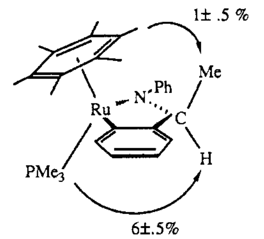
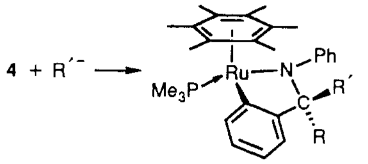


**Figure 1.** Proposed structure of **5b** showing observed $^1$H NOE enhancements. Within experimental error, irradiation of the $C_6Me_6$ protons does not enhance the benzylic proton, and irradiation of the $PMe_3$ protons does not enhance the benzylic methyl group.

metal cation, the imine carbon in **4a** should be susceptible to nucleophilic attack, giving an ortho metalated benzylphenylamide as the product. Related metallocycles, containing both M-aryl and M-O($\sigma$) bonds, have been synthesized by the reaction of 2-carboxylatobenzenediazonium or 2-sulfonatobenzenediazonium with low-valent platinum complexes.[9f]

When **4a** is allowed to react with 1 equiv of Li(*t*-BuO)$_3$AlH (THF, −20 °C), an immediate reaction occurs, producing the orange pentane-soluble product **5a** in ca. 95% yield:



(3)

**5a**, R = R′ = H
**b**, R = H, R′ = CH$_3$
**c**, R = CH$_3$, R′ = H
**d**, R = H, R′ = Ph

The $^1$H NMR spectrum of **5a** has a pair of doublets at 5.5 and 4.5 ppm that are assigned to the benzylic protons which are diastereotopic. The remainder of the $^1$H NMR spectrum (as well as the $^{13}$C and $^{31}$P spectra) is also consistent with the proposed structure of **5a**.[7b] Other strong nucleophiles such as lithium alkyls will also add to the imine carbon to give **5b–d**.[7b]

If the attacking nucleophile is different from the substituent already bonded to the imine carbon, then the formation of two sets of diastereomers is possible since both the Ru center and the benzylic carbon atom are chiral. When MeLi is added to a solution of **4a** in THF, only one product, **5b**, is observed by 300-MHz $^1$H NMR spectroscopy following workup. The structure of **5b** has been assigned with the aid of proton difference NOE spectroscopy and is shown in Figure 1 along with the observed NOE(s). Thus, **5b** is formed with ca. 100% diastereoselectivity. The other diastereomer, **5c**, can be synthesized by adding Li(*t*-BuO)$_3$AlH to **4b** followed by rapid workup of the reaction mixture. Under these conditions, **5c** is the only detectable product of the reaction. These experiments demonstrate that both methyl addition to **4a** and hydride addition to **4b** occur endo to the $C_6Me_6$ ring rather than between the "legs" of the piano stool. If compound **5c** is allowed to remain in solution, a slow isomerization ($t_{1/2} \simeq$ 18 h, 25 °C) occurs that converts it cleanly and completely to **5b**. This leads to the conclusion that while the regioselectivity of the nucleophilic attack is kinetically controlled and occurs endo to the $C_6Me_6$ group, **5b** is the thermodynamically more stable isomer of the pair of diastereomers (**5b** and **5c**).

Preliminary kinetic studies have been carried out on the isomerization of **5c** to **5b**. The reaction is first order in **5c**, and the activation parameters[10] are consistent with a considerable amount of bond breaking in the transition state. A mechanism involving loss of $PMe_3$ to form an unsaturated 16e intermediate that can trap $PMe_3$, resulting in a net racemization of the ruthenium center, would be consistent with these results. Since there are no examples of such racemization reactions that occur in complexes with ortho metalated ligands,[10] further studies are underway to elucidate the mechanism of this reaction in more detail.

