Inorg. Chem. **1999,** *38,* 3223−3227 **3223**

Interaction of Carbon Dioxide with $[IrH_2\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$[#]

Margaret A. McLoughlin,[§] Nancy L. Keder,[§] William T. A. Harrison,[*,†] Robert J. Flesher,[§] Hermann A. Mayer,[*,‡] and William C. Kaska[*,§]

Department of Chemistry, University of Western Australia, Nedlands, 6907, Australia, Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Germany, and Department of Chemistry, University of California, Santa Barbara, California 93106

Received June 24, 1998

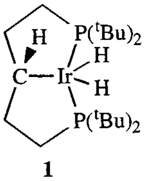
The pincer ligand dihydride complex $[IrH_2\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ interacts with carbon dioxide to give an isolable bicarbonate $[IrH(\kappa^2\text{-}O_2COH)\}\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ derivative and a metal hydride carbonyl compound. An intermediate metallo−formate complex can be detected by NMR spectroscopy. The reaction described is a reverse water gas shift process, $CO_2 + H_2 \rightleftharpoons CO + H_2O$.

Introduction

The interaction of coordination complexes with carbon dioxide and hydrogen is a potential route to effective utilization of CO_2[1−3] and the formation of useful carbon C_1 derivatives. Convenient methods that are currently being used to transform CO_2 are electrochemical,[4] photochemical,[5,6] and direct addition of hydrogen via transition metal hydrides.[7−14] Although metal hydride CO_2 reduction produces formic acid and formaldehyde, a major but often forgotten product in this reaction can be carbonylation of the transition metal complexes used in the process, the result of formic acid disproportionation. This method of metal carbonyl formation is not the most commonly used. However, the procedure is direct,[15] and a modified method is shown in eq 1 that consists of simply treating the ruthenium complex with formic acid.[16−21] Although Halpern showed the reaction to be bimolecular, the detailed process of carbon monoxide transfer to the metal could not be determined.[21]

$$K_2[RuCl_4] + HCO_2H \rightarrow K_2[Ru(CO)(H_2O)Cl_4] \qquad (1)$$

Pincer ligand complexes are a class of compounds which could reveal this method of carbonylation. These materials are most often characterized by a rigid molecular backbone with an extensive hydrophobic cavity surrounding the transition metal. This arrangement can promote unique and unusual chemical reactivity of the metal complex, especially with carbon dioxide.



1

The reactivity of the metal hydride bonds in pincer ligand dihydrides can be controlled by such a unique arrangement, and they can be replaced easily with a variety of reactive molecules.[22,23] Because of the hydrophobic cavity in **1**, the interaction of CO_2 with iridium can be expected to give a novel CO_2

---

[*] To whom correspondence thould be addressed. E-mail: H.A.M., hermann.mayer@uni-tuebingen.de; W.C.K., kaska@chem.ucsb.edu; W.T.A.H., wtah@chem.uwa.edu.

[#] Dedicated to Professor E. O. Fischer on the occasion of his 80th birthday.

[†] University of Western Australia.

[‡] Universität Tübingen.

[§] University of California.

(1) Miller, J. D. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2.
(2) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.
(3) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 255.
(4) Sullivan, B. P.; Krist, K.; Guard, H. E. *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Elsevier: New York, 1993.
(5) Mackor, A.; Koster, T. P. M.; Collin, J. P.; Jouaiti, A.; Sauvage, J. P. In *Proceedings 3rd EEC Workshop on Photochemical and Photobiological Research and Development*; Hall, D. O., Grassi, G., Eds.; Elsevier: London, 1989; p 1.
(6) Kubiak, C. P.; Ratliff, K. S. *Isr. J. Chem.* **1991**, *31*, 3.
(7) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.
(8) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.
(9) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.
(10) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: New York, 1988.
(11) Walther, D. *Nachr. Chem. Technol. Lab.* **1992**, *40*, 1214.
(12) Aresta, M.; Quaranta, E.; Tommasi, I. *New J. Chem.* **1994**, *18*, 133.
(13) Yi, C. S.; Liu, N. *Organometallics* **1995**, *14*, 2616.
(14) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.
(15) Keene, F. R.; Sullivan, B. P. In *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Sullivan, B. P., Krist, K., Guard, H. E., Eds.; Elsevier: New York, 1993; p 118.
(16) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372.
(17) Allen, D. L.; Green, M. L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 541.
(18) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.
(19) Koinuma, H.; Yoshida, Y.; Hirai, H. *Chem. Lett.* **1975**, 1223.
(20) Douglas, P. G.; Shaw, B. L., *J. Chem. Soc. A* **1969**, 1491.
(21) Halpern, J.; Kemp, L. W. *J. Am. Chem. Soc.* **1966**, *88*, 5147.
(22) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13.
(23) Gupta, M.; Kaska, W. C.; Cramer, R.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.

