

two isomers of these complexes were separated and identified spectroscopically.

### Summary and Conclusions

The behavior of the  $\{(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3) + \text{HC}\equiv\text{C-}t\text{-Bu}\}$  system is reminiscent of iron carbonyl-acetylene chemistry.<sup>30</sup> A large range of products is obtained, with a variety of cyclic ligands being constructed from the alkyne units and CO. It is unlike that observed in reactions of  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  with other alkynes where high specificity in product formation is generally observed. It seems likely that the different behavior of  $\text{HC}\equiv\text{C-}t\text{-Bu}$  is due to a combination of steric (*t*-Bu) and kinetic (H vs. *t*-Bu) effects that permit several alternative reaction pathways to develop simultaneously.

One feature of the set of products obtained in the present work is the variety of coordination modes observed for the pentadienone unit  $\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{C}(\text{O})-\text{C}(\text{R})=\text{C}(\text{R}')$  (R, R' = H or *t*-Bu). The fairly common "flyover bridge" attachment of an acyclic pentadienone is observed in two of the complexes (1 and 2). A closed cyclopentadienone ring is found in two other products. In one, it is attached in  $\eta^1, \eta^3$  manner (complex 5); in the other, there is an  $\eta^2, \eta^2$  attachment (complex 6). These are most unusual bonding modes for this type of ligand.

(30) Hubel, W. In *Organic Syntheses via Metal Carbonyls*; Interscience: New York, 1968; Vol. 1, p 273.

Perhaps the most unexpected feature of the reaction systems is the strange oxygenation of the metalladiene ring in complex 3. Such ring systems are generally very inert in binuclear complexes, although a variety of additions to mononuclear metalladiene rings have been reported.<sup>31</sup> We are not aware of previous observations of oxygenation of metalladiene rings involving either mononuclear or binuclear systems. Another novel feature of this reaction system is the cyclopentadienone ring opening that occurs when 5 is decarbonylated to give 2.

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**Registry No.** 1, 105969-35-5; 2, 105969-36-6; 3, 105945-01-5; 4, 105945-02-6; 5, 105945-03-7; 6, 105945-04-8;  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ , 71844-53-6;  $\text{HC}\equiv\text{C-}t\text{-Bu}$ , 917-92-0;  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{W})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ , 57872-13-6; Rh, 7440-16-6.

**Supplementary Material Available:** Tables of thermal parameters, ligand geometries, and equations for planes for complexes 4, 5, and 6 (12 pages); listing of structure factor amplitudes for complexes 4, 5, and 6 (69 pages). Ordering information is given on any current masthead page.

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## Reactions of Carbon Dioxide with the Electron-Rich Polyhydride Complex $[\text{Mo}(\text{dmpe})_2\text{H}_4]$

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The electron-rich polyhydride complex  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (1), formed by reduction of  $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$  under  $\text{H}_2$ , reacts with  $\text{CO}_2$  to give a complex manifold of products containing formate, carbon dioxide, and carbonate ligands. The final product of the reaction is  $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$  (2), in which reductive disproportionation of  $\text{CO}_2$  has led to formation of a carbonate ligand. Two other products have been identified in which only two of the initial hydrides have been retained, one of which is the crystallographically characterized bis(formate)  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$  (3). The complex crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 8.842$  (8) Å,  $b = 13.830$  (4) Å,  $c = 9.910$  (3) Å,  $\beta = 104.45$  (2)°,  $\rho_{\text{calcd}} = 1.38$  g cm<sup>-3</sup>,  $Z = 4$ , and  $R_w = 3.96\%$  and has an octahedral geometry with trans  $\eta^1$ -formate ligands. A precursor to 3 containing an  $\eta^2\text{-CO}_2$  ligand has been spectroscopically characterized as  $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$  (4). Two complexes formed early in the reaction sequence, before elimination of  $\text{H}_2$ , have been spectroscopically identified as  $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$  (5) and  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$  (6). The characteristic absorptions between 1600 and 2800 cm<sup>-1</sup> of the formate, carbonate, hydride, and carbon dioxide ligands in these molecules have been assigned on the basis of <sup>13</sup>C and deuterium-labeling studies.

### Introduction

Two of the characteristic reactions of carbon dioxide with transition-metal complexes are reversible insertion into a transition-metal hydride bond and reductive disproportionation into carbonate and carbon monoxide by electron-rich transition-metal complexes.<sup>1</sup> While examining<sup>2</sup> the chemistry of molybdenum complexes with the strongly

$\sigma$ -donating bis(chelate) phosphane  $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}-\text{H}_3)_2$  (dmpe), we have prepared an electron-rich polyhydride complex  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (1) which could a priori exhibit either of these reactions when treated with  $\text{CO}_2$ .

(1) (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* 1979, 28, 79. (b) Darensbourg, D. J.; Kudoroski, R. A. *Adv. Organomet. Chem.* 1983, 22, 129. (c) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 50.4.

(2) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Inorg. Chem.* 1986, 25, 1880.

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In practice the polyhydride nature of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  allows the compound to undergo a complex series of reactions with  $\text{CO}_2$  in which both reactivity patterns are observed. We have been able to identify most species within the reaction manifold, despite the lability of many of the complexes. The products include the formate hydride  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ , the carbonate hydride  $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$ , the  $\text{CO}_2$  complex  $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$ , and the bis(formate) complex  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$  (isomeric with the  $\text{CO}_2$  complex)—a rare example of a structurally characterized  $\eta^1$ -formate complex and the only reported bis(formate) which does not form a polymeric structure.

### Experimental Section

**General Data.** All manipulations were carried out under a dry, oxygen-free atmosphere of argon except where stated otherwise. Solvents were freshly distilled from drying agents before use as follows: sodium benzophenone ketyl for tetrahydrofuran (THF);  $\text{LiAlH}_4$  for pentane;  $\text{CaH}_2$  for toluene and benzene. Sodium amalgam (40%) was prepared by the literature method.<sup>3</sup>  $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$  was prepared as reported previously.<sup>2</sup>  $^{13}\text{CO}_2$  (92 atom %) was used as purchased from Merck, Sharpe, and Dohme.  $^1\text{H}$  NMR spectra were recorded on a Bruker WM-300 at 300 MHz or a Bruker AM-500 at 500 MHz, and the residual protons of the deuteriated solvents were used as internal standards.  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WM-300 at 74.47 and 121.5 MHz, respectively, and the  $^{13}\text{C}$  absorptions of the  $\text{C}_6\text{D}_6$  or  $\text{C}_6\text{D}_5\text{CD}_3$  solvents at  $\delta$  128.0 and 137.5 and the  $^{31}\text{P}$  absorption of external 85%  $\text{H}_3\text{PO}_4$  were used as calibrants. Microanalyses were performed as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, NY (Sch), or Galbraith Laboratories, Knoxville, TN (Gal). Gas chromatographic analyses for  $\text{H}_2$  were carried out on a Perkin-Elmer Sigma 300 using a 10.5 ft Carboxieve S-II column and TCD detection. Mass spectra were recorded on an AEI-MS9 using electron ionization at 60 eV. IR spectra of mull samples were recorded on a Perkin-Elmer 457A or 683, and solution IR spectra were recorded on a Nicolet 7199 FT spectrometer. All IR spectra were calibrated relative to the absorption of a polystyrene film at  $1601\text{ cm}^{-1}$ .

IR data are tabulated in the Results and Discussion and have been omitted from the Experimental Section in the interests of brevity and clarity. Details of the preparation of  $^{13}\text{C}$ - and D-labeled samples have been omitted from the Experimental Section unless they differ significantly from the preparations of the analogous unlabeled material (this was sometimes the case when changes in reaction stoichiometry necessitated other changes in the reaction conditions).

**$[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (1).** This compound was prepared and manipulated under an atmosphere of  $\text{H}_2$ , and exposure to ambient light was minimized. A solution of *trans*- $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$  (0.97 g, 2.09 mmol) in THF (20 mL) was added to ca. 12 g of 40% sodium amalgam under 20 mL of THF and placed under 1.5 atm of  $\text{H}_2$ . The mixture was vigorously stirred magnetically for 24 h and then allowed to settle for 12 h. The olive green solution was decanted off. Removal of the solvent gave a solid which was extracted with pentane ( $3 \times 30\text{ mL}$ ) to give a yellow-green solution. This was filtered and concentrated until saturated. Slow cooling (24 h) to  $-78^\circ\text{C}$  gave pale yellow cubes which were collected by filtration and shown to be 0.64 g (1.59 mmol, 77%) of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ :  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.41 (br s, 32, dmpe),  $-5.51$  (quin,  $J_{\text{P-H}} = 31.5\text{ Hz}$ , 4, MoH);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  51.0 (s). Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{MoP}_4$ : C, 36.01; H, 9.07. Found (Sch): C, 36.27; H, 8.35.

**$[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$  (2).** A pale yellow solution of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (0.435 g, 1.08 mmol) in benzene (30 mL) was degassed and placed under 20 psi of  $\text{CO}_2$  to give a burgundy brown solution.