The observation that nucleophilic attack occurs at the imine carbon of **4a,b** to give amide complexes demonstrates the viability of eq 1 as a method for the synthesis of metal amide complexes. The extraordinarily high diastereoselectivity of H$^-$ or R$^-$ addition to the imine carbon is reminiscent of the selectivities observed in reactions occurring at ligands coordinated to other three-legged piano-stool complexes.[11] We are currently exploring the generality of this reaction with other ortho metalated Schiff base complexes since the syntheses of monodentate amido complexes by this chemistry have not yet been successful. Results of studies on the reactions of **5b** with acetylene, carbon monoxide, and other unsaturated reagents will be reported separately.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

**Supplementary Material Available:** A $^1$H COSY NMR spectrum for $(\eta^6\text{-}C_6Me_6)\overline{Ru\leftarrow N(Ph){=}C(H)C}_6H_4(PMe_3)$ (**4a**) and $^1$H difference NOE spectra for $(\eta^6\text{-}C_6Me_6)\overline{RuN(Ph)C(H)(Me)C}_6H_4$ (isomer **5b**) (2 pages). Ordering information is given on any current masthead page.

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[9] (a) Bennet, R. L.; Bruce, M. I.; Goodall, B. L.; Igbal, M. Z.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1787. (b) Choo Yin, C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. (c) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (d) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (e) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 1986. (f) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464.

(10) The isomerization is first order in **5c** with $\Delta H^{\ddagger}$ = 24 kcal mol$^{-1}$ and $\Delta S^{\ddagger}$ = 40 cal mol$^{-1}$ K$^{-1}$: Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(11) For some representative examples see: Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C. *Tetrahedron* **1986**, *42*, 5123. Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

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# Ab Initio MO Study of $CO_2$ Insertion into a $Cu^I$–$CH_3$ Bond. Critical Difference from $CO_2$ Insertion into a $Cu^I$–H Bond

**Shigeyoshi Sakaki* and Katsutoshi Ohkubo**
*Department of Applied Chemistry*
*Faculty of Engineering, Kumamoto University*
*Kurokami, Kumamoto 860, Japan*

*Received May 31, 1989*

*Summary:* Several interesting differences are found between $CO_2$ insertion into a $Cu^I$–$CH_3$ bond and $CO_2$ insertion into a $Cu^I$–H bond, which come from the fact that an alkyl ligand possesses only a directional lone-pair orbital as a valence orbital while the hydride ligand has a spherical 1s orbital as a valence orbital.

0276-7333/89/2308-2970$01.50/0

**Table I. Relative Stability of Products and Activation Barriers of $CO_2$ Insertion into the Cu–$CH_3$ Bond of $Cu(CH_3)(PH_3)_2$ (kcal/mol)**

| | method/basis set | | | |
|---|---|---|---|---|
| | HF/ BS I | HF/ BS II | MP2/ BS II | HF/ BS III |
| rel stability[a] | | | | |
| **2A** | −13.8 | −21.3 | −2.7 | −41.7 |
| **2B** | −36.8 | −43.4 | −20.8 | −62.4 |
| **3** | −38.6 | −41.7 | −21.8 | −64.8 |
| activation barrier[b,c] | | | | |
| into Cu–$CH_3$ | 19 | 23 | 23 | 12 |
| into Cu–H[d] | 8 | 13 | 13 | 5 |

[a] Negative values mean the stabilization in energy relative to the reactants (sum of 1 and $CO_2$). [b] Analysis of harmonic frequencies was not carried out here. The activation energy listed is an approximated value. [c] The standard (energy zero) was taken at the C–C distance of 3.2 Å between C of $CO_2$ and C of $CH_3$, because the total energy was calculated to be the most stable at this point with the BS I and BS III sets. [d] Reference 4a.

