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Supplementary Material Available: Tables of crystal data and conditions for data collection, positional parameters, general temperature factors, bond distances, bond angles, and torsion angles (13 pages); listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Characteristic Features of CO_2 Insertion into a Cu–H Bond. An ab Initio MO Study

Sir:

One of the current interests in the chemistry of transition-metal CO_2 complexes is the activation of carbon dioxide via direct coordination to metal complexes and the subsequent conversion to organic substances.[1] In this regard, there is a need to elucidate the electronic structure, bonding nature, and reactivity of transition-metal CO_2 complexes, in the hope of finding ones that are useful for CO_2 fixation. Several MO studies of transition-metal CO_2 complexes have been carried out;[2,3] however, to our knowledge, an MO study of the CO_2 conversion to organic substances has not been reported.

In the present work, CO_2 insertion into a metal–hydride bond is investigated with an ab initio MO method. $CuH(PH_3)_2$ (**1**, Chart I) is chosen as a model,[4] because the CO_2 insertion into the Cu(I)–alkyl bond is well-known.[1e–i] Three complexes, $Cu(PH_3)_2(COOH)$ (**2**), $Cu(PH_3)_2(OCOH)$ (**3**), and $Cu(PH_3)_2(O_2CH)$ (**4**), are examined as possible products. This is the first example of a detailed MO study of the CO_2 insertion reaction, and several characteristic features of the reaction are clarified.

Chart I

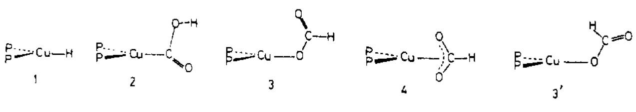

Table I. Relative Stabilities (kcal/mol) of Possible Products in CO_2 Insertion into the Cu–H Bond of $CuH(PH_3)_2$[a]

	basis set, method			
	small, HF	medium, HF	medium, MP2	large, HF
2	−15.5	−22.8	−19.8	−26.1
3	−37.4	−40.2	−29.0	−55.6
4	−36.8	−37.5	−29.1	−56.8

[a] The sum of the total energies of **1** and CO_2 is taken as a standard (zero energy).

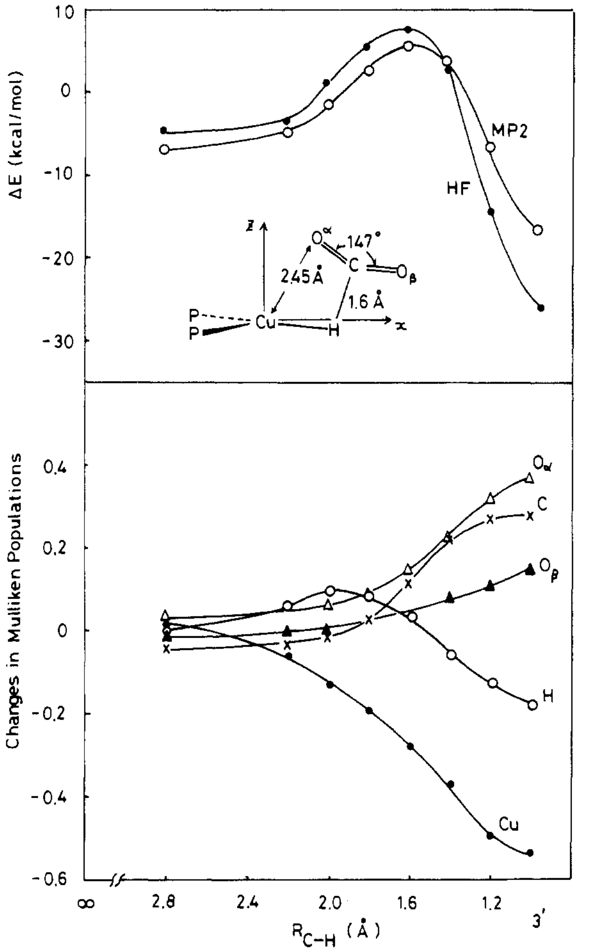

Figure 1. Changes in total energy and Mulliken populations caused by CO_2 insertion into the Cu–H bond (HF calculations with the medium basis set. The infinite separation of CO_2 and $CuH(PH_3)_2$ is taken as a standard (the value of zero on the ordinate scale).

