J. Am. Chem. Soc. **1995,** *117,* 11363−11364

Reaction of Carbon Dioxide and Heterocumulenes with an Unsymmetrical Metal−Metal Bond. Direct Addition of Carbon Dioxide across a Zirconium−Iridium Bond and Stoichiometric Reduction of Carbon Dioxide to Formate

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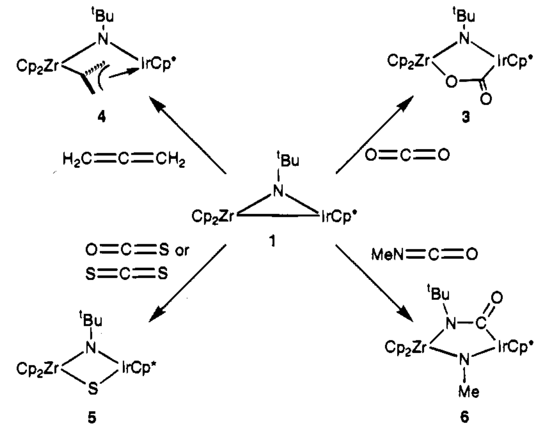
Received July 13, 1995

The use of carbon dioxide in large-scale metal-mediated catalytic processes has been quite limited so far.[1,2] Because of this, there is substantial interest in exploring and understanding the reactions of carbon dioxide and its analogues with transition metal complexes.[3] It seemed likely to us that the unsymmetrical metal−metal interaction in early−late heterobinuclear (ELHB) complexes might be ideal for inducing reactions with potentially polarizable organic molecules such as CO_2.[4] Although a plethora of ELHB complexes have been synthesized, few show cooperative reactivity, and far fewer ELHB complexes of CO_2 or heterocumulenes have been made or structurally characterized.[5]

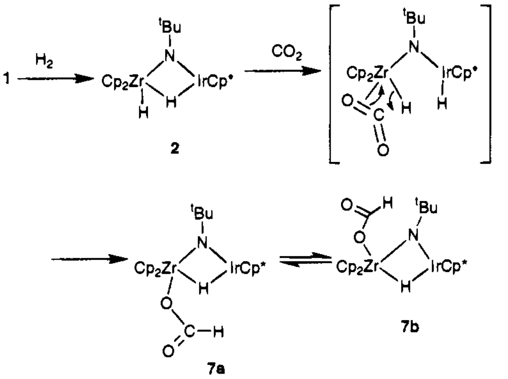
In this communication we report the following findings: (a) the ELHB complex $Cp_2Zr(\mu\text{-N}^t\text{Bu})IrCp^*$ (**1**) (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl)[6] reacts readily with CO_2 by direct addition of a carbon dioxide C=O bond across the Zr−Ir bond, leading to the unique simple heterobimetallacyclic complex **3**; (b) complex **1** reacts with other heterocumulenes with divergent results that depend on the heterocumulene structure; (c) CO_2 reacts with the ELHB dihydride $Cp_2Zr(H)(\mu\text{-H})(\mu\text{-N}^t\text{Bu})IrCp^*$ (**2**) by insertion into an M−H bond, leading to a heterobimetallic formato complex **7**; (d) the formato complex **7** can be converted stoichiometrically to formic acid.

Exposure of complex **1** to allene, heteroallenes, and CO_2 led to several different types of metal−metal insertion products. Reaction with CO_2 resulted in the clean insertion of carbon dioxide into the metal−metal bond to form $Cp_2Zr(\mu\text{-N}^t\text{Bu})(\mu\text{-OC(O)})IrCp^*$ (**3**) in 67% yield (Scheme 1). The product exhibited CO_2 stretching absorptions at 1569 and 1015 cm^{-1} in thf-d_8.[7,8] Reaction with allene gave a metastable intermediate that then converted into a 1:1 adduct. Despite several attempts we have so far not been able to obtain single crystals of the final product (68% yield), but its spectroscopic properties strongly suggest that it has structure **4** illustrated in Scheme 1. The allenyl protons were observed at 1.41 (C−H facing zirconium) and 2.50 (C−H facing iridium) ppm, and the allenyl carbons were observed at 96.2 (quaternary) and 38.3 (CH_2) ppm. The sulfur-containing CO_2 analogues COS and CS_2 both reacted rapidly with complex **1** at room temperature, giving (62 and 26% NMR yield, respectively) the sulfur-bridged compound $Cp_2Zr(\mu\text{-N}^t\text{Bu})(\mu\text{-S})IrCp^*$ (**5**),[9] possibly by initial insertion followed by elimination of CO and CS. In the case of COS, $Cp^*Ir(CO)_2$ was identified as the iridium-containing byproduct of the reaction (26% NMR yield),[10] but in the case of CS_2 several byproducts were formed. Methyl isocyanate in toluene gave yet a different product, leading to complex **6** (Scheme 1, identified by X-ray diffraction), in which the carbonyl group has migrated into the original $Ir{-}N^t\text{Bu}$ bond.

