Metal-Promoted Transformation of CO_2 into CO. X-ray Crystal Structure of the Nickel-Carbonate Complex $[O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2]Ni(O_2CO)\cdot 0.5H_2O\cdot C_6H_6$

Sir:

Metal-promoted transformation of CO_2 into CO can follow at *least* three different routes, which are summarized in (1)-(3).[1] The reaction principle that emerges from eq 1-3

$$L_nM + CO_2 \rightarrow L_nMO + CO \quad (1)$$

$$L_nM + CO_2 \rightarrow L_{n-1}MCO + LO \quad (2)$$

$$L_nM + 2CO_2 \rightarrow L_nMCO_3 + CO \quad (3)$$

is that a metal center and a ligand (eq 1,2) or CO_2 (eq 3), acting as oxygen acceptors, can be really active in the transformation of CO_2 into CO.

Here, we report an unusual metal-promoted reduction of carbon dioxide in which both a ligand and CO_2 function as oxygen sinks.

When CO_2 is bubbled through a tetrahydrofuran or benzene[2] suspension of the complex (triphos)Ni(η^2-CS_2)[3] (**1**) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane] at room temperature for 24 h, the original red-brown color of the solution changes to orange-yellow and yellow crystals of $[O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2]Ni(CO_3)$ (**2**) precipitate in 80% yield. Alternatively, CO_2 is bubbled through a methylene chloride solution of **1** and the mixture evaporated under CO_2 until **2** separates. Crystals suitable for an X-ray analysis[4] can be obtained by adding **1** to reagent grade benzene saturated with CO_2. Complex **2** crystallizes as **2**·$0.5H_2O\cdot C_6H_6$ (**2′**) upon standing for a period of 1-5 days.

The IR spectra (Nujol mull) of **2** and **2′** show bands in the C=O stretching region at 1660 and 1630 cm^{-1}. Absorptions at 1190 and 1120 cm^{-1} are also present, indicating the presence of the phosphine oxide group. The complexes react with HCl, evolving CO_2.

The molecular structure of complex **2′** is presented in Figure 1. The square-planar coordination sphere around the nickel atom consists of two phosphorus atoms of the triphos ligand and two oxygen atoms from the carbonate ion. To our knowledge there is no other structure of a nickel compound with carbonate acting as a bidentate ligand; thus, any detailed comparison is precluded. However no anomalous structural features are observed. The other phosphorus of the triphos molecule is not coordinated to the nickel atom. This phosphorus atom is involved in a P-O bond formed during the reaction. The P-O bond length is 1.38 (3) Å. The phosphine oxide groups of two molecules are engaged in a hydrogen-bonding network with water molecules located on the twofold axes of the lattice.

The $^{31}P\{^1H\}$ NMR spectrum of **2′** in $CDCl_3$ at 25 °C is consistent with the structure, showing resonances at 26.51 and 11.15 ppm (ratio 1:2), assigned to the phosphine oxide group and the two phosphorus atoms of triphos, respectively. Identical resonances are found for **2**.

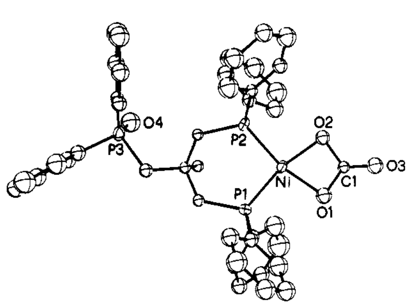
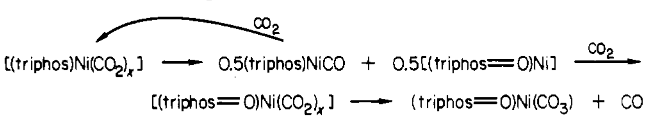


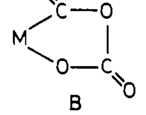
Figure 1. View of the molecular structure of (triphos=O)Ni(O_2CO). Bond lengths (Å): Ni-P(1), 2.143 (8); Ni-P(2), 2.153 (7); Ni-O(1), 1.95 (2); Ni-O(2), 1.91 (2). Bond angles (deg): P(1)-Ni-P(2), 98.1 (3); P(1)-Ni-O(1), 96.0 (6); P(2)-Ni-O(2), 96.2 (6); O(1)-Ni-O(2), 69.8 (8).