10.1021/ic980722f CCC: $18.00

coordination complex including a possible interaction with hydrogen. Precedent exists for such an interaction with CO_2 with the initial formation of a metallo−formate complex.[7,24−28] We now report an instance where reduction goes beyond that stage to a bicarbonate complex and a metal hydrido carbonyl complex via disproportionation.[29] This is a reverse of the water gas shift reaction.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (2)$$

Experimental Section

General Procedures. All experimental methods including purification of solvents, reagents, glassware, inert gas procedures, and synthesis of **1** have been described previously.[22,30,31] The carbon dioxide was the highest grade purity available from Matheson Corporation. Further drying was done by allowing it to stand over Phillips Catalyst[32] even though control experiments showed that the same results were obtained with gas directly from the cylinder. Contact of the CO_2 with glass was minimized by transporting it through flexible metal hose and glass to metal seals. The reactions of **1** with CO_2 were performed in NMR tubes so that dry CO_2 gas could be introduced and the tube sealed with a Young valve. After complex **3** crystallized, the solvent which contained **4** and **6** was removed by syringe under argon and analyzed separately. When the crystals of **3** were removed from the tube under argon and the tube cleaned with fresh solvent, the reaction with **1** could be performed again in the same tube with the same results. In this way the adverse effects of water could be minimized. Analysis of **4** was then performed in the NMR tube or samples were taken for mass spectral analysis. Low solubility of **3** in a benzene solution of **2** and **4** resulted in its precipitation before the product ratio could be determined by NMR. Since **3** and **4** are net disproportionation products from **2**, they should occur in equal amounts. We surmise that the 25 mg of **3** must have contained occluded solvent and/or CO_2 to give more than we should have observed. Analytical results were performed by Desert Analytics, Tuscon, AZ; the carbon analyses remained low despite the use of high temperatures and vanadium pentoxide catalyst. The atmospheric pressure chemical ionization (APCI) mass spectra were collected on a Fisons Instrument/VG platform electro spray instrument.

Reactions of $[IrH_2\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (1). A red C_6D_6 solution (0.6 mL) of **1** (30 mg, 0.054 mmol) was placed in a NMR tube and treated with $^{13}CO_2$-enriched gas.

$[IrHOC(O)H\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (2). ^1H NMR (C_6D_6, 500 MHz): δ −33.7 [t, $^2J(PH) = 13.0$ Hz, Ir−H], 1.1−1.5, 1.8, 2.3 [m, CCH_3, CH_2, CH], 9.4 [d, $^1J(CH) = 195.0$ Hz, OCOH]. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.45 MHz): δ 72.6 [s]. ^{13}C NMR (C_6D_6, 125.76 MHz): δ 171.4 [d, $^1J(CH) = 195.0$, OCOH].

