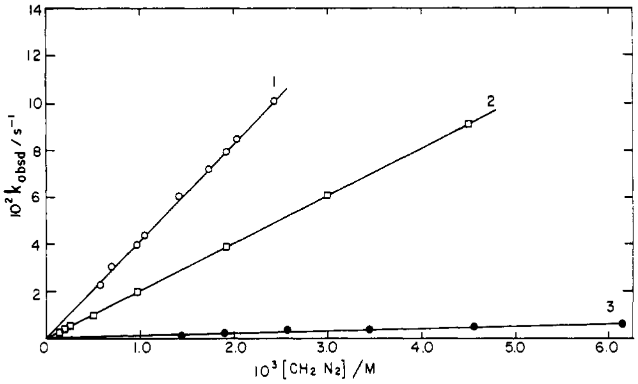

Figure 1. Pseudo-first-order rate constant for the reaction of eq 1, which varies linearly with the concentration of diazomethane in experiments having $[CH_2N_2]_0 >> [X_2Pt_2(\mu\text{-dppm})_2]_0$, the latter being varied (0.5–14) × 10^{-5} M for X = Cl. Data are shown for (1) $Pt_2Cl_2(\mu\text{-dppm})_2$, (2) $[Pt_2(Cl)(CO)(\mu\text{-dppm})_2](PF_6)$, and (3) $[Pt_2(CO)_2(\mu\text{-dppm})_2](PF_6)_2$.

Table I. Kinetic Data[a] for the Reaction of Dinuclear Pt(I) Complexes with Diazomethane

complex	range of $[CH_2N_2]$/M	k(2 °C)/ M^{-1} s^{-1}
$Pt_2Br_2(\mu\text{-dppm})_2$	(0.4–1) × 10^{-3}	204
$Pt_2I_2(\mu\text{-dppm})_2$	(0.2–1) × 10^{-3}	73
$Pt_2Cl_2(\mu\text{-dppm})_2$	(0.5–2.5) × 10^{-3}	41.2[b]
$Pt_2(Cl)(CO)(\mu\text{-dppm})_2^{+}$	(0.1–4.5) × 10^{-3}	20.6
$Pt_2(CO)_2(\mu\text{-dppm})_2^{2+}$	(1–6) × 10^{-3}	1.0
$Pt_2(C_5H_5N)_2(\mu\text{-dppm})_2^{2+}$	1 × 10^{-3}	$<10^{-2}$
$Pt_2(NH_3)_2(\mu\text{-dppm})_2^{2+}$	6 × 10^{-3}	$<10^{-2}$

[a] In CH_2Cl_2 containing up to 2% $(C_2H_5)_2O$ from the diazomethane solutions. Reactions were monitored spectrophotometrically, usually at two or more wavelengths, 240–430 nm. [b] Data as a function of temperature (six values, 2.0–25.0 °C) yield $\Delta H^{\ddagger}$ = 14.27 ± 0.24 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 0.94 ± 0.83 cal mol^{-1} K^{-1}.

include those bridged by a μ-methylene group, also referred to as "bridging carbene" complexes. In the structural unit $M\text{–}CH_2\text{–}M$, the two metals are often further joined by a metal–metal bond. The particular μ-methylene complexes that are the subject of this report have no such bond, the product being stabilized against dissociation by the bridging dppm ligands.

The reactions shown, and reactions of the analogous cationic complexes having one or two neutral ligands in place of halide,[6] were studied in purified dichloromethane. UV–visible spectrophotometry and product isolation showed that they proceed cleanly as written, with no detectable concentration of any reaction intermediate building up during the course of the reaction.[7,8] Kinetic data were obtained in experiments employing a large excess of diazomethane (Figure 1). Over wide concentration ranges a second-order rate law (eq 2) applies,

$$d[X_2Pt_2(\mu\text{-dppm})_2(\mu\text{-CH}_2)]/dt = k[X_2Pt_2(\mu\text{-dppm})_2][CH_2N_2] \quad (2)$$

leading to the rate constants summarized in Table I. The reactions were unaffected by oxygen or moisture.