This was stirred in the dark for 13.5 h to give a golden brown solution from which a noncondensable gas shown to be  $\text{H}_2$  (GC) was removed by use of a Toepler pump (19.3 mL, 0.86 mmol). A further 10 mL of benzene was added to redissolve a small quantity of a brown precipitate, and pentane (100 mL) was carefully layered on to the benzene. Diffusive mixing over 11 days in the dark led to precipitation of  $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$  (0.106 g, 0.23 mmol, 21%) as a mixture of brown nuggets and yellow needles which were shown to be identical by comparison of  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of mechanically separated samples. Analytical samples were prepared by recrystallization from benzene/pentane over 24 h:  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.12–1.17 (c, 32, dmpe),  $-6.23$  (dq,  $J = 49, 43\text{ Hz}$ , 2, MoH);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  53.7 (t,  $J = 8.5\text{ Hz}$ , 2), 30.8 (t,  $J = 8.5\text{ Hz}$ , 2). Anal. Calcd for  $\text{C}_{13}\text{H}_{34}\text{MoO}_3\text{P}_4$ : C, 34.07; H, 7.48; P, 27.04. Found (Gal): C, 33.75; H, 7.45; P, 28.28.

**Reaction of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  with  $^{13}\text{CO}_2$  in Benzene and Preparation of  $[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$ .** A pale yellow solution of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (0.048 g, 0.12 mmol) in benzene (10 mL) in a 40-mL vessel was degassed and  $^{13}\text{CO}_2$  (41.2 mL, 1.84 mmol) condensed into the vessel at  $-196^\circ\text{C}$ . The vessel was slowly warmed to ambient temperatures, and FT IR spectra of an aliquot were recorded after 7 and 21 min. The remainder of the solution was pressurized to 20 psi with Ar and stirred in the dark for 5.5 days.  $^{31}\text{P}$  and  $^{13}\text{C}$  spectra of the sample were recorded, and the solvent was removed to give  $[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$  as a yellow brown solid (mull IR):  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  163.3 (t,  $J_{\text{P-C}} = 9\text{ Hz}$ ,  $\text{CO}_3^{2-}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  53.7 (t,  $J = 8.5\text{ Hz}$ , 2), 30.8 (t of d,  $J = 8.5\text{ Hz}$ ,  $J_{\text{P-C}} = 8\text{ Hz}$ , 2).

**$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$  (3).** A pale yellow solution of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (0.046 g, 0.11 mmol) in pentane (20 mL) was placed under 20 psi of  $\text{CO}_2$  and left in the dark with minimal agitation for 10 days. The solution was then filtered under  $\text{CO}_2$  and cooled to  $0^\circ\text{C}$  under 20 psi of  $\text{CO}_2$ . Light brown crystals began to form after 12 h, and a first crop (0.015 g) was collected by filtration after 4.5 days. A second crop (0.011 g) was collected after 60 days, and the combined solids dried under vacuum to yield 0.026 g (0.05 mmol, 47%) of  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ :  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.36 ( $w_{1/2} = 84\text{ Hz}$ , 8,  $\text{CH}_2$ ),  $-9.63$  ( $w_{1/2} = 124\text{ Hz}$ , 24,  $\text{CH}_3$ ); mass spectrum,  $m/e$  (parent ion) 488 (for  $^{96}\text{Mo}$ );  $\mu_{\text{eff}}$  (NMR method,<sup>4</sup> toluene, 5%  $\text{Me}_4\text{Si}$ , diamagnetic correction<sup>5</sup>)  $2.54\ \mu\text{B}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{34}\text{MoO}_4\text{P}_4$ : C, 34.58; H, 7.05; P, 25.48. Found (Sch): C, 34.51; H, 7.04; P, 25.68.

**$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$  (4).** The pentane/benzene supernatant from the preparation of 2 above was concentrated to dryness under reduced pressure to give a brown solid, which was redissolved in 1:1 toluene/pentane (30 mL). The solution was cooled over 12 h to  $-78^\circ\text{C}$  to initiate crystallization, and the light orange, irregular cubes which formed were collected after 3 days at  $-78^\circ\text{C}$  and dried under vacuum to give 0.182 g (0.37 mmol, 34%) of a mixture containing (IR) traces of  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$  mixed with  $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$ :  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.71 (s, 1, OCHO), 2.0–0.5 (c, 32, dmpe),  $-6.18$  (quin,  $J_{\text{P-H}} = 38\text{ Hz}$ , 1, Mo-H);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  45.8 (s, dmpe);  $^{13}\text{C}$  NMR (sample prepared from  $^{13}\text{CO}_2$ ,  $\text{C}_6\text{D}_6$ )  $\delta$  224.6 (quin of d,  $J_{\text{P-C}} = 12\text{ Hz}$ ,  $J_{\text{C-H}} = 6\text{ Hz}$ ,  $\text{CO}_2$ ), 167.2 (d,  $J_{\text{C-H}} = 195\text{ Hz}$ , OCHO). Anal. Calcd for  $\text{C}_{14}\text{H}_{34}\text{MoO}_4\text{P}_4$ : C, 34.58; H, 7.05; P, 25.48. Found (Sch): C, 34.57; H, 6.99; P, 25.19.

**The Initial  $\text{CO}_2$  Adduct 5.** A filtered solution of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (0.224 g, 0.56 mmol) in pentane (30 mL) was degassed, placed under 20 psi of  $\text{CO}_2$ , and vigorously stirred magnetically in the dark. Within 1 h the solution changed from a pale yellow color to a burgundy brown and began to deposit a yellow solid. After 4 days the solution was light green and precipitation of the solid had ceased. The solid was collected by decantation, washed with pentane (20 mL), and dried under vacuum to give 0.073 g of yellow solid (0.16 mmol, 29%). See Results and Discussion for description of  $^{31}\text{P}$  and  $^1\text{H}$  NMR.  $^{13}\text{C}$  NMR (sample prepared from  $^{13}\text{CO}_2$ ,  $\text{C}_6\text{D}_5\text{CD}_3/\text{C}_6\text{H}_5\text{CH}_3$ , 195 K):  $\delta$  203.8 (d of t,  $J = 26$  and  $13\text{ Hz}$ ,  $\text{CO}_2$ ), 166.8 (d,  $J_{\text{C-H}} = 195\text{ Hz}$ , OCHO).

**Preparation of D- and  $^{13}\text{C}$ -Substituted  $\text{CO}_2$  Adduct and  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ .** In a typical procedure a solution of  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  (0.074 g, 0.56 mmol) in pentane (5 mL) was evacuated, and  $^{13}\text{CO}_2$  (37 mL, 1.66 mmol) was condensed into the vessel at  $-196^\circ\text{C}$  from a high vacuum gas handling line. The sealed vessel was warmed to ambient temperatures and stirred

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(4) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Bartle, K. D.; Jones, D. W.; Marici, S. *Croat. Chim. Acta* **1968**, *40*, 227.

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Table I. Summary of Crystallographic Data for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] (3)

Crystal Data	
space group	P2 <sub>1</sub> /n
a, Å	8.842 (2)
b, Å	13.830 (4)
c, Å	9.910 (3)
β, deg	104.45 (2)
V, Å <sup>3</sup>	1173.5 (5)
Z	4
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.38
μ, cm <sup>-1</sup> (Mo Kα)	8.3
Data Collection	
radiatn	Mo Kα
λ, Å	0.710 69
mode	θ-2θ
2θ range, deg	3.0-57.5
scan range, deg	0.8 (l), 0.9 (r)
scan speed, deg/min	3.0-16.0
scan/bkgd	0.75
exposure, h	87.92
reflctns	3795
Agreement Factors	
R <sup>a</sup>	0.0371
R <sub>w</sub> <sup>b</sup>	0.0396
g	0.000 95
max peak in final difference map, e Å <sup>-3</sup>	0.51 <sup>c</sup>

<sup>a</sup>  $R = \sum(|F_o - F_c|) / \sum(F_o)$ . <sup>b</sup>  $R_w = \sum(w^{1/2}|F_o - F_c|) / \sum(w^{1/2}F_o)$ ,  $w = (\sigma^2(F) + gF^2)^{-1}$ . <sup>c</sup> Largest peak is 0.5 Å from H13A. Next largest peak is 0.32 e Å<sup>-3</sup>.

for 3 days. The supernatant was removed by cannula filtration and the solid CO<sub>2</sub> adduct washed with pentane (10 mL) and dried under vacuum. The supernatant was concentrated under vacuum to give a yellow oil shown (IR) to be primarily <sup>13</sup>C-labeled [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] contaminated by some labeled [Mo(dmpe)<sub>2</sub>(CO)<sub>2</sub>(OCHO)H].