$[IrH(\kappa^2\text{-}O_2COH)\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (3). Crystals of the bicarbonate complex **3** were isolated from a pentane or benzene solution after standing for 2 weeks. ^1H NMR (CD_2Cl_2, 500 MHz): δ −33.5 [t, $^2J(PH) = 11.2$ Hz, IrH], 1.2−1.4 [m, CH_3, CH_2], 2.8 [s, CH], 11.7 [br, s, O_2COH]. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.45 MHz): δ 72.4 [s]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.76 MHz): δ 14.6 [s, CH], 24.9 [A part of an AXX′ pattern, $N = |^1J(PC) + {}^3J(PC)| = 26.9$ Hz, CH_2P], 29−30 [m, $\mathit{C}CH_3$], 35.8 [m, $\mathit{C}CH_3$], 44.4 [A part of an AXX′ pattern, $N = |^2J(PC) + {}^4J(PC)| = 13.2$ Hz, $\mathit{C}H_2$], 161.9 [s, OOCOH]. MS (FD) for $C_{22}H_{47}O_3P_2Ir$: calcd *m/e* 613.78, found 550, M^+ loss of CO_3. IR (cm^{-1}, KBr): 2698, 2652 ν (OH), 1587 ν (C=O), 1469 δ (OHO). Anal. Found: C, 42.36; H, 7.57. Calcd for $C_{22}H_{47}O_3P_2Ir$: C, 43.19; H, 7.41. Yield: 25 mg (76). Mp: 188−193 °C (dec).

Crystal Structure Determination of 3. A very thin, translucent, platelike crystal coated with Paratone N was mounted inside a glass capillary under inert gas. Intensity data were collected in the $\theta-2\theta$ scanning mode for $0° < 2\theta < 45°$. Three standard reflections were monitored every 100 observations for intensity variation, but no significant variation in these standards was observed. Crystal absorption was monitored by φ-scans, but no absorption correction was applied. The raw intensities were reduced to F and $\sigma(F)$ values using a Lehmann−Larsen profile-fitting routine,[33] and normal corrections for Lorentz and polarization effects were made. The systematic absences ($h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$) uniquely identified the space group as centrosymmetric $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14). A total of 3739 reflections ($+h$, $+k$, $\pm l$) were measured, of which 1191 reflections were used in the structure solution and refinement (reflections with $I < 4\sigma(I)$ considered unobserved). All of the data collection and reduction routines were based on the UCLA crystallographic computing package.[34]

The structure was solved by a combination of direct methods and Fourier syntheses. A direct-methods solution for the heavy atoms (Ir and P) of the complex was obtained from the SHELXS-86,[35] and the remaining non-hydrogen atoms were located from Fourier difference maps following refinement of the known atom positions. All of the hydrogen atoms were positioned geometrically ($d(C-H) = 1.0$ Å, $\theta(H-C-H) = 109.5°$). The least squares, Fourier, and subsidiary calculations were performed using the Oxford CRYSTALS[36] system. The final full-matrix refinement was against F and included atomic positional parameters, anisotropic temperature factors for Ir and P, and isotropic thermal factors for the remaining non-hydrogen atoms. All of the hydrogen atoms were refined as "riding" on their respective carbon atoms. Neutral-atom scattering factors, taking account of anomalous dispersion terms, were obtained from the *International Tables for X-Ray Crystallography*.[37] Final residuals, of $R(F) = 0.0862$ and $R_w(F) = 0.1002$ [$w_i = 1/\sigma^2(F)$], were calculated. Although the poor data quality and low data-to-parameter ratio limit the precision of the refinement, we believe that the atomic connectivity for this material is unambiguously established.

---

(24) Bo, C.; Dedieu, A. *Inorg. Chem.* **1989**, *28*, 304.

(25) Hutschka, F.; Dedieu, A.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742.

(26) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.* **1990**, *112*, 9252.

(27) Sakai, S.; Musashi, Y. *Inorg. Chem.* **1995**, *34*, 1914.

(28) Whittlesey, M. K.; Perutz, R.; Moore, M. H. *Organometallics* **1996**, *15*, 5166.

(29) Sullivan, B. P.; Meyer, T. J.; Caspar, J. V.; Johnson, S. R. *Organometallics* **1981**, *3*, 1241.

(30) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

(31) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816.

(32) Krauss, H. L.; Stach, H. *Z. Anorg. Allg. Chem.* **1969**, *366*, 34.

(33) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580.