$CO_2$ conversion into organic substances with transition-metal complexes is of current interest in the chemistry of $CO_2$ fixation.[1] In this regard, $CO_2$ insertion into metal–hydride (M–H) and metal–alkyl (M–R) bonds is an attractive subject of research,[1a,b,d] because many catalytic reactions of transition-metal complexes include a similar insertion reaction as a key elementary step.[3] The MO method is expected to offer a variety of information about the $CO_2$ insertion. However, an MO study of $CO_2$ insertion into an M–R bond has not been reported yet, to our knowledge, while only a few MO studies of $CO_2$ insertion into M–H bonds have been reported.[4] Because M–R and M–H bonds differ remarkably in chemical reactivity,[5] an MO study of $CO_2$ insertion into the M–R bond is also necessary for finding a good transition-metal catalyst useful for $CO_2$ fixation.

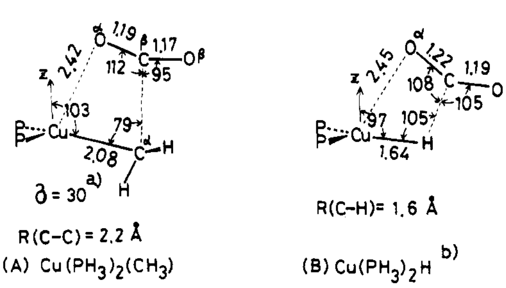

**Figure 1.** Geometries of the $CO_2$ insertion reaction system around the transition state (bond distances in angstroms and bond angles in degrees). (a) Angle between the lone-pair orbital and the Cu–C bond; (b) The BS I and BS II sets give this transition state on the HF and MP2 level, but the BS III set gives an earlier transition state at $R$(C–H) = 1.8 Å.[4]

In this work, $CO_2$ insertion into an M–R bond is first investigated with an ab initio MO method. $Cu(CH_3)(PH_3)_2$ (1) was chosen as a reactant, because similar Cu(I)–alkyl complexes are well-known to undergo $CO_2$ insertion into the Cu–alkyl bond.[2c,d,h] It is our intention with this theoretical work to provide detailed information about $CO_2$ insertion by comparing $CO_2$ insertion into the $Cu^I$–$CH_3$ bond with $CO_2$ insertion into the $Cu^I$–H bond.

MO calculations were carried out with Gaussian 82[6] and IMSPACK[7] programs, where three kinds of basis sets were used.[8–10] Geometries of the reactant **1**, products **2B** and **3** (se eq 1), and the reaction system **1** + $CO_2$ were optim-

1 2A 2B 3

(1)

ized with the small basis set (BS I)[8] on the Hartree–Fock (HF) level.[11a–d] Better basis sets (BS II[9] and BS III[10]) were used to obtain more reliable results about the reaction.[11c,d]

There are three possible products, i.e., a carboxyl type compound, $Cu(\eta^1\text{-}COOCH_3)(PH_3)_2$, and two carboxylate type compounds, **2** and **3**. Of these products, the carboxyl type compound is excluded from discussion, because a Cu(I)–carboxyl type compound is in general much less

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(1) For example: (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Culter, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (e) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (g) Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, 1981.

(2) (a) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896. (b) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58; *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784. (c) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1973**, *49*, C57; **1976**, *113*, 187. (d) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1974**, *72*, 145. (e) Koinuma, H.; Yoshida, Y.; Hirai, H. *Chem. Lett.* **1975**, 1223. (f) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 863. (g) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984. (h) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1978**, *100*, 632. (i) Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349; *Organometallics* **1982**, *1*, 1685. (j) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285. (k) Darensbourg, D. J.; Kudaroski, R. *J. Am. Chem. Soc.* **1984**, *106*, 3672. (l) Darensbourg, D. J.; Ovalless, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750. (m) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654. (n) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 924. (o) Cocolios, P.; Guilard, R.; Bayeul, D.; Lecomte, C. *Inorg. Chem.* **1985**, *24*, 2058. (p) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 746. (q) Kojima, F.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1986**, *108*, 391. (r) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 6425. (s) Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 977. (t) Darensbourg, D. J.; Sanchez, K. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 290. (u) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1987**, *109*, 3330. (v) Darensbourg, D. J.; Gotsch, G.; Wiegreffe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827. (w) Darensbourg, D. J.; Darensbourg, M. Y.; Goh, L. Y.; Ludvig, M.; Wiegreffe, P. *J. Am. Chem. Soc.* **1987**, *109*, 7539. (x) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.