MO calculations were carried out with Gaussian 82[5] and IMSPACK[6] programs, where three kinds of basis sets were employed:

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(1) For example: (a) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 8. (b) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (c) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (d) Beverwijk, C. D. M.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1973**, *49*, C59. (e) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896. (f) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58. (g) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1974**, *72*, 145. (h) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *113*, 187. (i) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784. (j) Koinuma, H.; Yoshida, Y.; Hirai, H. *Chem. Lett.* **1975**, 1223. (k) Inoue, S.; Sasaki, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1975**, 718; *Chem. Lett.* **1976**, 863. (l) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984. (m) Kojima, F.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1986**, *108*, 391. (n) Fishe, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (o) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315. (p) Jubran, N.; Ginzburg, G.; Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251. (q) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 924. (r) Hawecker, J.; Lehn, J. M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. (s) Willer, I.; Mandler, D.; Riklin, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1022. (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; *Inorg. Chem.* **1986**, *25*, 1603. (v) Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 977. (w) Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 205.

(2) (a) Sakaki, S.; Kudou, N.; Ohyoshi, A. *Inorg. Chem.* **1977**, *16*, 202. (b) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760. (c) Sakaki, S.; Dedieu, A. *J. Organomet. Chem.* **1986**, *314*, C63; *Inorg. Chem.* **1987**, *26*, 3278.

(3) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

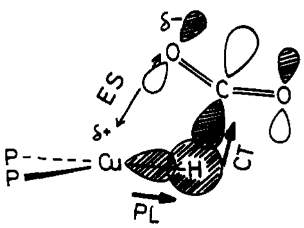
(4) A CO_2 insertion into the Cu–H bond of $Cu(BH_4)(PH_3)_2$ and $Cu(BH_4)$(triphos) has been reported,[1q] but no report has been published on a CO_2 insertion into $CuH(PH_3)_2$. We examined a CO_2 insertion into $CuH(PH_3)_2$ as a model of Cu–alkyl complexes.

(5) 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. The program used is implemented with the effective core potential calculation of L. R. Kahn, which was supplied by P. J. Hay.

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

0020-1669/88/1327-2020$01.50/0

Scheme I



the small basis set[7] was used for optimization of geometries, and the medium[8] and large basis sets[9] were used for determining energetics and bonding. All these basis sets are of double-ζ quality for valence electrons, except that a minimal basis set was used for PH_3 only in the small basis set. The geometries of reactants and products were optimized with the energy gradient method,[10a] and the geometry change during the reaction was optimized with parabolic fitting of total energies.

As shown in Table I, **2** is less stable than **3** and **4**. This is probably due to electrostatic repulsion between $Cu^{\delta+}$ and $C^{\delta+}$. The compound **4** has been experimentally proposed to be the most stable among **2**–**4**.[1q] Although **4** is calculated to be slightly less stable than **3** at the Hartree–Fock (HF) level with the medium basis set, MP2 calculations indicate **3** and **4** are of nearly the same energy.[11] Furthermore, **4** is calculated to be slightly more stable than **3** with the large basis set. Thus, it is reasonably concluded that **4** is the final product of the CO_2 insertion into $CuH(PH_3)_2$ and that **3** is only slightly higher in energy than **4**. Because **4** is significantly more stable than the reactants (a sum of the total energies of **1** and CO_2), the CO_2 insertion is exothermic.

In the CO_2 insertion reaction, the distance between C of CO_2 and H of $CuH(PH_3)_2$ is taken as a reaction coordinate, since the C–H bond is newly formed during the CO_2 insertion.[10b,c] As shown in Figure 1, the CO_2 insertion proceeds with an activation barrier of about 13 kcal/mol at both the HF and the MP2 levels with the medium basis set.[12] Just after CO_2 insertion, the geometry of the reaction system (**3′**) is similar to **3**, where **3′** differs from **3** only in the orientation of the OCOH group. The geometry of **3′** is less stable than that of **3** by 13–14 kcal/mol[13] and **3′** isomerizes to **3** with no barrier (the small basis set). Further isomerization from **3** to **4** proceeds easily with a very small barrier (2 kcal/mol; the small basis set).