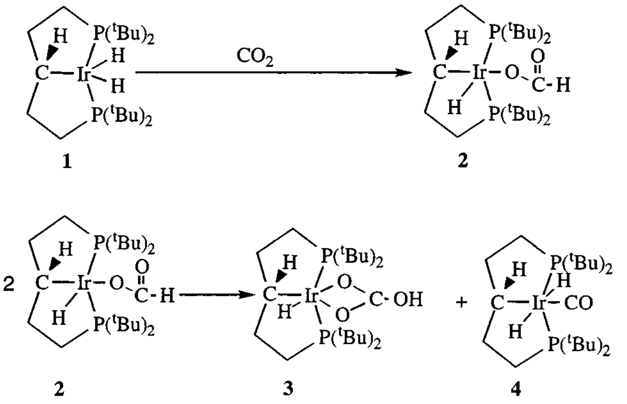
(34) Data collection, developed by C. E. Strouse, Department of Chemistry, UCLA, Los Angeles, CA.

(35) Sheldrick, G. M., Crystallography Department, University of Göttingen, Germany, 1986.

(36) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Oxford University: Oxford, 1990.

(37) Cromer, D. T. *International Tables for X-Ray Crystallography*; Kynock Press: Birmingham, 1974; Vol. IV, Table 2.

Scheme 1



$[IrH_2(CO)\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (4). ^1H NMR (C_6D_6, 500 MHz): δ −3.0 [m], −10.4 [m], −7.2, −7.9 [m] $^{31}P\{^1H\}$ NMR (C_6D_6, 202.45 MHz): δ 94.7, 83.9, 85.6 [s]. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz): δ 194.1 [t, *C*O, J_{PC} = 5.7 Hz]. MS (APCI) for $C_{22}H_{45}P_2OIr$ calcd *m/z* 581.78, found 580 M^+ (581.76 *m/z* − 2H). Selective decoupling of the *tert*-butyl and methylene resonances at 202.45 MHz in the $^{31}P\{^1H\}$ NMR spectrum splits the peak at δ 94.1 into a three-line pattern $^2J(PH)$ = 11.6 Hz, which is consistent with the presence of two inequivalent trans hydrogen atoms on the iridium with the same phosphorus−hydride interaction. The peaks at δ 85.3 and 83.6 both have five-line patterns with different $^2J(PH)$ values. The five-line pattern is consistent with inequivalent cis hydrogen atoms on the iridium.

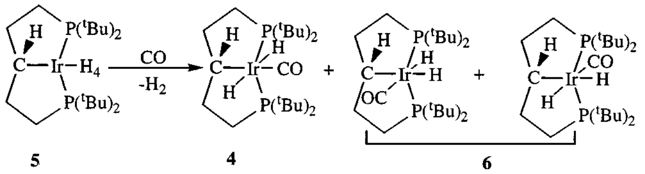
Results

A benzene or pentane solution of the red dihydride $[IrH_2\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (**1**) changes to yellow brown when treated with very dry CO_2 in a sealed tube. Pale yellow crystals of the iridium bicarbonate complex **3**, $[IrH(\kappa^2\text{-}O_2COH)\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$ (Scheme 1), are deposited over a period of 2 weeks, and isomers of the carbonyl dihydride **4** remain in solution.

The ^{13}C NMR gated decoupled spectrum of the red pentane or benzene solution of **1** and $^{13}CO_2$ within the first 1 min of interaction shows an observable formate species **2** with a doublet resonance at δ 171.4 ($^1J(CH)$ = 195 Hz). In the ^1H NMR spectrum the formate hydrogen atom resonance appears at δ 9.32[12,22,38] whereas the triplet at δ −33.7 ($^2J(PH)$ = 13.0 Hz) is typical for a hydrogen atom bound to iridium. A $^{31}P\{^1H\}$ NMR spectrum of the initial reaction solution shows a single resonance at δ 72.6.