**Formation of a Mixture of Solid [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>H<sub>2</sub>] (6) and the Initial CO<sub>2</sub> Adduct.** A degassed solution of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] (0.037 g, 0.09 mmol) in benzene (5 mL) was swirled with CO<sub>2</sub> (20 psi) for 45 s and plunged into dry ice/acetone. The benzene was sublimed off over 20 h at -40 to -35 °C and 10<sup>-3</sup> torr to yield 0.029 g (0.06 mmol, 66%) of a bright yellow mixture (mull IR) of the initial CO<sub>2</sub> adduct and [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>H<sub>2</sub>]: <sup>1</sup>H NMR of sample prepared from <sup>13</sup>CO<sub>2</sub> (300 MHz, C<sub>6</sub>D<sub>6</sub>, 283 K) δ 8.87 (d, J<sub>C-H</sub> = 196 Hz, 2, OCHO), 2.0-0.5 (c, 32, dmpe), -7.80 (c, 2, Mo-H); <sup>1</sup>H NMR of sample prepared from <sup>13</sup>CO<sub>2</sub> (300 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 200 K) δ 8.89 (d, J<sub>C-H</sub> = 196 Hz, 2, OCHO), 1.6-0.6 (c, 32, dmpe), -8.10 (quin, J<sub>P-H</sub> = 48 Hz, 2, Mo-H); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 54.2 (t, 2, J = 14.5 Hz), 29.1 (t, 2, J = 14.5 Hz); <sup>13</sup>C NMR (sample prepared from <sup>13</sup>CO<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>) δ 167.1 (d, J<sub>C-H</sub> = 195 Hz, OCHO).

**X-ray Crystallography. General Data.** Crystals were handled under argon and sealed in glass capillaries for diffraction studies. The data were collected on a Nicolet R3 diffractometer by using graphite-monochromated Mo Kα radiation. The final unit cell parameters were determined by a least-squares treatment of the setting angles of 12 sets of accurately centered Friedel pairs. Lorentz and polarization corrections were applied by using the SHELXTL programs.<sup>6</sup> Atomic scattering factors were based on literature values for Mo<sup>7</sup> and on those in the SHELXTL program for other atoms. Weights were taken as  $w = (\sigma^2(F) + gF^2)^{-1}$ .

**Structure Solution and Refinement.** Crystals of [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] suitable for a single-crystal X-ray diffraction study were prepared by recrystallization from pentane. The parallelepiped-shaped crystal studied measured approximately 0.25 mm on each side. Reflections taken from a rotation photograph indicated that the unit cell had two angles measuring

Table II. Atomic Coordinates and Thermal Parameters for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>]<sup>a</sup>

atom	x	y	z	U <sub>equiv</sub>
Mo(1)	0	0	0	48 (1)
P(1)	2363 (2)	1269 (1)	1129 (2)	72 (1)
P(2)	926 (2)	-191 (1)	2431 (1)	68 (1)
Ox(1)	-1736 (5)	1083 (3)	-85 (4)	81 (2)
C(11)	1645 (9)	2499 (4)	602 (7)	115 (5)
Ca	-3319 (9)	1372 (5)	-943 (8)	97 (4)
Ha	-3511 (78)	2005 (38)	-635 (56)	106 <sup>b</sup>
Ox(2)	-4383 (6)	1055 (4)	-2088 (6)	167 (4)
C(21)	2763 (10)	671 (5)	3533 (6)	116 (5)
C(22)	-750 (10)	103 (6)	2810 (8)	122 (5)
C(12)	4404 (9)	1251 (7)	1150 (11)	181 (9)
C(23)	1885 (10)	-1309 (4)	3398 (6)	116 (4)
C(13)	3220 (15)	1317 (7)	2957 (7)	229 (8)

<sup>a</sup> Fractional atomic coordinates (×10<sup>4</sup>). The equivalent isotropic U (Å<sup>2</sup> × 10<sup>3</sup>) is defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor. See Figure 1 for atom designations. <sup>b</sup> U<sub>iso</sub> (Ha) = 1.2 U<sub>equiv</sub> (Ca).

approximately 90°; the monoclinic symmetry was confirmed by the presence of mirror symmetry uniquely along the b axis in axial photographs. No higher order unit cell could be found with either the P3 program or TRACER. A trial data collection indicated the unit cell to be P2<sub>1</sub>/n, and a single quadrant of data (hkl): +h, +k, ±l was collected. Full details of the data collection are presented in Table I. No decrease in intensity was observed for the check reflections during data collection. The position of the Mo (which was known to be on a special position) and of the atoms bound directly to Mo were revealed by the SOLV direct methods of SHELXTL.<sup>6</sup> Refinement of atomic positions revealed the positions of all non-hydrogen atoms on subsequent difference maps. The hydrogens of the dmpe ligands were placed in positions (Table S-II in the supplementary material) calculated from those of the adjacent carbon atoms with r(C-H) = 0.96 Å and U<sub>iso</sub> = 1.2 U<sub>equiv</sub>; the methyl hydrogens were refined as free-to-rotate rigid groups. The formate hydrogen, Ha, was located in a difference map after all other hydrogen atoms had been placed in their calculated positions. The positional parameters of the formate hydrogen were allowed to refine, and led to a reasonable C-H bond distance (0.99 (6) Å) from the formate carbon, Ca, with the expected large esd's in its positional parameters. Refinement was continued to convergence (Δ/σ < 0.1) by using the blocked-cascade least-squares procedure of SHELXTL. Final atomic positional parameters are presented in Table II, and anisotropic thermal parameters are given in Table SI of the supplementary material.

## Results and Discussion

The reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub> is complex and leads to a manifold of six observable products. Identifying these species is complicated by the tendency of many to convert to species later in the sequence under typical separation conditions. We have, however, been able to use the sensitivity of the reaction to the nature of the solvent and other reaction variables to isolate analytical samples of three of the compounds, and with the spectroscopic characteristics of these materials to hand we have been able to identify two of the remaining complexes in the system. After a brief discussion of the synthesis of the starting tetrahydride 1, the characterization of the isolable products of the reaction of 1 with CO<sub>2</sub> will be presented, and the probable nature of some of the more labile intermediates in the reaction will then be discussed.

**Preparation of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] (1).** A number of eight-coordinate tetrahydridotetraphosphane complexes of molybdenum have been prepared by hydride reduction of Mo(IV) [MoCl<sub>4</sub>L<sub>2</sub>] complexes in the presence of excess phosphane<sup>8,9</sup> or by addition of H<sub>2</sub> to Mo(0) [Mo(PAr<sub>2</sub>C-

(6) Sheldrick, G. M. *SHELXTL User's Manual, Issue 4.0*; Nicolet: Madison, WI, 1981.

(7) *International Tables for X-Ray Crystallography*; Ibers, J., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72-98.

(8) Penella, F. *Inorg. Synth.* 1974, 15, 42.

(9) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* 1982, 21, 1273.

**Table III. Bond Lengths (Å) within  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]^a$** 

Mo(1)–P(1)	2.467 (1)	Mo(1)–P(2)	2.472 (2)
	Mo(1)–Ox(1)	2.102 (4)	
Ox(1)–Ca	1.247 (7)	Ca–Ox(2)	1.203 (9)
	Ca–Ha	0.993 (61)	
P(1)–C(11)	1.793 (6)	P(2)–C(21)	1.836 (6)
P(1)–C(12)	1.788 (11)	P(2)–C(22)	1.807 (11)
P(1)–C(13)	1.811 (8)	P(2)–C(23)	1.816 (6)
	C(21)–C(13)	1.304 (14)	

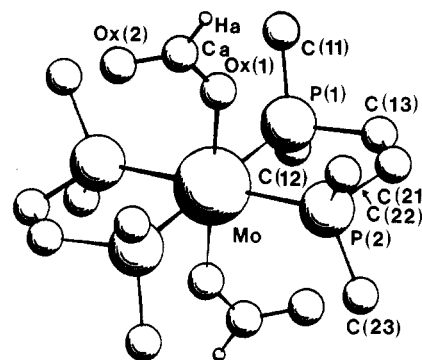
<sup>a</sup> See Figure 1 for atom designations.

$\text{H}_2\text{CH}_2\text{PAR}_2)_2(\text{N}_2)_2]$  complexes.<sup>10</sup> The ability of 40% sodium amalgam to reduce  $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]^2$  suggested that a similar complex might be available with dmpe as a chelating diphosphane ligand by conducting the reduction under  $\text{H}_2$ . This proved to be the case, and thermally stable but highly air-sensitive **1** could be prepared in 77% yield in this manner. The complex does not give a parent ion in the mass spectrum (the highest peak corresponds to  $[\text{Mo}(\text{dmpe})_2\text{H}_2]^+$ ) but was unambiguously characterized as a tetrahydride by  $^{31}\text{P}$  NMR spectra: the singlet observed at  $\delta$  51.0 in broad-band  $^1\text{H}$ -decoupled spectra splits into a quintet<sup>11</sup> when the decoupling irradiation is reduced to a narrow band of frequencies centered at  $\delta$  1.5.