Because the CO_2 insertion into the Cu–H bond has been completed at **3′** and the highest barrier is involved in the reaction from **1** to **3′**, this reaction is examined in more detail. Around the transition state ($R_{\mathrm{C-H}} = 1.6$ Å), the $CuH(PH_3)_2$ moiety is slightly distorted[14] but the CO_2 is very distorted (OCO angle 147°). The O^{α} atom of CO_2 is about 2.4 Å distant from the Cu atom (see Figure 1 for the O^{α} atom). These results suggest that the CO_2 insertion has a rather early transition state with four-center-like character. Mulliken populations (Figure 1) also show the following interesting changes during the reaction: (1) The population of the H ligand increases as CO_2 approaches $CuH(PH_3)_2$, attains the maximum at $R_{\mathrm{C-H}} = 2.0$ Å, and then decreases gradually. (2) The electron population of the CO_2 moiety increases and the electron population of the $CuH(PH_3)_2$ moiety decreases as CO_2 approaches. (3) The electron population of the O^{α} atom increases more than that of the O^{β} atom does. The first result suggests that the polarization in the $CuH(PH_3)_2$ moiety is important at the early stage of the reaction, in which electrons of the $CuH(PH_3)_2$ moiety are withdrawn toward the Lewis acid center of CO_2. The second result indicates the importance of the charge-transfer interaction from $CuH(PH_3)_2$ to CO_2. The third result means the reaction system receives some of the stabilization arising from the electrostatic attraction between $Cu^{\delta+}$ and $O^{\delta-}$.

The above-mentioned electron redistributions and interactions are schematically summarized in Scheme I. These results suggest that the CO_2 insertion into an M–X bond proceeds easily when the X group is electron-rich and the metal part can increase polarization. This agrees with the experimental result that CO_2 readily inserts into the W–OR bond of $W(CO)_5(OR)^-$, where the OR^- ligand is highly electron-rich.[1t]

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[7] The (3s 2p 5d/2s 2p 2d),[7a] MIDI-3,[7b] (4s/2s)[7c] and STO-2G[7d] sets were used for the Cu atom, the CO_2 part, the H ligand, and the PH_3 ligand, respectively: (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 *Method 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.

[8] The (3s 2p 5d/2s 2p 2d),[8a] (9s 5p/3s 2p),[8b] (4s/3s),[8c] and MIDI-3[8d] sets were used for the Cu atom, the CO_2 part, the H ligand, and the PH_3 ligand, respectively: (a) Reference 7a. (b) Reference 7c. (c) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (d) Sakai, S.; Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1981**, *2*, 108.

[9] The (14s 11p 6d/5s 4p 3d) set was used for the Cu atom, while the same basis sets as the medium basis set were employed for the other atoms: Watchers, A. J. *J. Chem. Phys.* **1970**, *52*, 1033. Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

[10] (a) The geometry of PH_3 was taken from the experimental studies 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) The Cu–H, C–O^{α}, C–O^{β}, and Cu–P distances and the (*z*-axis)–Cu–H, Cu–H–C, H–C–O^{α}, H–C–O^{β}, and P–Cu–P angles were optimized independently, with an assumption of C_s symmetry (see the coordinate system in Figure 1).[10c] This approach seems reasonable by considering that Cu(I) tends to form a tetrahedral-like four-coordinate complex. (c) The deviation from C_s symmetry was examined in two ways: in the first, the CO_2 moiety was rotated around the C–H bond; in the second, the CO_2 moiety was rotated around the Cu–H bond. Both geometry changes destabilize the reaction system.

[11] The MP2 calculations were carried out with a frozen-core approximation. The other important result found by the MP2 calculations is that the exothermicity of the reaction is decreased very much by introducing electron correlation effects. This will be investigated in more detail.

[12] An activation barrier smaller than 13 kcal/mol is expected to be calculated with the large basis set, because the large basis set calculations predict greater exothermicity for this reaction than the medium basis set calculations do.

[13] Values are 16 kcal/mol from the HF calculation with the medium basis set, 12 kcal/mol from the MP2 calculation with the medium basis set, and 14 kcal/mol from the HF calculation with the large basis set.

[14] The Cu–H distance is lengthened by 0.05 Å, and the H ligand is pushed down from the CuP_2 plane by 0.28 Å. The destabilization caused by this distortion is very small (less than 1 kcal/mol).