The reaction was further probed by NMR spectroscopy for 13 days at 25 °C as crystals of **3** slowly precipitated (Scheme 1). Resonance peaks assigned to **2** were slowly replaced by those of **4** and **6**. The $^{31}P\{^1H\}$ spectrum of the reaction mixture shows major resonances at δ 94.1 and 83.6. These are identified as the trans carbonyl dihydride **4** and one of the corresponding cis carbonyl dihydrides **6**, respectively. Identification of **4** and its isomers is confirmed by treating **5** with carbon monoxide as reported by Shaw.[39] (See Scheme 2.)

Scheme 2



With excess CO at atmospheric pressure for 24 h the $^{31}P\{^1H\}$ spectrum shows a major peak at δ 94.1, minor peaks at δ 83.6 and 85.3, and very minor peaks at δ 95.8, 52.4, and −30. Under a pressure of 3 atm only two peaks are observed, at δ 94.1 and 85.3. Selective decoupling of the *tert*-butyl and methylene resonances shows that the ^{31}P NMR peak at δ 94.1 has a three-line pattern, $^2J(PH)$ = 11.6 Hz, which is consistent with the presence of two inequivalent trans hydrogen atoms on the iridium. A similar decoupling experiment shows that the $^{31}P\{^1H\}$ resonances at δ 85.3 and 83.6 both have five-line patterns with different $^2J(PH)$ values. The five-line pattern is in agreement with inequivalent cis hydrogen atoms on the iridium. Shaw originally assigned the δ 94.1 peak to a monocarbonyl or a dicarbonyl species with no hydrogen atoms on the iridium, $[Ir(CO)\{(^tBu_2)PCH_2CH_2CHCH_2CH_2P(^tBu_2)\}]$.[39] The $^{31}P\{^1H\}$ resonance positions of the two cis dihydride isomers are in accordance with those observed by Shaw.

The ^1H NMR spectrum of the reaction mixture which contains **4** and one of its isomers shows multiplets at δ −3.0 and −10.0. Authentic **4** and its isomers made by treating **5** with low-pressure carbon monoxide also exhibit peaks at δ −3.0 and −10.0 and smaller peaks at δ −10.80 and −12.4. Treating **5** with CO at high pressure gives a product with only resonances at δ −3.0 and −10.0. Selective decoupling $^1H\{^{31}P\}$ of the δ 94.1 peak showed a modification of the three-line pattern at δ −3.0. This is consistent with the conclusion that the trans hydride resonance at δ −3.0 is coupled to the ^{31}P resonance at δ 94.1. Similar decoupling of the δ 85.3 peak shows a modification of the cis dihydride δ −10.0 resonance. The high-pressure reaction of **5** with CO must promote the formation of only the trans isomer and one of the cis dihydride isomers **6**.

The $^{13}C\{^1H\}$ NMR spectrum of the iridium carbonyl dihydride **4** in the reaction mixture shows a resonance for the carbonyl group at δ 194.0; however, the fine structure was not resolved. The $^{13}C\{^1H\}$ NMR spectrum of authentic material prepared according to Shaw's procedure allowed us to resolve the fine structure as a triplet δ 194.8 ($^2J(PC)$ = 7.6 Hz). Only one $^{13}C\{^1H\}$ resonance was observed. This is presumably the more abundant trans isomer.

An APCI mass spectrum of the reaction solution revealed the presence of **4** (parent ion peak at 581.76 *m/z* − 2H) in solution after filtration of **3** from the mixture.

X-ray molecular analysis of **3** shows the crystals to be a bicarbonate complex. (See Tables 1 and 2.) The most significant feature of the structure is the molecular packing which shows a "dimerization" of two molecules via O(32)−H···O(31)′ hydrogen bonds (d(O−O) = 2.53 Å) around a crystallographic inversion center at ($^1/_2$,0,0). The geometry around the iridium atom exhibits a distorted octahedral Ir(III) center with a bicarbonate moiety in a plane perpendicular to the iridium ligand plane. There is a hydrogen atom trans to one of the coordinated

---

(38) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223.

(39) Errington, R. J.; Shaw, B. L. *J. Organomet. Chem.* **1982**, *238*, 319.