Scheme I



In the attempt of building a possible reaction mechanism, the following experimental pieces of information are noteworthy: (i) The reaction of **1** with CO_2 in methylene chloride leads in the beginning (4-5 h) to the formation of the complex (triphos)NiCO[5] (**3**), which optionally can be precipitated in 30-40% yield as yellow crystals by adding ethanol to the solution. Alternatively, the evaporation of the reaction mixture to dryness affords a yellow-brown solid. The IR spectrum of this material shows bands at 1895 cm^{-1} (CO stretching of the carbonyl of **3**) and in the region of the phosphine oxides.[6] (ii) When a methylene chloride solution of the carbonyl complex **3** is reacted with carbon dioxide, **2** is obtained. (iii) As a general observation, when a metal complex having triphos and a coligand such as CO, CS_2, CSe_2, SCNPh, or SO_2 is treated with an excess of a similar coligand, the displacement reaction (triphos)MX + Y → (triphos)NiY + X (M = Co, Ni; X, Y = CO, CS_2, CSe_2, SCNPh, SO_2) takes place.[7] Accordingly, the result at point ii does not necessarily imply a reaction between CO and CO_2 to give carbonate, but rather the formation of a initial CO_2 adduct that later evolves to the carbonate complex. (iv) As an alternative to the η^1 or η^2 coordination of CO_2 (A), dimerized head-to-tail adducts (B) are

A



B

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[1] For a comprehensive description and reference list of reactions of CO_2 with transition-metal complexes see: Sneeden, R. P. A. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford 1982; Vol. 8, p 225.

[2] Research purity grade CO_2 was obtained from Matheson and dried by passage through a 2 × 40 cm column of activated 3-Å molecular sieves. Tetrahydrofuran and benzene were refluxed under N_2 over sodium-benzophenone ketyl and were distilled immediately prior to use.

[3] For the synthesis see: Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768. For the structure see: Bianchini, C.; Masi, D.; Mealli, C.; Meli, A. *Inorg. Chem.* in press.

[4] Crystal data for $C_{42}H_{39}NiO_4P_3\cdot 0.5H_2O\cdot C_6H_6$: fw 844.52, monoclinic, *C*2, $a = 24.928$ (5) Å, $b = 15.258$ (3) Å, $c = 11.833$ (2) Å, $\beta = 90.91$ (2)°, $V = 4500.1$ A^3, $Z = 4$, $\rho_{calcd} = 1.249$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å. The structure was solved by heavy-atom techniques and refined to $R = 0.078$ ($R_w = 0.076$) for 1171 reflections with $I > 3\sigma(I)$ collected on a Philips PW 1100 diffractometer. Absorption corrections have been applied. Anisotropic temperature factors for the nickel and phosphorus atoms and contributions from the hydrogen atoms have been included during the refinement. The phenyl rings were treated as rigid groups.

[5] Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1965**, 812.

[6] Similar IR absorptions have been observed for a number of nickel complexes with the bidentate $O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2$ ligand.

[7] (a) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A. *J. Organomet. Chem.* **1983**, *247*, C29. (b) Bianchini, C.; Innocenti, P.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1983**, 1777. (c) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1309.

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sometimes observed. We have repeatedly experienced that triphos is not able to stabilize CO_2 adducts either of type A or of type B.[3,8] Thus, whichever species (triphos)Ni$(CO_2)_x$ is on the way of being formed, an easy degradation does follow. (v) The water molecules found in the crystal lattice of **2′** are to be ascribed to the use of reagent grade benzene. We have found that the carbonate–nickel complex is formed regardless of the trace amounts of water in the solvent. In particular, the anhydrous complex **2** is obtained by using dehydrated solvents. Thus, the presence of traces of water in our system does not seem to have the same importance as in the formation of other carbonate complexes from CO_2,[9] but rather serves to improve the crystallization process. By contrast, significant amounts of water in the reaction mixture have been found to inhibit the formation of the carbonate complex. These points suggest an overall process shown in Scheme I.

The above results indicate that none of the pathways (1)–(3) taken separately fully describe the transformation of CO_2 within our system. In fact, not only a carbonate complex and carbon monoxide are formed as in eq 3[10] but also a phosphine group of the ligand is oxidized as in eq 2.[11] Unfortunately, we have not been able to characterize any metal–CO_2 adduct; however, it seems reasonable to accept the idea of the intermediacy of $L_3M(CO_2)_x$ and $L_2M(CO_2)_x$ adducts at different times in the course of the reaction. This agrees well with the assumption that the nature of the metal–ligand fragment is of critical importance in determining not only the coordination mode[8] but also the pattern of CO_2 fragmentation.

Acknowledgment. This work was supported by a grant from the CNR program Chimica Fine e Secondaria.

Registry No. **1**, 60294-99-7; **2′**, 90914-29-7; CO_2, 124-38-9.