**Isolation and Characterization of  $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$  (**2**).** The final product of the reaction of **1** with  $\text{CO}_2$  under most conditions is the unusual carbonate dihydride **2**, which can be isolated in analytically pure form when the reaction is carried out in benzene.

Formulation of the product as  $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$  is consistent with the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the complex. The high-field absorption assigned to the hydride ligands in  $^1\text{H}$  NMR spectra could be interpreted on the assumption that four  $^{31}\text{P}$  and two  $^1\text{H}$  nuclei formed an  $\text{AA}'\text{M}_2\text{XX}'$  spin system ( $\text{X}, \text{X}' = \text{H}$ ) with  $J_{\text{AM}} = J_{\text{A}'\text{M}} = 8.5$  Hz,  $J_{\text{AX}} = J_{\text{A}'\text{X}} = J_{\text{MX}} = J_{\text{M}'\text{X}} = 43$  Hz,  $J_{\text{AX}'} = J_{\text{A}'\text{X}} = 49$  Hz,  $J_{\text{AA}'} < 2$  Hz, and  $J_{\text{XX}'} < 2$  Hz.<sup>12</sup> The  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum of the compound contained two triplet resonances as anticipated on this model, and the presence of two hydride ligands was confirmed by reducing the  $^1\text{H}$  decoupling irradiation to a narrow band of frequencies centered at  $\delta$  1.5. This gave a  $^{31}\text{P}$  spectrum in which the two dmpe resonances appeared as partially resolved triplets of triplets.<sup>14</sup>

The  $\text{CO}_2$ -derived ligand was identified as a carbonate group by NMR and IR studies of **2** and of  $^{13}\text{C}$ - and D-labeled samples.  $^{13}\text{C}$  NMR spectra of a sample prepared from 92% enriched  $^{13}\text{CO}_2$  contained a triplet at  $\delta$  163.3 assigned to the carbonate carbon selectively coupling to



**Figure 1.** SNOOPI drawing of  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ , indicating atomic nomenclature. Atoms have been drawn at 50% of their covalent radii, and dmpe hydrogen atoms have been omitted for clarity.

**Table IV. Bond Angles (deg) within  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]^a$** 

d			
P(1)–Mo(1)–P(2)	79.9 (1)	P(1)–Mo(1)–P(2 <sub>a</sub> )	100.1 (1)
P(1)–Mo(1)–Ox(1)	84.3 (1)	P(1)–Mo(1)–Ox(1 <sub>a</sub> )	95.7 (1)
P(2)–Mo(1)–Ox(1)	84.2 (1)	P(2)–Mo(1)–Ox(1 <sub>a</sub> )	95.8 (1)
Mo(1)–P(1)–C(11)	117.0 (2)	Mo(1)–P(2)–C(21)	109.2 (3)
Mo(1)–P(1)–C(12)	123.1 (3)	Mo(1)–P(2)–C(22)	117.1 (2)
Mo(1)–P(1)–C(13)	109.1 (4)	Mo(1)–P(2)–C(23)	122.7 (3)
C(11)–P(1)–C(12)	100.4 (4)	C(21)–P(2)–C(22)	102.2 (4)
C(11)–P(1)–C(13)	101.7 (4)	C(21)–P(2)–C(23)	101.0 (3)
C(12)–P(1)–C(13)	102.8 (5)	C(22)–P(2)–C(23)	101.7 (4)
P(1)–C(13)–C(21)	121.8 (6)	P(2)–C(21)–C(13)	119.3 (5)
Mo(1)–Ox(1)–Ca	136.7 (5)	Ox(1)–Ca–Ox(2)	127.3 (8)
Ox(1)–Ca–Ha	109.4 (26)	Ha–Ca–Ox(2)	122.1 (27)

<sup>a</sup> Atoms with numbers having "a" subscripts are symmetry generated by the center of inversion. See Figure 1 for atom designations.

two of the dmpe P nuclei with  $J_{\text{P-C}} = 9$  Hz. This interpretation was supported by the  $^{31}\text{P}$  NMR spectrum of this sample, in which the  $\delta$  53.7 peak showed the corresponding doublet pattern but the  $\delta$  30.8 peak was unchanged. An alternative assignment of the carbon resonance to a formate ligand (which could absorb in the same region—see below) was ruled out by two observations: the  $^{13}\text{C}$  resonance of **2** did not exhibit the single bond  $^1\text{H}$  coupling characteristic of formates (see below) in gated spectra, and the principal  $\nu_{\text{C=O}}$  for the carbonate ligand at  $1601\text{ cm}^{-1}$  shifted  $40\text{ cm}^{-1}$  with  $^{13}\text{C}$  substitution but was unaffected by deuterium substitution.<sup>15</sup>

**Isolation and Characterization of  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$  (**3**).** The bis(formate) complex was isolated as an analytically pure crystalline material by reacting  $[\text{Mo}(\text{dmpe})_2\text{H}_4]$  with  $\text{CO}_2$  in pentane under conditions such that agitation of the solution was minimized. The complex was primarily characterized by a single-crystal X-ray diffraction study, which established that the complex has two  $\eta^1$ -formate ligands arranged in a trans geometry as illustrated in Figure 1. The bond lengths and bond angles within the complex are presented in Tables III and IV, respectively, and details of the structure determination are given in the Experimental Section and in the supplementary material.

The  $\eta^1$ -formate ligands are the most interesting feature of the structure. Formate, like most carboxylate ligands, tends to be a bis(chelate) or bridging ligand, and relatively

(15) This supports assignment as a carbonate and rules out assignment as a formate  $\text{C}=\text{O}$  stretch, since in this system these characteristically exhibited  $7\text{--}10\text{ cm}^{-1}$  shifts on deuteration (see IR section below).

(10) Archer, L. J.; George, T. A. *Inorg. Chem.* 1979, 18, 2079.

(11) The splittings observed in  $^{31}\text{P}$  spectra during such experiments are typically less than the corresponding splittings in the  $^1\text{H}$  spectra, as a consequence of partial decoupling of the hydrides on the metal.

(12) This is a reasonable coupling scheme for a fluxional eight-coordinate complex. The coupling constants are also reasonable and led to an excellent PANIC<sup>13</sup> simulation of the observed spectrum. The coupling scheme implies that one (M) pair of P atoms are chemically and magnetically equivalent (they could, for example, be mutually trans: strong coupling of these two spins would not significantly affect the anticipated spectrum), while the other (A) pair are magnetically inequivalent with respect to the metal hydrides. The magnetic inequivalence of the A  $^{31}\text{P}$  nuclei and of the hydride ligands could, for example, be accounted for if A and A' are cis and X and X' are cis within a plane perpendicular to the M–Mo–M axis. Accidental degeneracy of  $J_{\text{AX}}$  and  $J_{\text{MX}}$  is not unreasonable within this model, since X would be cis with respect to the A  $^{31}\text{P}$  and both M  $^{31}\text{P}$ .

(13) *Aspect 2000 NMR Software Manual*; Bruker Instruments: Billerica, MA, 1979.

(14) PANIC<sup>13</sup> simulation of this spectrum was consistent with origin from the spin system deduced from the  $^1\text{H}$  NMR data with partial  $^1\text{H}$  decoupling reducing all P–H coupling constants by ca. 50%.

few  $\eta^1$ -formate complexes have been structurally characterized to date.<sup>16</sup> The Mo—Ox(2) distance of 3.540 (8) Å is unambiguously nonbonding, and, as in the case of most (but not all<sup>16d,e</sup>) of the reported  $\eta^1$ -formate structures, the C—O bond lengths are consistent with the conventional bonding description (MoO—CH=O). The failure of the formate ligands to bridge Mo<sup>2+</sup> sites in the lattice contrasts markedly with the polymeric structures established for the formate dihydrates<sup>17</sup> and anhydrous formates<sup>18</sup> of many divalent metals and with the extensive chemistry of dinuclear Mo(II) carboxylates with quadruple metal–metal bonds.<sup>19</sup>

Initial characterization of 3 was hampered by its paramagnetism, which corresponds to an effective magnetic moment in solution of 2.54  $\mu_B$ . This is close to the spin-only value for an approximately octahedral d<sup>4</sup> complex with two unpaired electrons and no major Jahn–Teller distortion and is consistent with the observed solid-state structure. It is also similar to the value which we have reported for the closely related molecule *trans*-[Mo(dmpe)<sub>2</sub>Cl<sub>2</sub>], and, as in that case, the dmpe ligands of the molecule give rise to observable (although broad) resonances in <sup>1</sup>H NMR spectra despite the paramagnetism of the molecule. Similar behavior has been reported for other d<sup>4</sup> octahedral complexes<sup>20</sup> and demonstrated to result from the temperature-independent paramagnetism of the complexes.<sup>21</sup> A similar interpretation may apply in the present case, although detailed magnetic and NMR studies would be required to confirm this.

