Reactivity of Iridium PCP Pincer Complexes toward CO and CO_2. Crystal Structures of $IrH(\kappa^2\text{-}O_2COH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ and $IrH(C(O)OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}\cdot H_2O$

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The reactivity of a series of PCP pincer complexes with carbon monoxide and carbon dioxide has been studied. The reactions of CO_2 with PCP pincer iridium complexes provide the 16-electron complex $Ir(\eta^2\text{-}CO_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**2**). Analogously, reactions with CO yield the 16-electron monocarbonyl compound $Ir(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**4**). When $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1b**) is reacted with CO_2, the hydrido bicarbonate complex $IrH(\kappa^2\text{-}O_2COH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**3**) is obtained. Analogously, when $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1a**) is reacted first with CO_2 and then with H_2O, the reaction affords the same species (**3**). Thus, compound **3** can be obtained irrespective of the order of addition of the substrates CO_2 and H_2O to **1a**. Similarly, the reaction of **1b** with CO affords the insertion product $IrH(C(O)OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**5**). The identities of **3** and **5** have been confirmed by single-crystal X-ray structure determinations.

Introduction

In recent years increasing attention has been focused on the activation of small molecules using transition-metal complexes.[1] Application of this method to molecules that are normally thought to be inert has been of special interest. Among these, carbon dioxide is an excellent example.[2] Since it is a main byproduct of industrial emissions, carbon dioxide can be found in excess in the atmosphere. Scientists have envisioned CO_2 as a possible starting material for the synthesis of fine chemicals.[3] Consumption of CO_2 in this manner would be beneficial in the context of global warming.[4] Furthermore, carbon dioxide species have been postulated and identified as important intermediates in catalytic reactions such as the Fischer−Tropsch process.[5]

We have demonstrated previously that the iridium PCP pincer complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ is an excellent catalyst for the dehydrogenation of aliphatic C−H,[6] O−H,[7] and N−H[8] bonds and showed that this complex is able to activate molecules such as dinitrogen[9] and water.[10] Thus, it was of interest for us to explore whether $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ and the series of other PCP pincer complexes $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}]_2(\mu\text{-}N_2)$[9] and $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$[10] could activate carbon dioxide. For comparative purposes, reactions with carbon monoxide have been also studied. Carbon monoxide has been successfully employed in a variety of catalytic reactions,[11] perhaps the most famous and useful being hydroformylation, which combines carbon monoxide and hydrogen with an olefin to provide aldehydes as final products.[11]

Results and Discussion

Reactions with Carbon Dioxide. Treatment of a pentane solution of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1a**) with a 15-fold excess of *tert*-butylethylene (tbe) under 1 atm of carbon dioxide at 25 °C yields a mixture of two

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(1) Murai, S., Ed. *Activation of Unreactive Bonds and Organic Synthesis*; Springer-Verlag: Berlin, 1999.
(2) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988.
(3) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259. (b) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.
(4) Siegenthaler, U.; Sarmiento, J. L. *Nature* **1993**, *365*, 119.
(5) (a) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. (b) Aresta, M.; Quaranta, E.; Tommasi, I. *New J. Chem.* **1994**, *18*, 133. (c) Ibers, J. A. *Chem. Soc. Rev.* **1982**, 57. (d) Vol'pin, M. E.; Kolomnikov, I. S. *Pure Appl. Chem.* **1973**, *33*, 567.
(6) (a) Gupta, M.; Hagen, C.; Kaska, W. C.; Flesher, R.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2083. (b) Gupta, M.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (c) Xu, W.-W.; Rossini, G.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krough-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273. (d) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 1. (e) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1997**, 2083.
(7) Redón, R.; Morales-Morales, D.; Wang, Z.; Lee, D.-W.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823.
(8) Chen, W.; Morales-Morales, D. Jensen, C. M. *J. Mol. Catal. A: Chem.* **2002**, *189*, 119.
(9) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1.
(10) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics.* **2001**, *20*, 1144.
(11) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; Chapters 7 and 22.