Scheme 1



Dihydrogen does not react with **3** at 1 atm and room temperature, and at elevated pressures decomposition to several unidentified species occurs. Allowing the system to interact with H_2 first and CO_2 subsequently, however, was more productive. Thus $Cp_2Zr(H)(\mu\text{-H})(\mu\text{-N}^t\text{Bu})IrCp^*$ (**2**), the product formed by addition of dihydrogen to complex **1**,[6] reacts readily with carbon dioxide, leading to the two diastereomeric heterobimetallic formato complexes $Cp_2Zr(OC(O)H)(\mu\text{-N}^t\text{Bu})(\mu\text{-H})IrCp^*$ (**7a,b**) (eq 1)[11] in 75% overall yield from **1**. Carbon



(1)

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(1) *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J., Eds.; Kluwer Academic: Dordrecht, 1990; Vol. 314.

(2) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, pp 225−283.

(3) (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661 and references therein. (b) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev.* **1990**, *59*, 344 and references therein. (c) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.

(4) The concept of activating CO_2 by simultaneous interaction with electron-rich and electron-deficient metal centers was pioneered by Floriani et al., although in their case the metals were not bonded to each other. See: Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1974**, 615. Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405.

(5) The only fully characterized ELHB CO_2 complex that we know of to date was made by Cutler and co-workers; Pinkes, J. R.; Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1994**, *13*, 21.

(6) (a) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7890. (b) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822.

(7) These IR data are quite similar to the data for the CO_2 stretches observed for the structurally related complex $Cl(4\text{-}^t\text{Bu-py})(Ph_3P)_2Ir(\mu\text{-O})(\mu\text{-CO}_2)Os(O)_2(4\text{-}^t\text{Bu-py})_2$ described by Collins and co-workers: Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352.

(8) This is unlike Cutler's CO_2 insertion complex $Cp_2Zr(Cl)(\mu\text{-CO}_2)M(CO)_2Cp$ (M = Fe, Ru), in which the CO_2 moiety forms a symmetrical allenyl-like bridge between the zirconium and group VIII metal. See ref 5.

(9) Baranger, A. M.; Hanna, T. A.; Bergman, R. G. *J. Am. Chem. Soc.*, in press.

(10) $Cp^*Ir(CO)_2$ was identified by comparison of its ^{1}H and ^{13}C NMR spectra to those of an authentic sample.

(11) Note that the structures as drawn are not intended to imply any mechanism of isomer interconversion. Further investigation will be necessary to elucidate mechanistic details.

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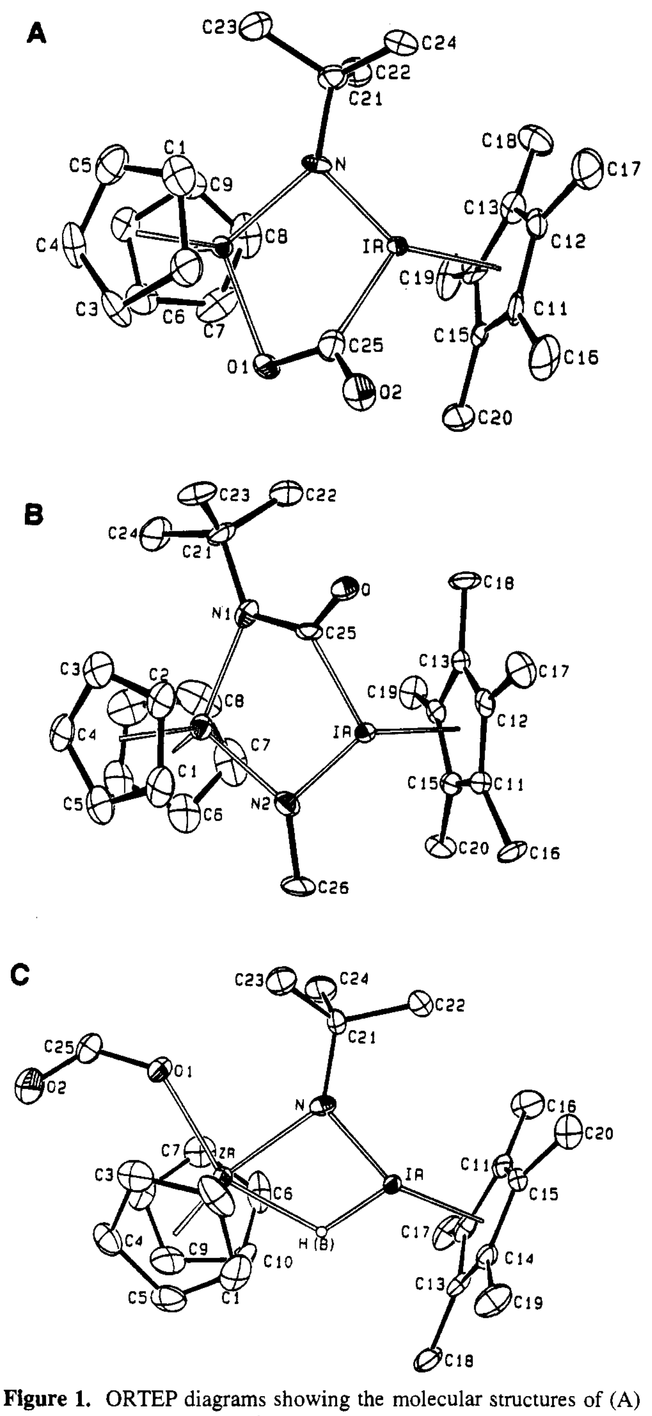
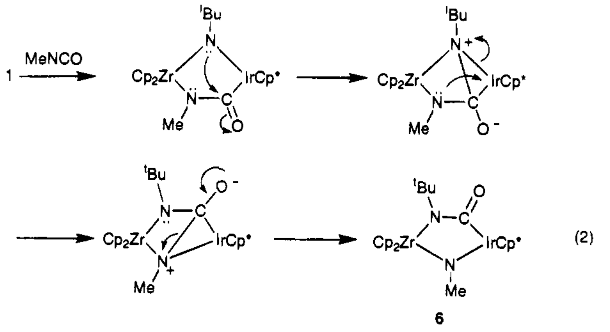