Table 1. Crystallographic Data for **3**

formula	$C_{22}H_{47}P_2O_3Ir$
M_r	610.76
a (Å)	14.178(3)
b (Å)	15.541(3)
c (Å)	12.217(3)
β (deg)	103.00(1)
V (Å^3)	2622.9
ρ_{calc} (g/cm^3)	1.55
Z	4
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
F(000) (e)	1232
μ (cm^{-1})	52.1
radiation	0.710 73 Å (Mo Kα)
temp (°C)	25(2)
R (F_o)^a (%)	8.62
R_w (F_o)^b (%)	10.02

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w_i = 1/\sigma_i^2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ir(1)−P(1)	2.31(1)	P(2)−Ir(1)−P(1)	165.9(5)
Ir(1)−P(2)	2.32(1)	C(3)−Ir(1)−P(2)	86.4(15)
Ir(1)−C(3)	1.99(5)	C(3)−Ir(1)−P(1)	81.7(15)
Ir(1)−O(30)	2.42(3)	O(30)−Ir(1)−O(31)	57.8(11)
Ir(1)−O(31)	2.29(3)	O(30)−Ir(1)−C(3)	115.1(17)
O(31)−C(30)	1.29(5)	O(30)−Ir(1)−P(1)	95.4(8)
O(32)−C(30)	1.43(5)	O(31)−Ir(1)−C(3)	172.0(16)
O(30)−C(30)	1.27(5)	O(30)−Ir(1)−P(2)	96.5(8)

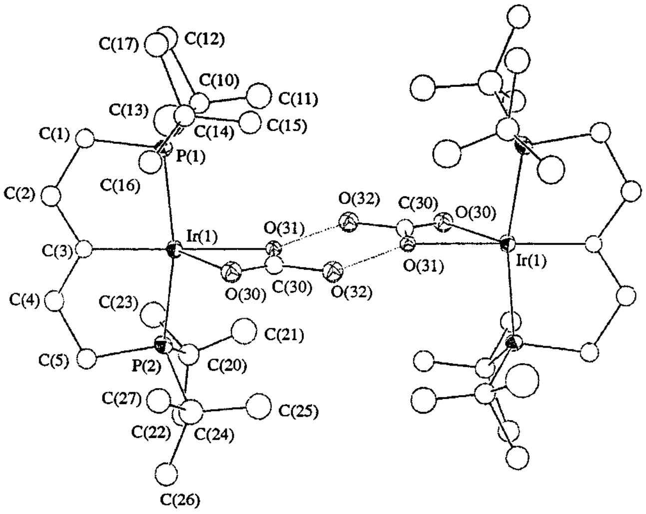


Figure 1. Partial ortep representation of **3** as a bicarbonate dimer with atom labels.

oxygen atoms which may account for the long iridium oxygen distance. (See Figure 1.)

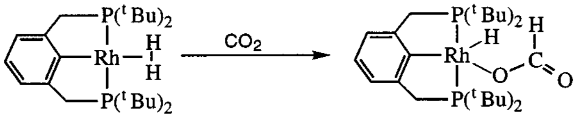
The interatomic distances within the η^2 bicarbonato ligand are similar to those reported by Ibers and Otsuka[40] and Nicholas[41] except for the bicarbonate oxygen.

The bicarbonate carbon atom of **3** was identified at δ 161.9 in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H NMR shows a triplet at δ −33.5 (^2J(PH) = 11.50 Hz) for the Ir−H and a broad OH resonance for the bicarbonate at δ 11.7. Nicholas reported the bicarbonate resonance at δ 7.25 for [Rh(κ^2-O_2COH)(CO)(Ph_3P)$_2$].[41]

An infrared spectrum of the bicarbonate complex showed a very weak Ir−H band at 2000 cm^{-1} and υ (asym) (CO_2^-) carbonate band at 1587 cm^{-1} and υ (sym) (CO_2^-) at 1469 cm^{-1} which is similar to the known Rh complex, reported by Ibers and Otsuka.[40] The O_2COH vibrations ν(OH) at 2652 and 2696 cm^{-1} are similar[40,42,43] as well.