**Characterization of [Mo(dmpe)<sub>2</sub>(CO<sub>2</sub>)(OCHO)H] (4), a Precursor to [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>].** The most logical immediate precursor to the bis(formate) 3 would be a complex containing one formate ligand, one CO<sub>2</sub>, and a hydride ligand, and we have indeed been able to obtain evidence for the intermediacy of a complex formulated as [Mo(dmpe)<sub>2</sub>(CO<sub>2</sub>)(OCHO)H] (4) in the formation of 3. The complex was obtained from the mother liquor of the pentane/benzene mixture from which 2 precipitated and could be isolated by stripping this solution, redissolving the material in a toluene/pentane mixture, and cooling the new solution slowly to –78 °C. Complex 4 converts into 3 rapidly in solution and slowly in the solid state, and we have been unable to obtain solutions of the material which do not contain significant quantities of 3. Mull IR spectra do, however, indicate that fresh solid samples are relatively clean, and elemental analysis of this material is consistent with that expected for a mixture of the isomeric species 3 and 4.

The presence of a single hydride ligand and two dmpe ligands in 4 was established by the combined <sup>1</sup>H and <sup>31</sup>P spectra of an NMR sample of the solid prepared under CO<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>. The <sup>31</sup>P{<sup>1</sup>H} spectrum contained a single resonance attributable to 4, which was split into a doublet in spectra recorded with narrow band decoupling (centered at  $\delta$  1.5) of the dmpe protons. The presence of a high-field quintet of the appropriate intensity in <sup>1</sup>H NMR spectra

confirmed that this doublet splitting was a consequence of coupling to a single metal hydride and that all four dmpe P nuclei are equivalent. Since it is unlikely that the ground-state structure of the complex contains chemically equivalent P nuclei, this indicates that the molecule is fluxional.<sup>22</sup> The magnitude of  $J_{P-H}$  in 4 was similar to that observed in 1.

The presence of a coordinated CO<sub>2</sub> ligand in 4 was suggested by examination of <sup>13</sup>C NMR spectra of a solution prepared by reacting 1 with 5 equiv of 92% enriched <sup>13</sup>CO<sub>2</sub> for 10 days in benzene-*d*<sub>6</sub> in a sealed NMR tube. In addition to the carbonate resonance of 2 (the principal product under these conditions) and resonances assigned to 6 (see below) the <sup>1</sup>H-decoupled spectrum contained a singlet at  $\delta$  167.2 and a quintet ( $J = 12$  Hz) at  $\delta$  224.6. In <sup>1</sup>H-coupled spectra the singlet exhibited single-bond coupling of 195 Hz, consistent with assignment to a formate ligand, while the quintet showed only weak long-range coupling ( $J_{C-H} = 6$  Hz) to the hydride on Mo. This indicates that the second ligand is not a formate, and assignment as an  $\eta^2$ -CO<sub>2</sub> ligand containing a C directly bonded to Mo is consistent with the observed P–C coupling<sup>23</sup> and leads to a reasonable 18-electron configuration for the complex. Assignment of the  $\delta$  224.6 resonance to a carbonate ligand, which would also lack a directly bonded hydrogen, is implausible on two counts: (a) long-range coupling to a metal hydride is unlikely in a carbonate complex (and is not observed in 2); (b) this chemical shift is more plausibly associated with a CO<sub>2</sub> ligand than a carbonate (see below).

An alternative formulation in which the CO<sub>2</sub> acts as an  $\eta^1$  (Lewis acidic) ligand and the formate as a bis(chelate) ligand is difficult to reconcile with the IR characteristics of the complex (see below), since the CO<sub>2</sub> stretching frequencies are in the correct region for an  $\eta^2$ -CO<sub>2</sub> and would be high for an  $\eta^1$ -CO<sub>2</sub> (cf. 1740 cm<sup>-1</sup> for [Ni(PCy<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>]<sup>24</sup> and 1610 cm<sup>-1</sup> for [Rh(diars)<sub>2</sub>(CO)<sub>2</sub>Cl]<sup>25</sup>).  $\nu_{C=O}$  for the formate is also in the correct region for an  $\eta^1$ -formate (see below) and would be high for a bis(chelate) formate.

**The Initial CO<sub>2</sub> Adduct [Mo(dmpe)<sub>2</sub>(CO<sub>2</sub>)(OCHO)H<sub>2</sub>] (5).** The complexes discussed so far occur late in the sequence of reactions which follow addition of CO<sub>2</sub> to [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] (1) and are all formed after the loss of one molecule of H<sub>2</sub> from the starting tetrahydride. We have also, however, obtained evidence for the formation of two complexes which, in stoichiometric terms, involve the addition of two molecules of CO<sub>2</sub> to 1. The first of these probably contains a coordinated CO<sub>2</sub> and is one of the most interesting molecules in the system. Unfortunately, however, it is also one of the most labile and has only been partially characterized.

The initial CO<sub>2</sub> adduct can be reproducibly obtained as a solid by reaction of 1 with CO<sub>2</sub> in pentane. As reported above this reaction gives a solution of 3 over a period of 10 days if care is taken to avoid agitating the reaction. If, however, the solution is magnetically stirred, a yellow precipitate is formed which can be collected after 3–5 days in 29% yield.<sup>26</sup> A Nujol mull of this material has a dis-

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(21) Gunz, H. P.; Leigh, G. J. *J. Chem. Soc. A* 1971, 2229.

(22) Fluxionality would be anticipated for this molecule since it is probably seven-coordinate. Reversible broadening of the <sup>31</sup>P resonance was observed when a sample of 4 was cooled to 200 K, but the low-temperature limit could not be attained.

(23) The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this sample, which incidentally confirmed the composition of the mixture of materials obtained under these conditions, exhibited the complementary splitting of the  $\delta$  45.8 resonance into a doublet with  $J_{P-C} = 12$  Hz.

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(25) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* 1983, 105, 5914.

tinctive IR spectrum, one feature of which is a weak band at  $1843\text{ cm}^{-1}$  indicative of the presence of Mo–H groups (cf.  $1800\text{ cm}^{-1}$  in 2).

NMR spectra in benzene were of limited utility in characterizing this material. The principal absorption in the high-field region of the  $^1\text{H}$  NMR spectrum of a freshly prepared solution in benzene- $d_6$  did exhibit a quintet at  $\delta -5.07$ , confirming the presence of one or more hydride ligands coupled to four equivalent  $^{31}\text{P}$  nuclei. The complex was, however, unstable in this solvent, decomposing in ca. 30 min to another complex (see below) which was itself labile.  $^{31}\text{P}$  NMR spectra of this sample did not exhibit any resolved resonances attributable to the initial adduct, but there was a broad hump from  $\delta 32$  to  $45$  of considerable integrated intensity which decayed on a similar time scale to the high field hydride. This suggested that the symmetry of the hydride resonance, as in the case of the  $\text{CO}_2$  complex 4, reflected a low-energy fluxional process which happens to be too slow to equilibrate the P resonances at 298 K. This interpretation was confirmed by  $^{31}\text{P}$  NMR spectra in toluene- $d_8$  at 200 K of a sample of the adduct prepared in situ by reaction of 1 with  $^{13}\text{CO}_2$ . This exhibited a well-resolved but complex spectrum, which appears to be that of the complex below the low-temperature limit but which could not be analyzed in detail since it was partially obscured by absorptions of unreacted 1 and of small quantities of materials later in the reaction sequence.

The most informative spectra of the initial adduct were  $^{13}\text{C}$  NMR spectra in toluene- $d_8$ /toluene at 195 K of the  $^{13}\text{C}$ -enriched sample prepared in situ. In addition to a formate resonance at  $\delta 174.9$  ( $J_{\text{C-H}} = 192\text{ Hz}$ —this resonance will be discussed below), these contain a complex resonance at  $\delta 203.8^{27}$  which lacks single-bond coupling to  $^1\text{H}$  in uncoupled spectra and a resonance of equal intensity at  $\delta 166.8$  with  $J_{\text{C-H}} = 195\text{ Hz}$  in uncoupled spectra. These resonances indicate the presence of a coordinated  $\text{CO}_2$  and of a formate ligand<sup>28</sup> and suggest that the complex is most probably  $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$  (5).<sup>29</sup> Similar resonances<sup>30</sup> could be observed in  $^{13}\text{C}$  spectra recorded in benzene- $d_6$ , and these decayed at a rate similar to that of the  $^1\text{H}$  and  $^{31}\text{P}$  resonances of 5 under these conditions.