Figure 1. ORTEP diagrams showing the molecular structures of (A) $Cp_2Zr(\mu\text{-}N^tBu)(CO_2)IrCp^*$ (**3**), (B) $Cp_2Zr(\mu\text{-}N(^tBu)C(O))(\mu\text{-}NMe)IrCp^*$ (**6**), and (C) $Cp_2Zr(OC(O)H)(\mu\text{-}N^tBu)(\mu\text{-}H)IrCp^*$ (**7b**).

dioxide inserts selectively into the terminal Zr—H bond to make the terminal formato complex, with no evidence of insertion into the bridging hydride. The carbonyl stretching absorptions for **7** are typical for terminal formato complexes,[12] with the asymmetric stretch at 1624 cm^{-1} and the symmetric stretch at 1293 cm^{-1} (Nujol), and the formato carbons resonate at 166 ppm in the ^{13}C NMR spectrum. In the proton NMR spectrum the protons attached to the carbonyl group appear to be coincident at 9.06 ppm, but the bridging hydride is observed at −5.23 ppm for the minor isomer (10%) and −8.07 ppm (in C_6D_6) for the major one (90%). Spin saturation transfer between these hydrides is observed at 50 °C in the proton NMR, confirming the solution isomerization. An X-ray diffraction study of the major isomer (Figure 1) showed that the two C—O bonds are clearly different, one exhibiting a typical single-bond length of 1.276(8) Å, and the other a double-bond length of 1.208(8) Å, as expected for a formato group.[3a,b]

To explore the possibility of converting the formato complexes to CO_2 reduction products, we examined their reaction with basic reagents. We found that treatment of **7** with phenyllithium led to lithium formate (30% yield)[13] and regenerated **1** (37% yield[14]).

We have not yet carried out in-depth investigations of the mechanisms of these reactions, and so at present we can only speculate on how they proceed. In the case of **1**, it seems likely that the CO_2, allene, and heterocumulene transformations are related to one another. We propose that they occur by initial coordination of X=C=Y to the complex (where X or Y = O, probably via interaction of the organic reactant with the Zr center), followed by addition of the C=X or C=Y bond across the Zr—Ir bond. Subsequent elimination or rearrangement steps then lead to **3**, **4**, and **5**. A plausible pathway for the conversion of **1** to **6** is shown in eq 2. In the case of **2**, we believe that CO_2 reacts by initial coordination to Zr, followed by migratory insertion involving a C=O and Zr—H bond (eq 1).[15] Work is in progress aimed at obtaining further information about these mechanisms and at discovering a way to make the CO_2-to-formate conversion catalytic.[16]



(2)

Acknowledgment. We thank Dr. F. J. Hollander, director of the UC Berkeley X-ray diffraction facility (CHEXRAY), for determination of the X-ray crystal structures. We thank our reviewers for pointing out several pertinent references and for their helpful comments, especially with regard to the proposed structure of **4**. We are grateful to the NSF for support of this work through Grant No. CHE-9113261, and to the Johnson Matthey Aesar/Alfa Co. for a generous loan of iridium chloride.

Supporting Information Available: Experimental details, spectroscopic and analytical data on complexes **3**–**4** and **6**–**7**, tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, intramolecular distances and angles for compounds **3**, **6**, and **7**, and suggested pathway for conversion of **1** to **6** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.

[13] The presence of lithium formate in the reaction product was established by ^1H and ^{13}C NMR analysis of the reaction products in D_2O.

[14] Both yields were determined by integration of ^1H NMR peaks versus an internal standard. For the yield of lithium formate, the NMR solvent was D_2O and the internal standard was ethylene glycol. For the yield of **1**, the NMR solvent was C_6D_6 and the internal standard was trimethoxybenzene.

[15] CO_2 insertion into a zirconium hydride bond has been inferred in the reaction of $Cp_2Zr(H)Cl$ with CO_2 to form $[Cp_2ZrCl]_2O + CH_2O$. Although the CO_2 insertion complex was not detected, the analogous dicyclohexylcarbodiimide insertion complex was fully characterized. See: Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877. Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

[16] For a recent review of homogeneous hydrogenation of carbon dioxide, see: Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.