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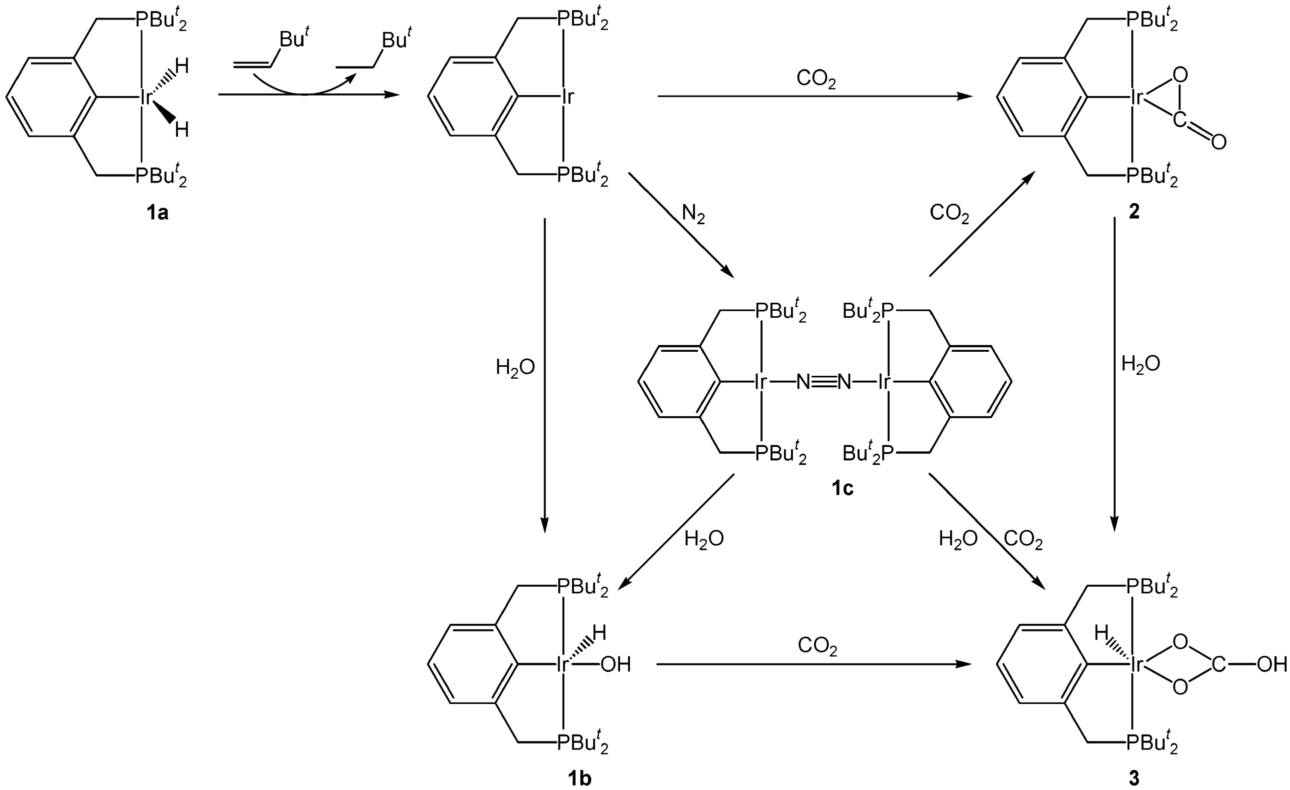
Scheme 1. PCP Pincer Complexes: Reactivity with CO_2



complexes: a very air- and moisture-sensitive reddish orange carbon dioxide complex, Ir(η^2-CO_2){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**2**), and a relatively air-stable pale yellow hydrido bicarbonato complex, IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**3**). The product ratio of **2** to **3** is dependent upon the amount of water vapor present in the carbon dioxide. The initial product of this reaction is very likely the η^2-CO_2 complex **2**, which reacts further with water to produce the bicarbonato complex **3**. This compound can also be obtained in major yield from the reaction of the hydrido hydroxy complex IrH(OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**1b**) with carbon dioxide. Thus, the bicarbonato product **3** is obtained regardless of the order of the carbon dioxide–water reaction sequence. Similar results are obtained when the dinitrogen complex [Ir{C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}]$_2$(μ-N_2) (**1c**) is reacted under 1 atm of CO_2/H_2O at 25 °C.