The initial adduct should be considerably more stable in pentane than in benzene or toluene, since its preparation took several days in this solvent. This was confirmed by examining  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra of a solution of 1 in pentane sealed in an NMR tube under 92% enriched  $^{13}\text{CO}_2$ . Resonances very similar to those of 5 in aromatic solvents were observed and had a lifetime of days at ambient temperatures.<sup>31</sup>

The mull IR spectrum of 5 (see below) provides the only

ambiguity in its spectroscopic characteristics. In addition to the Mo–H stretching absorption mentioned above, the spectrum contains absorptions at  $1628$  and  $1612\text{ cm}^{-1}$  which probably arise from stretching modes of  $\text{C}=\text{O}$  bonds. Assignment of the  $1612\text{ cm}^{-1}$  band to the formate  $\text{C}=\text{O}$  bond was confirmed by characteristic isotope shifts of  $38$  and  $10\text{ cm}^{-1}$ , respectively, following  $^{13}\text{C}$  and D substitution, but assignment of the  $1628\text{ cm}^{-1}$  band to the coordinated  $\text{CO}_2$ , although supported by the  $^{13}\text{C}$  isotope shift of  $40\text{ cm}^{-1}$ , was apparently inconsistent with an isotopic shift of  $4\text{ cm}^{-1}$  following D substitution. It should be noted, however, that this is much smaller than the  $10\text{ cm}^{-1}$  secondary isotope effect observed for other formate absorptions in this system, and the shift probably occurs because the  $1628\text{ cm}^{-1}$  band has been shifted from its true position by Fermi resonance with the  $1612\text{ cm}^{-1}$  band. This interpretation is strongly supported by the lack of any D shift for the corresponding absorption in pentane, which at  $1685\text{ cm}^{-1}$  is much further from the formate band.

**Formation of  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$  (6).** As mentioned above, the initial  $\text{CO}_2$  adduct converts rapidly into a new complex, which is itself labile with respect to conversion to 4, 3, and eventually 2, in benzene or toluene at ambient temperatures. Although it was too labile to allow isolation of analytical samples, a mixture of the new complex and 5 could be obtained in the solid state by swirling a benzene solution of 1 under  $\text{CO}_2$  (20 psi) for 45 s, freezing the solution, and subliming off the benzene at  $-40\text{ }^\circ\text{C}$ .

NMR spectra recorded in benzene- $d_6$ <sup>32</sup> established that the new complex was  $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$  (6). The presence of two triplets in  $^{31}\text{P}\{^1\text{H}\}$  spectra indicated that there are two chemically distinct types of dmpe P, and the further triplet splitting in spectra recorded with narrow band decoupling of the dmpe protons (centered at  $\delta 1.5$ ) suggested the presence of two hydride ligands on the Mo. This was confirmed by analysis of the complex absorption in  $^1\text{H}$  NMR spectra at  $\delta -7.8$  assigned to the metal hydrides, which indicated that the four  $^{31}\text{P}$  and two  $^1\text{H}$  nuclei form an  $\text{AA}'\text{M}_2\text{XX}'$  spin system (X, X' = H) with  $J_{\text{AM}} = J_{\text{A'M}} = 14.5\text{ Hz}$ ,  $J_{\text{AX}} = J_{\text{A'X'}} = 45\text{ Hz}$ ,  $J_{\text{MX}} = J_{\text{M'X'}} = 59\text{ Hz}$ , and  $J_{\text{AX'}} = J_{\text{A'X}} = 52\text{ Hz}$ .<sup>33</sup>  $^1\text{H}$  NMR spectra also contained a resonance at  $\delta 8.87$  (equal in intensity to the hydride resonances and with a  $^{13}\text{C}$  coupling of  $196\text{ Hz}$  appropriate for single bond coupling to an  $\text{sp}^2\text{ C}$ ) which suggested the presence of two formate ligands. This was confirmed by the  $^{13}\text{C}\{^1\text{H}\}$  spectrum of a  $^{13}\text{C}$ -enriched sample, which consisted of a single resonance at  $\delta 167.1$  which split into a doublet with  $J_{\text{C-H}} = 195\text{ Hz}$  in the absence of  $^1\text{H}$  decoupling.

**Attempts To Crystallographically Characterize the Initial  $\text{CO}_2$  Adduct.** The ability to prepare solid samples of the initial  $\text{CO}_2$  adduct, together with the limited number of structurally characterized  $\text{CO}_2$  complexes, led to extensive efforts to characterize the adduct crystallographically. Diffraction quality crystals were prepared from a sample of 1 in pentane which was stirred under  $\text{CO}_2$  for 24 h. After removal of the precipitated 5 by filtration, the *unstirred* mother liquor deposited orange brown cubic

(26) The influence of agitation on the course of the reaction is probably a crystallization effect, in which stirring promotes nucleation of the initial adduct. The adduct is relatively stable if it is precipitated but in solution rapidly converts to other species in the reaction sequence.

(27) This resonance approximates a doublet of triplets, suggesting that four  $^{31}\text{P}$  nuclei and the  $^{13}\text{C}$  form an  $\text{A}_2\text{BCX}$  coupling system with  $J_{\text{A-X}} = 13\text{ Hz}$ ,  $J_{\text{B-X}} = 26\text{ Hz}$ , and  $J_{\text{C-X}}$  too small to observe. This would be consistent with the complex nature of the  $^{31}\text{P}$  spectrum, and the average  $J_{\text{P-C}}$  of  $13\text{ Hz}$  is similar to the value of  $12\text{ Hz}$  observed for the  $\text{CO}_2$  carbon in 4.

(28) The formate resonance is coincident with that of 6 (see below), but  $^{31}\text{P}$  spectra establish that this sample contains little 6. Conversely, we have  $^{31}\text{P}$  and  $^{13}\text{C}$  spectra of samples of 6 containing little 5.

(29) We have no direct evidence for the number of hydride ligands in 5, but, if the  $\text{CO}_2$  is an  $\eta^1$  (Lewis acid) ligand, three hydrides would make 5 an 18-electron complex and distinguish 5 from 4.

(30)  $\delta 203.4$  with  $J_{\text{C-H}} = 0$  and  $\delta 167.1$  with  $J_{\text{C-H}} = 195\text{ Hz}$ . The  $\text{CO}_2$  resonance is a quintet with  $J_{\text{P-C}} = 15\text{ Hz}$  at 298 K.

(31)  $\delta 199.2$  with  $J_{\text{C-H}} = 0$  and  $\delta 165.5$  with  $J_{\text{C-H}} = 198\text{ Hz}$ . As in the case of room-temperature benzene spectra, the  $\text{CO}_2$  resonance is a quintet with  $J_{\text{P-C}} = 15\text{ Hz}$ .

(32) The best resolved NMR spectra of this molecule were obtained from material prepared from 92% enriched  $^{13}\text{CO}_2$  and were recorded in benzene- $d_6$  at 283 K. The complex was more stable in toluene- $d_8$  at 200 K, and integrations are based on spectra recorded under these conditions. These spectra were consistent with the benzene spectra except that the metal hydride absorption was less well resolved and approximated a quintet.

(33) These coupling constants are physically reasonable and led to a good PANIC<sup>13</sup> simulation of both the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the complex. The coupling scheme implies that one (M) pair of P atoms are chemically and magnetically equivalent while the other (A) pair are magnetically inequivalent with respect to the metal hydrides.

crystals over a period of 48 h. The IR spectrum of a Nujol mull of these crystals established that the bulk of the sample was 5 rather than 6, and a diffraction study was attempted. This suggested that the complex contained two dmpe ligands, two hydrides, a formate, and an η<sup>1</sup>-O coordinated CO<sub>2</sub>. The latter is an unprecedented coordination mode for CO<sub>2</sub>, but this cannot be the correct structure since "[Mo(dmpe)<sub>2</sub>(CO<sub>2</sub>)(OCHO)H<sub>2</sub>]" would be a paramagnetic complex while 5 and 6 are diamagnetic and the bulk of the crystalline sample was established to be diamagnetic by a Faraday balance measurement. It seems probable that the "CO<sub>2</sub>" ligand is in fact a formate and that an initial crystal of 5 converted to 6 before or during the diffraction study,<sup>34,35</sup> but despite extensive efforts experimental difficulties prevented us from obtaining evidence supporting this hypothesis, and little weight can be attached to the diffraction results.<sup>36</sup>

**<sup>13</sup>C NMR Characteristics of Carbon Dioxide, Formate, and Carbonate Ligands.** We have based distinctions between coordinated CO<sub>2</sub> ligands, formates, and carbonates on less ambiguous data than chemical shifts (such as the large single-bond J<sub>C-H</sub> anticipated for formates), but it is reassuring to note that the resonances assigned to CO<sub>2</sub> ligands in 4 and 5 occur in the region in which such resonances have been previously observed (δ 206.1, [Mo(CO<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>],<sup>37</sup> and δ 200.5, [Nb(η-C<sub>5</sub>H<sub>5</sub>Me)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)(CO<sub>2</sub>)],<sup>38</sup>). This is considerably downfield of free CO<sub>2</sub> (δ 132.2<sup>39</sup>), and somewhat below where formate ([Re(η-C<sub>5</sub>H<sub>5</sub>)(NO)(PPh<sub>3</sub>)(OCHO)]: δ 171.4<sup>40</sup>) and carbonate ([UO<sub>2</sub>](CO<sub>3</sub>)<sub>6</sub>]<sup>6-</sup>: δ 168.7 and 167.3<sup>41</sup>) resonances have been reported. It is clear that formates and carbonates can not be distinguished on chemical shift grounds,<sup>42</sup> but the positions of the resonances assigned to coordinated carbonate in 2 and to formates in 4, 5, and 6 are consistent with the quoted literature values and with each other.