(3) For example: (a) Crabtree, R. M. *The Organometallic Chemistry of the Transition Metals*; Wiley-Interscience: New York, 1988; Chapter 7. (b) Hartley, F. R., Patai, S., Eds. *The Chemistry of the Metal-Carbon Bond*; Wiley: Chichester, England, 1985; Vol. 3.

(4) (a) Sakaki, S.; Ohkubo, K. *Inorg. Chem.* **1988**, *27*, 2020; **1989**, *28*, 2583. (b) Bo, C.; Dedieu, A. *Inorg. Chem.* **1988**, *28*, 304.

(5) For instance: (a) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482. (b) Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1983**, *78*, 986. (c) Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1983**, *105*, 5557. (d) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (e) Rabaa, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327.

(6) Binkley, J. S.; Frisch, M.; Reghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. "Gaussian 82"; Carnegie-Mellon Quantum Chemistry Archive; Carnegie-Mellon University: Pittsburgh, PA, 1983. Several subroutines for effective core potential calculation supplied by P. J. Hay have been added to Gaussian 82 by Dr. N. Koga and Prof. K. Morokuma.

(7) Morokuma, K.; Kato, S.; Kitaura, K.; Ohmine, I.; Sakai, S.; Obara, S. "IMSPACK"; IMS Computer Program Library No. 0372; The Institute for Molecular Science: Okazaki, Japan, 1980.

(8) In the small basis set (BS I), (3s2p5d/2s2p2d),[8a] MIDI-3,[8b] (4s/2s),[8c] and STO-2G[8d] were used for the Cu atom, the C and O atoms, the H atom, and the $PH_3$ ligand, respectively, where the core orbitals of Cu were replaced by effective core potential.[8a] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205. (c) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; p 1. (d) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

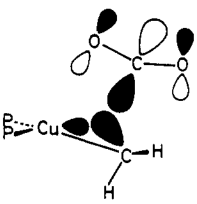
(9) In the medium basis set (BS II), (3s2p5d/2s2p2d),[8a] (9s5p/3s2p),[9a] (4s/2s),[8c] and MIDI-3[9b] were used for the Cu atom, the C and O atoms, the H atom, and the $PH_3$ ligand, respectively. (a) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (b) Sakai, S.; Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1981**, *2*, 108.

(10) In the largest basis set (BS III), the (14s11p6d/5s4p3d) set was used for the Cu atom, while the same basis sets as for the BS II set were employed for the other atoms: Wachters, A. J. *J. Chem. Phys.* **1970**, *52*, 1033. Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

stable than Cu(I)–carboxylate type compounds.[4] As compared in Table I, all the calculations show that **2A** is much less stable than **2B** and **3**. Although only the HF/BS II calculation indicates **2B** is more stable than **3**, **3** is calculated to be more stable than **2B** with the most reliable BS III set at the HF level. Introduction of electron correlation effects with the MP2 method[12] stabilizes **3** more than **2B**, as shown by comparing HF/BS II and MP2/BS II calculations.[13] Thus, it is reasonably concluded that **3** is a final product.

Unfortunately, relative stabilities of the reactants (**1** and $CO_2$) and products depend significantly on the basis set and electron correlation effects. An HF calculation with the most reliable BS III set yields a rather large exothermicity of about 65 kcal/mol. Introduction of electron correlation effects with the MP2 method, however, remarkably reduces the exothermicity by about 20 kcal/mol, where the BS II set is used.[13] Also, the exothermicity of the model reaction system $Cu(CH_3) + CO_2 \rightarrow Cu(\eta^2\text{-}O_2CCH_3)$ was calculated to decrease by 19 kcal/mol upon introducing electron correlation effects with the SD-CI method.[14] Thus, a decrease in the exothermicity by introduction of electron correlation effects is reasonably estimated to be about 20 kcal/mol, and consequently, the exothermicity of the $CO_2$ insertion examined would be estimated at about 45 kcal/mol.