Discussion

A characteristic feature of all metal hydrides is CO_2 insertion into the metal hydride bond. Although the exact mode of carbon dioxide insertion is not completely certain,[44] prior complex formation can occur.[45] Chaudret[46] has shown that η^2 hydrogen ruthenium complexes generate only formates with CO_2. The pincer ligand η^2 hydrogen[22] complex [RhH$_2${(^{t}Bu$_2$)PCH$_2$C$_6$H$_3$-CH$_2$P(^{t}Bu$_2$)}] (**7**) and [RhH$_2${(^{t}Bu$_2$)PCH$_2$CH$_2$CHCH$_2$P(^{t}Bu$_2$)}] (**8**)[47] both interact with CO_2 to give formate complexes although the formate of **7** reacts further to give a metallo hydride hydroxo species and a metal carbonyl compound. Unlike the present work, however, no bicarbonate complex can be isolated. Thus complex **1** shows a different behavior than its rhodium analogues **7** and **8** by forming a bicarbonate complex with CO_2.



7

(3)

The isolation of **3** and **4** from the reaction mixture suggests that the formate moiety undergoes disproportionation. The mechanism of CO_2 disproportionation in transition metal carbon dioxide chemistry is poorly understood because of extraneous factors involved including those of adventitious water. Even so, the process is not common.[4,17,48] Nicholas[41] et al. have proposed a metal-promoted disproportionation of CO_2 followed by H transfer to give a bicarbonate and CO which in the present case would also give **4**. This is a likely possibility in the reaction of **1** with CO_2. Another possibility is the deinsertion of CO from the formate complex to produce a metal hydroxo species which would interact with CO_2 to give **3**, although the formation of 4 is then difficult to explain. Since complex **2** persists long enough to be detected by $^{31}P\{^1H\}$ ^{13}C and ^1H NMR spectroscopy, the disproportionation of formate ion could occur according to a scheme proposed by Elliott and Sealock[48] in which two formate ions associate and subsequently undergo disproportionation. Previous studies show that the hydrogen atoms in **1** are not static.[31] They are fluxional, and the ipso hydrogen atom has an agostic interaction with the iridium atom. We suggest that this agostic interaction may be strong enough to influence the dissociation of the formate ion as an ion pair thus preventing it from forming an η^2 complex. This formate ion pair can simultaneously undergo an unsymmetrical disproportion to give **3** and **4**, although this may be unlikely on electrostatic grounds.

---

(40) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

(41) Hossain, S. F.; Nicholas, K. M.; Teas, C. L.; Davis, R. E. *J. Chem. Soc., Chem. Commun.* **1981**, 268.

(42) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(43) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3831.

(44) Hutschka, F.; Dedieu, A.; Eichberger, M.; Fornika, R.; Leitner, W. *J. Am. Chem. Soc.* **1997**, *119*, 4432.

(45) Fu, P. F.; Fazlur-Rahman, A. K.; Nicholas, K. M. *Organometallics* **1994**, *13*, 413.

(46) Christ, M. L.; Sabo-Etienne, S.; Chung, G.; Chaudret, B. *Inorg. Chem.* **1994**, *33*, 5316.

(47) Vigalok, A.; Ben-Davis, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839.

(48) Elliot, D. C.; Hallen, R. T.; Sealock, L. J., *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 41.

The interaction of Pincer complexes of rhodium and iridium with CO_2 gives a variety of different products which are now identified. Kinetic studies on these interesting reduction reactions can lead to a better mechanistic understanding of CO_2 reduction and disproportionation reactions.

Acknowledgment. Support of this research by the Office of Naval Research and the University Energy Wide Research Group (California Energy Studies Program) is gratefully acknowledged. H.A.M. thanks the Fonds der Chemischen Industrie, Frankfurt/Main, Germany, for support. We also acknowledge the helpful comments and suggestions by Professor Dennis Mitchell, Los Angeles City College, throughout this project.

Supporting Information Available: Tables with full crystallographic details, bond distances, bond angles, atomic positional parameters, and general displacement parameter expressions for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC980722F