**Infrared Characteristics of the Functional Groups Produced in the Reaction between [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] and CO<sub>2</sub>.** Metal hydride, formate, carbonate, and coordinated CO<sub>2</sub> functional groups would all be expected to have characteristic IR absorptions in the region between 1600 and 2800 cm<sup>-1</sup>. These absorptions were, however, of limited use in initial characterization of complexes formed from the reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub>, partly because the functional groups have similar frequencies in many of the complexes and partly because many of the

absorptions were sensitive to the sample medium. It has subsequently proved possible, however, to use <sup>13</sup>C- and D-labeling studies to assign the IR absorptions of the complexes in the 1600–2800 cm<sup>-1</sup> region, and the results of this analysis are presented in Table V. The assignments are consistent with the NMR and crystallographic studies, and, in some cases, as pointed out above, provide critical confirmation of the presence of certain functional groups.

Examining the effects of deuterium substitution on the IR spectra of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] derivatives was complicated because [Mo(dmpe)<sub>2</sub>D<sub>4</sub>] could only be obtained in, at best, ca. 60 atom % purity. Reduction of [Mo(dmpe)<sub>2</sub>Cl<sub>2</sub>] with 40% sodium amalgam under D<sub>2</sub> invariably gave material containing Mo–H groupings (IR), and the presence of a broad band at 1975 cm<sup>-1</sup> in the region characteristic of saturated C–D bonds suggested that this occurred because 1 is an exceptionally reactive C–H activation and exchange catalyst which catalytically deuterates its own dmpe ligands. It is not surprising that [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] is a C–H activation and exchange catalyst, given that the closely related early transition-metal polyhydride [Ta(dmpe)<sub>2</sub>H<sub>5</sub>] undergoes facile hydride exchange with benzene.<sup>43</sup> The ability of the complex to activate the saturated C–H bonds of dmpe is, however, unusual, although [Mo(η-C<sub>5</sub>H<sub>5</sub>)(dmpe)H<sub>3</sub>], a formally isoelectronic Mo(IV) complex, has been reported to catalyze exchange between hydrogen in ligated dmpe and deuterium in benzene-d<sub>6</sub>.<sup>44</sup> Further details of the characteristics of 1 as a C–H activation catalyst will be reported later.

Our initial assumptions when labeled material was used to assign the IR absorptions of complexes were as follows: that <sup>13</sup>C labeling of CO<sub>2</sub>, carbonate, or formate ligands should shift their C=O stretching absorptions, and the C–H stretching absorptions of formate ligands, by an amount approximating that predicted by the simple harmonic oscillator model<sup>45</sup> but should not affect the stretching absorptions of metal hydride bonds in the same molecule; that deuterium labeling of the metal hydrides should similarly affect metal hydride stretching absorptions and the C–H stretching frequencies of derived formates, but should not affect C=O stretching absorptions.

In practice, <sup>13</sup>C substitution shifted ν<sub>C=O</sub> ca. 40 cm<sup>-1</sup> for coordinated CO<sub>2</sub> (predicted 38 cm<sup>-1</sup> for an absorption at 1700 cm<sup>-1</sup>), 40 cm<sup>-1</sup> for the carbonate (predicted 36 cm<sup>-1</sup>), and ca. 38 cm<sup>-1</sup> for the formates (predicted 36 cm<sup>-1</sup> for 1612 cm<sup>-1</sup> band). <sup>13</sup>C labeling also had the predicted small effect (8 cm<sup>-1</sup>) on ν<sub>C-H</sub> for formate ligands.

Deuterium labeling shifted ν<sub>Mo-H</sub> as predicted, although it was not possible to determine by how much since the Mo–D region (ca. 1300 cm<sup>-1</sup>) was obscured by stronger absorptions. Deuterium labeling also shifted ν<sub>C-H</sub> for formates, but again the magnitude of the effect could not be determined, in this case because the weak formate C–D stretches could not be distinguished from the C–D stretches of partially deuterated dmpe (see above). Deuterium labeling did not change ν<sub>C=O</sub> for carbonate or CO<sub>2</sub> ligands (with the exception of the solid-state spectrum of the initial CO<sub>2</sub> adduct: see above). Formates did not completely conform to this elementary model and exhibited small (7–10 cm<sup>-1</sup>) shifts in the frequencies of the C=O stretching absorptions on deuterium substitution. These second-order effects are not unreasonable in the case of η<sup>1</sup>-formate ligands and are similar to those reported pre-

(34) The structure would not refine when an additional hydrogen was added to the "CO<sub>2</sub>" ligand in the appropriate position to convert this into a formate ligand, but the structure also lacked a vacant site on the metal which could accommodate a third hydride.

(35) The stability of 5 in the solid state was variable and depended on the sample. IR spectra of mulls indicated that some powdered samples converted to 6 in a matter of weeks, but crystalline samples were in general stable for months. Conversion to 6, may, however, be accelerated in the X-ray beam.

(36) If the structure is that of [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>H<sub>2</sub>], the coordination sphere is a distorted dodecahedron which approximates a tetrahedron of P ligands interpenetrated by a tetrahedral array of two hydrides and two formates. This would be consistent with the P and H ligands of 6 forming the observed AA'M<sub>2</sub>XX' coupling system.

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**Table V. Infrared Absorptions (cm<sup>-1</sup>) of the Functional Groups in Products Derived from the Reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub> and of Their <sup>13</sup>C- and D-Labeled Analogues in Nujol, Benzene, and Pentane<sup>a</sup>**

complex	$\nu_{\text{O}_2\text{C-H(D)}}$	$\nu_{\text{Mo-H}}$	$\nu_{\text{CO}_2}$	$\nu_{\text{CO}_3}$	$\nu_{\text{OCH(D)O}}$
Nujol					
[Mo(dmpe) <sub>2</sub> H <sub>4</sub> ] (1)			1743 w sh, 1725 w sh, 1701 m, 1679 ms		
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )H <sub>2</sub> ] (2)			1800 w br	1656 w, 1601 s	
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )D <sub>2</sub> ]				1656 w, 1601 s	
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>3</sub> )H <sub>2</sub> ]			1800 w br	b, 1561 s	
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> ] (3)	2704 w				1614 s
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> ]	c				1604 s
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> ]	2696 w				1576 s
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H] (4)	2682 w	1891 w br	1787 ms, 1744 s		1614 s
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>2</sub> )(O <sup>13</sup> CHO)H] <sup>d</sup>	not obsd	not obsd	1747, 1704		1576
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H <sub>3</sub> ] (5)	2689 w	1843 w br	1628 s		1612 s
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCDO)D <sub>3</sub> ]	c		1624 s <sup>e</sup>		1602 s
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>2</sub> )(O <sup>13</sup> CHO)H <sub>3</sub> ]	2682 w	1843 w br	1588 s		1574 s
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> H <sub>2</sub> ] (6)	not obsd	1757 w, 1740 w			1653 s
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> D <sub>2</sub> ]	no solid samples				
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> H <sub>2</sub> ]	no solid samples				
Benzene					
[Mo(dmpe) <sub>2</sub> H <sub>4</sub> ] (1)		f			
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )H <sub>2</sub> ] (2)		f		1655 w, 1636 s	
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )D <sub>2</sub> ]				1655 w, 1636 s	
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>3</sub> )H <sub>2</sub> ]		f		not obsd, 1590 s	
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> ] (3)	2702 w				1618 s
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> ]	c				1611
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> ]	not obsd				1580
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H] (4)	2702	f	1794, <sup>g</sup> 1745 <sup>g</sup>		1618
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H <sub>3</sub> ] (5)	not obsd	f	1667 s		1629
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>2</sub> )(O <sup>13</sup> CHO)H <sub>3</sub> ]	not obsd	f	1625 s		1587
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> H <sub>2</sub> ] (6)	not obsd	f			1618
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> D <sub>2</sub> ]	c				1611
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> H <sub>2</sub> ]	not obsd	f			1580
Pentane					
[Mo(dmpe) <sub>2</sub> H <sub>4</sub> ] (1)			1702 sh, 1685 s		
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )H <sub>2</sub> ] (2)	insoluble in pentane				
[Mo(dmpe) <sub>2</sub> (CO <sub>3</sub> )D <sub>2</sub> ]	insoluble in pentane				
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>3</sub> )H <sub>2</sub> ]	insoluble in pentane				
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> ] (3)	2702 w				1624 s
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> ]	c				1614
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> ]	not obsd				1586
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H] (4)	2702	not obsd	1812, 1768		1624
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)H <sub>3</sub> ] (5)	not obsd	not obsd	1685 s		1624
[Mo(dmpe) <sub>2</sub> (CO <sub>2</sub> )(OCHO)D <sub>3</sub> ]			1685 s		1614
[Mo(dmpe) <sub>2</sub> ( <sup>13</sup> CO <sub>2</sub> )(O <sup>13</sup> CHO)H <sub>3</sub> ]	not obsd	not obsd	1643 s		1586
[Mo(dmpe) <sub>2</sub> (OCHO) <sub>2</sub> H <sub>2</sub> ] (6)	not obsd	not obsd			1624
[Mo(dmpe) <sub>2</sub> (OCDO) <sub>2</sub> D <sub>2</sub> ]					1614
[Mo(dmpe) <sub>2</sub> (O <sup>13</sup> CHO) <sub>2</sub> H <sub>2</sub> ]	not obsd	not obsd			1586