Chart I



As $CO_2$ approaches **1**,[15] the geometry of the reaction system (**1** + $CO_2$) becomes similar to that of **2A**. In this step of the reaction, a rather high activation barrier[16] was calculated, as shown in Table I, whereas conversion from **2A** to **3** was calculated to occur without a barrier. Thus, the step going to **2A** from **1** seems important in the $CO_2$ insertion. The activation barrier for this step is somewhat dependent on the basis set but is only slightly dependent on the electron correlation effects (Table I). In all the calculations, this step requires an activation energy higher than that for $CO_2$ insertion into the $Cu^I$–H bond of $CuH(PH_3)_2$[4a] by about 7–11 kcal/mol (Table I). This result clearly shows that $CO_2$ insertion into the $Cu^I–CH_3$ bond occurs less easily than insertion into the $Cu^I$–H bond. The geometry around the transition state (Figure 1) is critically different between $CO_2$ insertion into the $Cu^I–CH_3$ bond and insertion into the $Cu^I$–H bond, as follows: the former has a much larger $z$–Cu–$CH_3$ angle ($z$ = $z$ axis) and a smaller Cu–$C^\alpha$–$C^\beta$ angle than the latter (see Figure 1 for $C^\alpha$ etc.). These differences result from the fact that a directional lone-pair orbital is only a valence orbital of the $CH_3$ ligand and a spherical (nondirectional) 1s orbital is a valence orbital of the H ligand. Around the transition state, $CO_2$ starts to interact with the lone-pair orbital of the $CH_3$ ligand. Because this lone-pair orbital needs to maintain the overlap with acceptor orbitals of $Cu(PH_3)_2$ as much as possible, $CO_2$ better approaches the $CH_3$ ligand in the region near the $Cu^I–CH_3$ coordinate bond (i.e., with a small Cu–$C^\alpha$–$C^\beta$ approach angle), and the $CH_3$ ligand shifts its position with a turning of the lone-pair orbital, as pictured in Chart I. In the $CO_2$ insertion into the $Cu^I$–H bond, on the other hand, the H ligand can interact with $CO_2$ because of the nondirectional 1s valence orbital, even if $CO_2$ attacks the H ligand with a large Cu–H–C approach angle (Figure 1). This means that $CO_2$ does not need to attack the H ligand with a small Cu–H–C approach angle. Also, the H ligand can maintain sufficient overlap between its 1s orbital and acceptor orbitals of $Cu(PH_3)_2$, even if the H ligand does not shift its position. Consequently, the $z$–Cu–H angle is near 90° around the transition state. These differences are also considered a reason that the $CO_2$ insertion into the $Cu^I–CH_3$ bond needs a higher activation energy than the insertion into the $Cu^I$–H bond.

Finally, electronic structure at the transition state is investigated with an energy decomposition analysis.[17] The CTPLXA term,[18a] which includes charge transfer from $Cu(CH_3)(PH_3)_2$ to $CO_2$, accumulates electrons between C