The significant features of these results are as follows: (1) The rate drops off sharply when both halides are replaced by neutral amine and pyridine ligands, and even the carbonyl complex reacts only 2% as rapidly as the slowest of the halides. (2) Relatively smaller (and irregular) rate variations are found among the dihalides, Cl (41) < Br (204) > I (73 M^{-1} s^{-1}). (3) The rate constants are characterized by an activation entropy which is nearly zero. These points argue against a mechanism in which the rate-limiting step is attack of the methylene group of $N{\equiv}N^{+}\text{—}^{-}CH_2$ on the electropositive metal center: Such a mechanism would be facilitated by replacement of the negative halide by a neutral ligand and, being a bimolecular, bond-making process, would be characterized by a substantial, negative value of ΔS^{*}.

Rather, the data suggest rate-limiting transfer of an electron pair from the metal–metal bond to the methylene group of diazomethane. Both effects described are in accord with this formulation. The value of $\Delta S^{*} \approx 0$ is the result of offsetting contributions from organizational terms and from the weakening of the N–C bond preceding the liberation of N_2. The clear implication is that diazomethane acts as an electrophile toward the metal–metal bond. To our knowledge, this is the first such demonstration. Initial coordination to platinum through nitrogen seems unlikely in that it would appear not to facilitate the overall chemical change represented by eq 1. Further work on related reactions is in progress.

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(7) The UV–visible spectra of these complexes, which do not appear to have been reported previously, are quite characteristic. Complete details will be published in the full paper, but the following is typical: $Cl_2Pt_2(\mu\text{-dppm})_2(\mu\text{-CH}_2)$ λ_{max} 376 (ε 5.2 × 10^3 M^{-1} cm^{-1}), 308 (shoulder) (7.5 × 10^3), and 264 nm (2.6 × 10^4). The product solutions from kinetic determinations have absorption spectra that agree precisely with those of the authentic crystalline μ-methylene complexes in every instance. The rate constants were, in every case, independent of the monitoring wavelength.

(8) Cationic μ-CH_2 complexes of this family do not appear to have been prepared and characterized previously. The compound $[Pt_2(PPh_3)_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2](PF_6)_2$ has λ_{max} 372 cm (ε 5.7 × 10^3 M^{-1} cm^{-1}). ^1H NMR (CD_2Cl_2 with Me_4Si reference): μ-CH_2 (2 H), δ 1.2, multiplet; CH_2 of dppm (4 H), δ 3.6 and 5.05, multiplets (i.e., the latter CH_2 groups are inequivalent in the A-frame product as compared to the case in the starting complex). ^{31}P NMR (^1H decoupled, CD_2Cl_2 with H_3PO_4 reference): $(Ph_2P)_2CH_2$, δ 20.8; Ph_3P, δ 32.76.

Characterization of a Unique Electrochemical Oxidation Catalyst: The Difluoro Complex of Iron(III) Tetraphenylporphyrin

Sir:

It has been known for some time that two fluoride ions will bind to iron(III) porphyrins in aprotic solvents to form six-coordinate high-spin complexes.[1-3] More recently it has been reported that reductive electrochemistry of $(TPP)FeF_2^-$ is distinctive in that the two fluoride ions shift the iron(III) → iron(II) couple to −1.10 V (all potentials are referenced to the saturated calomel electrode).[3,4] By comparison the couple for the monofluoro complex is −0.50 V.[3] We have found that the oxidation of $(TPP)FeF_2^-$ is also unique, as the first oxi-

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(4) Porphyrin abbreviations: TPP, *meso*-tetraphenylporphyrin; TPP(*p*-OCH_3), *meso*-tetrakis(*p*-methoxyphenyl)porphyrin; OEP, octaethylporphyrin. Abbreviations for salts: $Bu_4NF{\cdot}3H_2O$, tetrabutylammonium fluoride trihydrate; Bu_4NClO_4, tetrabutylammonium perchlorate.

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