Supplementary Material Available: Listings of final positional and thermal parameters with standard deviations for (triphos=O)Ni$(O_2CO)\cdot 0.5H_2O\cdot C_6H_6$ (4 pages). Ordering information is given on any current masthead page.

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[8] Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

[9] Carmona, E.; Gonzales, F.; Poveda, M. L.; Marin, J. M.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3365.

[10] Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7606. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

[11] Aresta, M.; Nobile, C. F. *Inorg. Chim. Acta* **1977**, *24*, L49. Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944. Ito, T.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1398. Nicholas, K. M. *J. Organomet. Chem.* **1980**, *188*, C10.

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Bonding and Conformational Relationships in the "Open Metallocenes": Solid-State Structures of Bis(2,4-dimethylpentadienyl) Compounds of Vanadium and Chromium

Sir:

Recently we have demonstrated that a fairly extensive series of thermally stable, yet chemically reactive, bis(pentadienyl)metal compounds ("open metallocenes") exists.[1] This new series of related molecules clearly affords us a key opportunity to explore structural trends in metal–pentadienyl compounds and thereby gain important insight into their bonding. Structural characterization of the bis(2,4-dimethylpentadienyl) complexes of vanadium and chromium is presented herein and does indeed provide some useful information concerning these "open metallocenes", particularly as a comparison to related cyclopentadienyl and allyl analogues.

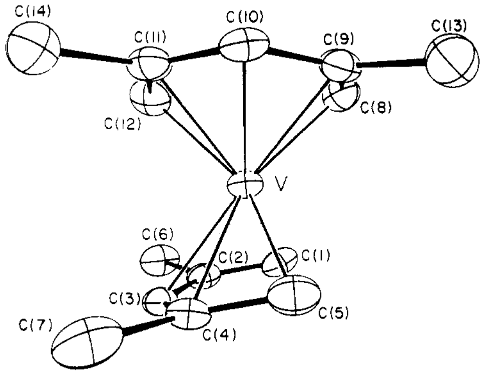

Figure 1. Perspective view of bis(2,4-dimethylpentadienyl)vanadium. The 30% probability ellipsoids are shown.

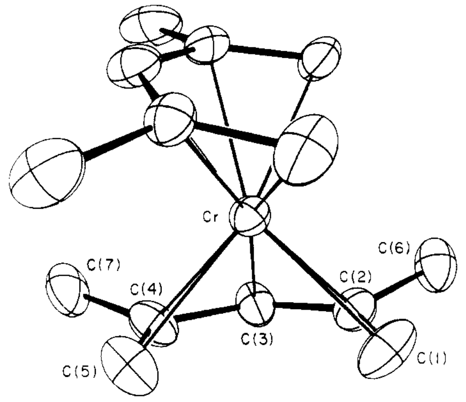

Figure 2. Perspective view of bis(2,4-dimethylpentadienyl)chromium. The 30% probability ellipsoids are shown. The molecule lies on a twofold rotational axis.

Table I. Bonding Parameters[a]

parameter	V	Cr	Fe
A. For $M(2,4\text{-}C_7H_{11})_2$ Compounds			
conformation angle	89.8	82.9	59.7
M–C(1,5)	2.179 (4)	2.166 (6)	2.108 (5)
M–C(2,4)	2.231 (4)	2.162 (5)	2.073 (4)
M–C(3)	2.236 (5)	2.167 (7)	2.084 (3)
M–C (av)	2.211 (2)	2.165 (4)	2.089 (1)
M–CM	1.632 (2)	1.594 (4)	1.508 (2)
C–C (internal)	1.415 (4)	1.414 (8)	1.416 (4)
C–C (external)	1.389 (4)	1.378 (8)	1.406 (4)
C(1)–C(2)–C(3)	124.7 (4)	125.2 (8)	124.1 (3)
C(2)–C(3)–C(4)	130.2 (3)	127.4 (8)	125.5 (3)
C(3)–C(4)–C(5)	125.0 (3)	123.5 (8)	120.7 (3)
C(1)- -C(5)	3.05 (1)	2.93 (1)	2.785 (5)
B. For $M(C_5H_5)_2$ Compounds			
M–C	2.280 (5)	2.169 (4)	2.064 (3)
C–C	1.434 (3)	1.431 (2)	1.440 (2)
M–CM	1.928 (6)	1.798 (4)	1.660 (10)

[a] Angles are given in degrees; distances are given in angstroms.

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[1] (a) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. (b) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (c) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (d) Stahl, L.; Ernst, R. D. *Organometallics* 1983, *2*, 1229.

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