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(11) (a) The geometry of $PH_3$ was taken from an experimental study of the free $PH_3$ molecule without further optimization: Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: Toronto, 1967; Vol. 3, p 610. (b) Because the energy gradient calculation is very time-consuming for this reaction system, optimization with parabolic fitting of total energies was carried out on the following geometrical parameters: in **1**, the Cu–C distance; in **2B** and **3**, the Cu–$O^\alpha$, C–$O^\alpha$, C–$O^\beta$, and C–C distances and Cu–$O^\alpha$–C, $O^\alpha$–C–$O^\beta$, and $O^\alpha$–C–C angles; in the **1** + $CO_2$ reaction system, Cu–C, C–$O^\alpha$, and C–$O^\beta$ distances and Cu–$C^\alpha$–$C^\beta$, C–C–$O^\alpha$, and C–C–$O^\beta$ angles (see eq 1 and Figure 1 for $C^\alpha$, $O^\alpha$, etc.). (c) These bond distances and bond angles were optimized independently, in which optimized values are consistent within about 0.02 Å for bond distances and about 5° for bond angles. (d) **2A** was not optimized, because **2A** was calculated to isomerize to **2B** with no barrier. The geometry of **2A** was assumed from that of **2B**, where only the orientation of $\eta^1$-$OCOCH_3$ was altered, the geometries of the other parts being kept fixed. (e) To examine how the more extensive basis set influences the geometry, $R$(Cu–C) of $Cu(CH_3)(PH_3)_2$ and $R$(Cu–O) of $Cu(\eta^2\text{-}O_2CCH_3)$ were optimized with the better BS III set, where geometries of the other parts were fixed. Both $R$(Cu–C) and $R$(Cu–O) lengthen by ca. 0.05 Å upon going to BS III from BS I, as expected. This deviation of the geometry increases the total energy of these compounds by ca. 0.3 kcal/mol in the HF/BS III calculation. Thus, the exothermicity of the reaction changes little, even if we employ geometries optimized with the better BS III set. (f) Electron correlation effects on the geometry were examined in the model systems $Cu(CH_3)$ and $Cu(\eta^2\text{-}O_2CCH_3)$, because real systems are too large to carry out geometry optimization at a correlated level. Here, $R$(Cu–C) of $Cu(CH_3)$ and $R$(Cu–O) of $Cu(\eta^2\text{-}O_2CCH_3)$ were optimized at the HF and MP2 levels, with use of the BS III set, where geometries of the other parts were fixed. Introduction of electron correlation effects shortens $R$(Cu–C) and $R$(Cu–O) by 0.085 and 0.03 Å, respectively. The exothermicity is calculated with the MP2 method to be 26.9 kcal/mol for the geometries optimized at the HF level and 26.0 kcal/mol for the geometries optimized at the MP2 level. This difference is not large, and the discussion presented here seems reliable, at least semiquantitatively.

(12) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum. Chem., Symp.* **1976**, *10*, 1. (c) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum. Chem.* **1978**, *14*, 545. (d) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(13) The BS III set is too large for MP2 calculations. To save CPU time, MP2 calculations were carried out with the medium BS II set.

(14) (a) Preliminary SD–CI calculations were carried out with the MELD program.[14b,c] (b) Davidson, E. R.; McMurchie, L.; Elbert, S.; Langhoff, S. R.; Rawlings, D.; Feller, D. "Program of MELD"; University of Washington: Seattle, WA, 1983. This program was brought to IMS by Davidson, as: IMS Computer Center Library No. 030; Institute for Molecular Science: Okazaki, Japan. (c) A double-ζ basis set[14d] was used for Cu, and the geometries of $Cu(CH_3)$ and $Cu(\eta^2\text{-}O_2CCH_3)$ were assumed to be the same as in the **1** + $CO_2$ reaction system. (d) The basis set for Cu was taken from the No. 3 contraction of ref 10a, and basis sets for the other atoms were the same as in the BS III set.

(15) The C–C distance between C of $CH_3$ and C of $CO_2$ was taken as a reaction coordinate of the $CO_2$ insertion, because products **2** and **3** have a newly formed C–C bond.

(16) The activation barrier was estimated as a energy difference from the total energy at $R$(C–C) = 3.2 Å, because the total energy is calculated to be the most stable at $R$(C–C) = 3.2 Å with the BS I and BS III sets and the geometry at this distance is almost the same as that at $R$(C–C) = 3.6 Å.