<sup>a</sup> Many of the absorptions in pentane or benzene were determined from mixtures of materials (particularly in the case of labeled samples). This sometimes resulted in the overlap of absorptions from different species, and intensity estimates have been omitted in such cases. All assignments are consistent with the labeling studies, as discussed in the text. The notation "not obsd" indicates that a weak absorption would have been anticipated from this functional group in a complex, but that experimental limitations precluded observation of the absorption. In every case in which a strong absorption was anticipated an appropriate band was observed with appropriate isotopic shifts. <sup>b</sup> The <sup>13</sup>C=O band corresponding to the weak 1656 cm<sup>-1</sup> absorption in unlabeled **2** was obscured by the strong 1601 cm<sup>-1</sup> absorption of some unlabeled **2** in the sample. <sup>c</sup> Formate C-D stretches were in general obscured by absorptions assigned to partially deuterated dmpe ligands. <sup>d</sup> This sample was contaminated by some **3**. <sup>e</sup> See Results and Discussion for the origin of this shift. <sup>f</sup> Weak absorptions in the 1800 cm<sup>-1</sup> region would have been obscured in this solvent. <sup>g</sup> Recorded in benzene-*d*<sub>6</sub>, which has a window in this region.

viously for a tungsten formate.<sup>46</sup> The sensitivity of the formate  $\nu_{\text{C=O}}$  to deuterium substitution assisted in many of the spectral assignments.

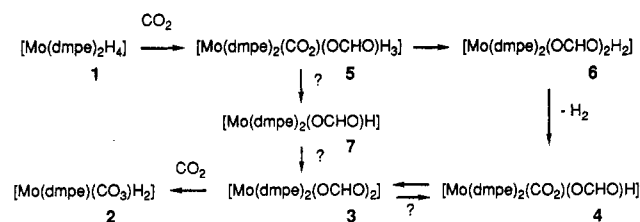
The overall positions of the metal hydride, formate, carbonate, and coordinated CO<sub>2</sub> absorptions, as established by labeling studies, fall within the expected ranges. The metal hydride and coordinated CO<sub>2</sub> stretching frequencies are quite sensitive to the precise nature of each complex and have overlapping ranges of 1679–1891 and 1628–1787 cm<sup>-1</sup>, respectively. The principal carbonate absorption of **2** (1601 cm<sup>-1</sup>) and the  $\nu_{\text{C=O}}$  bands of the formates, with a narrow spread of 1614–1628 cm<sup>-1</sup>, fall somewhat below these ranges but are themselves similar in energy. The

positions of the formate absorptions are very similar to that of the  $\eta^1$ -formate [Re( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(NO)(PPh<sub>3</sub>)(OCHO)]<sup>40</sup> (1616 cm<sup>-1</sup>) and somewhat above those reported for bis(chelate) transition-metal formates (such as [Ru(PPh<sub>3</sub>)<sub>3</sub>(OCHO)H]:  $\nu_{\text{C=O}}$  = 1565 cm<sup>-1</sup><sup>47</sup>), as would be expected from the established effects of coordination mode on the IR spectra of carboxylate complexes.<sup>48</sup>

**Sequence of Formation of the Complexes Derived from the Reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub> (Scheme I) and Evidence for the Formation of a Bis(chelate) Formate Complex, [Mo(dmpe)<sub>2</sub>-**

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Scheme I. Most Probable Relationships between Complexes Derived from the Reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub>

(OCHO)H] (7). The early stages of the reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] with CO<sub>2</sub> are sufficiently slow in pentane to permit the reaction to be monitored by using the characteristic IR absorptions of the products from 1500 to 2400 cm<sup>-1</sup>. Spectra of a solution of 1 recorded 1, 4.5, 8, and 20.5 h after exposure to an atmosphere of CO<sub>2</sub> established that only traces of unreacted 1 were left after 4.5 h (at which point the concentration of the initial CO<sub>2</sub> adduct 5 was at its maximum) and that all of the material had been converted to 6 or 3 (whose spectra can not be distinguished in this region in pentane) after 20.5 h.

IR spectra in pentane also, however, indicated the formation, at a rate comparable with the formation of 5, of a further complex characterized by a strong absorption at 1558 cm<sup>-1</sup>. This is below the C=O stretching region for η<sup>1</sup>-formates in this system but within the range in which a bis(chelate) formate might be expected to absorb. Assignment to a bis(chelate) formate was supported by introduction of deuterium and <sup>13</sup>C labels, which shifted the absorption to 1548 and 1520 cm<sup>-1</sup>, respectively. The <sup>13</sup>C NMR resonance observed at δ 174.9 immediately after <sup>13</sup>CO<sub>2</sub> was reacted with 1 in toluene/toluene-*d*<sub>8</sub> at 195 K (see Discussion above of the initial CO<sub>2</sub> adduct) is most reasonably assigned to the new formate complex, confirming that the complex is an early product in the reaction manifold in toluene as well as in pentane.

The bis(chelate) formate was never obtained as a solid, and no conditions were discovered under which it was a major product of the reaction of 1 with CO<sub>2</sub>. The new complex may be [Mo(dmpe)<sub>2</sub>(OCHO)H] (7), but it is unclear where such a complex would fit into the reaction pathway (unless it provides an alternate pathway from 5 to 3—see Scheme I), and in the absence of <sup>1</sup>H NMR or other data on the number of hydride ligands in the complex identification as 7 must remain tentative.

The synthetic results indicate that the other complexes which contain only two of the original hydride ligands (4, 3, and 2) are formed later in the reaction sequence than the complexes containing all four of the original hydrides (5 and 6). The remaining hydrogen is lost as H<sub>2</sub>, and the rapidity with which 5 and 6 convert into complexes later in the reaction sequence in benzene is indicated by the observation that close to an equivalent of H<sub>2</sub> is evolved after only 13.5 h (see preparation of 2 in the Experimental Section). The loss of H<sub>2</sub> appears to be essentially irre-

versible, and we have seen no evidence for complex 4, 3, or 2 reverting to complex 5 or 6.

Interconversions within the characterized complexes retaining only two of the original hydrides may be more complex. The conversion of 4 to 3 was observed in the solid state (IR), in benzene solution (<sup>1</sup>H NMR), and in pentane solution (IR) as indicated above. The surprisingly high yield of 4 (which was not a major species in situ NMR studies) from pentane/toluene at -78 °C, however, suggests that this may be a reversible reaction, i.e., that although 4 was never the major species in the mixture, it was isolated in good yield because it was the only species in the reaction manifold which was both insoluble and accessible under these conditions.

The carbonate complex 2 could reasonably be formed from the bis(formate) 3 (although the reaction may require reversal of one of the CO<sub>2</sub>/Mo-H insertion reactions to give an intermediate CO<sub>2</sub> complex), and it was confirmed in a separate experiment that 3 converts into a mixture of 3 and 2 in benzene (IR) under 20 psi CO<sub>2</sub> over 7 days.

### Conclusion

Although we have not determined the fate of the equivalent of CO which should be produced, the carbonate ligand in [Mo(dmpe)<sub>2</sub>(CO<sub>3</sub>)H<sub>2</sub>], the final product of the reaction of [Mo(dmpe)<sub>2</sub>H<sub>4</sub>] (1) with CO<sub>2</sub>, is probably formed by reductive disproportionation of CO<sub>2</sub> by an electron-rich intermediate species which acts as if it contains "[Mo(dmpe)<sub>2</sub>H<sub>2</sub>]". The availability of such a species indicates that the insertions of CO<sub>2</sub> into Mo-H bonds which result in the formation of the formate ligands in precursors such as 3, 4, 5, and 6 are readily reversible, as has been reported in the case of some other CO<sub>2</sub>/M-H insertions.<sup>47,48</sup> It is the reversibility of the CO<sub>2</sub> insertions, together with the presence of four hydride ligands in 1, that allows the observation of such a wide range of intermediate formate and carbon dioxide complexes from the reaction of 1 with CO<sub>2</sub>.

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**Supplementary Material Available:** Table S-I, anisotropic temperature factors for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>], Table S-II, calculated hydrogen parameters for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>], and Figure S-1, thermal ellipsoids (30% probability) for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] (3 pages); Table S-III, structure factor tables for [Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] (5 pages). Ordering information is given on any current masthead page.

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