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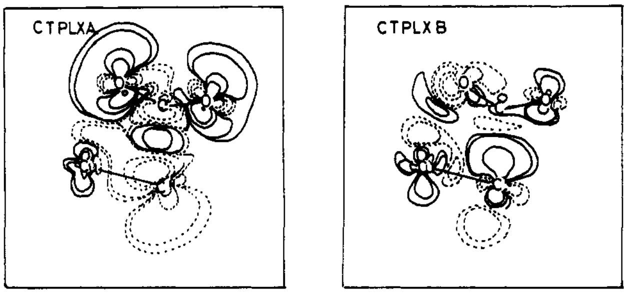

**Figure 2.** Difference density maps ($\Delta\rho = \rho(\text{CTPLXA}) - \rho[Cu(CH_3)(PH_3)_2] - \rho[CO_2]$) of CTPLXA and CTPLXB interactions:[17,18] (—) increase in density; (- - -) decrease in density.

of $CH_3$ and C of $CO_2$, as shown in Figure 2. The CTPLXB term,[18b] which includes charge transfer from $CO_2$ to $Cu(CH_3)(PH_3)_2$, accumulates electrons between Cu and $O^\alpha$ of $CO_2$.[18c] This is the first clear evidence that the $CO_2$ insertion proceeds via a four-center-like transition state.

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(18) (a) CTPLXA includes charge transfer from $Cu(CH_3)(PH_3)_2$ to $CO_2$ as a main contributor, polarization of $CO_2$, and their coupling terms. (b) CTPLXB includes charge transfer from $CO_2$ to $Cu(CH_3)(PH_3)_2$ as a main contributor, polarization of $Cu(CH_3)(PH_3)_2$, and their coupling term. (c) The difference density map of CTPLXB exhibits several complicated features; for instance, the electron density is increased in some regions between Cu and $O^\alpha$ atoms but is decreased in other regions between Cu and $O^\alpha$ atoms. These features are interpreted in terms of several orbital mixings, as follows: (i) The $CO_2$ $n\pi$ and $\pi$ orbitals overlap with the empty Cu $4p_z$ orbital in a bonding way to form a charge transfer interaction, which would increase the electron density in the region of the Cu $4p_z$ orbital (rather far from Cu). (ii) At the same time, the $CO_2$ $\pi$ and $n\pi$ orbitals overlap with the stable and doubly occupied Cu $d_z{}^2$ orbital in an antibonding way, which would decrease the density in the region of the Cu $3d_z{}^2$ orbital (rather close to the Cu atom). (iii) $CO_2$ $n\pi$ and $\pi$ orbitals form a charge transfer interaction with the Cu $4p_z$ orbital. In the virtual space, the Cu $4p_z$ orbital undergoes antibonding mixing with the more stable $CO_2$ $n\pi$ and $\pi$ orbitals. This mixing enlarges the $O^\alpha$ $p_\pi$ orbital but decreases the $O^\beta$ $p_\pi$ orbital in the virtual space, because the O $p_\pi$ orbital has different phases in $n\pi$ and $\pi$ orbitals. Thus, in the occupied space, the electron density decreases on the $O^\alpha$ atom but increases on the $O^\beta$ atom, since orbital contribution in the occupied space is reverse to that in the virtual space. (iv) Because CTPLXB includes the polarization of the $Cu(CH_3)(PH_3)_2$ part, the electron cloud of this part is withdrawn toward the positively charged C atom, which would increase the electron density on the $CH_3$ ligand. A detailed discussion will be presented in our subsequent full paper.

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# Regioselectivity in Electrophilic Addition to a 3-Oxaplatina(II)cyclobutane Complex. Metallacycle Ring-Opening Reactions and Synthesis of a Platinum(IV) 3-Oxametallacyclobutane Complex

**James F. Hoover and Jeffrey M. Stryker**[*,1]
*Department of Chemistry, Indiana University*
*Bloomington, Indiana 47405*

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*Summary:* Electrophilic addition to a 3-oxaplatina(II)cyclobutane complex is directed either to the metal or to the ring oxygen, depending on the nature of the electrophile. Reaction at the metal center gives a stable Pt(IV) oxametallacyclobutane complex, while reaction at the oxygen leads to ring-opened products.

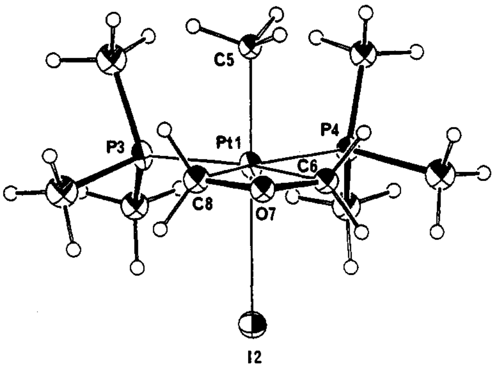
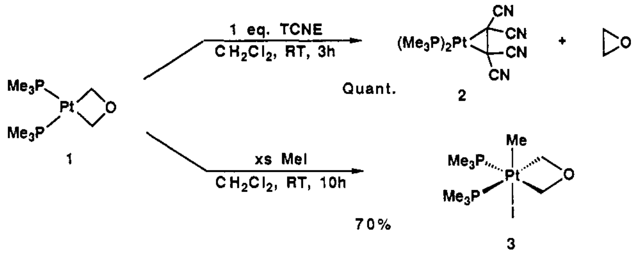


**Figure 1.** ORTEP drawing of 3. Selected bond distances (Å): Pt(1)-I(2), 2.771 (2); Pt(1)-C(5), 2.074 (24); Pt(1)-C(6), 2.106 (25); Pt(1)-C(8), 2.078 (25); Pt(1)-P(3), 2.372 (6); Pt(1)-P(4), 2.369 (6); C(6)-O(7), 1.50 (3); C(8)-O(7), 1.44 (3). Selected bond angles (deg): C(6)-Pt(1)-C(8), 66.5 (10); Pt(1)-C(6)-O(7), 93.9 (13); Pt(1)-C(8)-O(7), 97.2 (15); C(6)-O(7)-C(8), 102.4 (17); P(3)-Pt(1)-C(8), 97.1 (7); P(4)-Pt(1)-C(6), 95.9 (7); P(3)-Pt(1)-P(4), 100.6 (2); C(5)-Pt(1)-P(3), 92.2 (7); C(5)-Pt(1)-P(4), 91.3 (7); C(5)-Pt(1)-C(6), 88.9 (9); C(5)-Pt(1)-C(8), 86.8 (9); I(2)-Pt(1)-C(5), 175.7 (6); I(2)-Pt(1)-P(3), 90.50 (18); I(2)-Pt(1)-P(4), 91.54 (16); I(2)-Pt(1)-C(6), 87.6 (7); I(2)-Pt(1)-C(8), 89.6 (7). Least-squares dihedral plane angle (deg): [Pt(1)-C(8)-C(6)]-[C(6)-O(7)-C(8)], 1.1. Final residuals: $R(F) = 0.058$ and $R_w(F) = 0.057$.

**Scheme I**



We recently reported the first synthesis of the 3-oxametallacyclobutane structural class by dehydrative ring closure of an unprecedented bis(hydroxymethyl) complex of platinum(II).[2] Because of the extensive chemistry reported for all-carbon platinacyclobutanes,[3,4] these platinum complexes were considered ideal for probing the effect of noncoordinating oxygen substitution on metallacycle stability and reactivity. Here we report that oxaplatinacyclobutane complexes react with electrophiles with high selectivity in one of several reactivity manifolds, depending on the nature of the electrophile.

The trimethylphosphine-substituted 3-oxaplatina(II)cyclobutane complex 1 (Scheme I) was selected for initial investigation, maximizing electron density at the metal center and anticipating optimized stabilization of the Pt(IV) oxidation state. The reaction of complex 1 with 1 equiv of tetracyanoethylene (TCNE) at room temperature led, however, to reductive elimination of the metallacycle with quantitative formation of the known $(Me_3P)_2Pt(TCNE)$ complex 2[5] and ethylene oxide as the

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