The η^2-CO_2 complex **2** was characterized by ^{31}P NMR and infrared spectroscopy. Evidence for the presence of coordinated CO_2 is provided by the solid-state (KBr) infrared spectrum. Very strong absorbances are observed at 1756 and 1149 cm^{-1}, which correspond respectively to the asymmetric and symmetric stretches of the carbonyl group. Very similar carbonyl absorptions (1740 (vs), 1150(s) cm^{-1}) have been observed for the nickel complex Ni(η^2-CO_2)(PCy_3)$_2$.[12]

To our knowledge, complex Ir(η^2-CO_2){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**2**) is the first η^2-CO_2 iridium complex to be isolated. Generally, formato complexes are obtained from the reaction of metal hydride complexes with carbon dioxide.[13] Thus, it appears that **2** results from an initial reductive elimination of H_2 from IrH_2{C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}, which is followed by interception of the resulting 14-electron complex by CO_2 (Scheme 1).

The bicarbonato complex **3** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy. The presence of the bicarbonate ligand in **3** is supported by NMR and IR spectroscopy data. In the ^{13}C NMR spectrum, the resonance of the carbon of the bicarbonate moiety is observed at 162.2 ppm. The solid-state (KBr) infrared spectrum of **3** contains a broad absorption at 2655 cm^{-1} corresponding to the O–H vibration. This very low frequency apparently results from hydrogen bonding between the bicarbonate ligands. Similar interactions have been noticed previously for RhH_2(κ^2-O_2COH)($PPr^i{}_3$)$_2$.[14] Characteristic absorptions for the bicarbonato ligand[14,15] were observed at 1580 (carbonyl stretch) and 1482 cm^{-1} (OHO in-plane bending), respectively. The presence of bicarbonate is also supported by a broad OH resonance at 11.62 ppm in the ^{1}H NMR spectrum, which is similar to the resonances for previously reported bicarbonato complexes.[14,15] A resonance is observed for the hydride ligand in the ^{1}H NMR spectrum at −30.4 ppm (t, J_{PH} = 13.7 Hz), but no absorption was observed in the IR spectrum for the Ir–H vibration, due to very low intensity.[16]

The molecular structure of **3** was elucidated through a single-crystal X-ray structure determination (Figure

(12) (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708.

(13) (a) Hutschka, F.; Dedieu, A.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742. (b) Sakaki, S.; Musashi, Y. *Inorg. Chem.* **1995**, *34*, 1914. (c) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.* **1990**, *112*, 9252. (d) Bo, C.; Dedieu, A. *Inorg. Chem.* **1989**, *28*, 304. (e) Christ, M. L.; Sabo-Etienne, S.; Chung, G.; Chaudret, B. *Inorg. Chem.* **1994**, *33*, 5316. (f) Tsai, J.-C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (g) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839.

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

(15) Edwards, A. J.; Elipe, S.; Esteurelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.

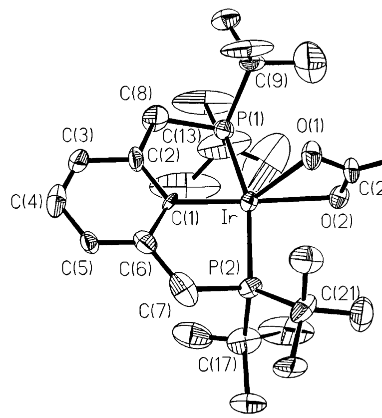


Figure 1. Molecular structure of $IrH(\kappa^2\text{-}O_2COH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**3**) (50% probability). The hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for $IrH(\kappa^2\text{-}O_2COH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (3) and $IrH(C(O)OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}\cdot H_2O$ (5)

	3	5
formula	$C_{25}H_{45}O_3IrP_2$	$C_{25}H_{47}O_3IrP_2$
formula wt	647.75	649.75
temp, K	293(2)	293(2)
cryst syst	orthorhombic	tetragonal
space group	*Pbca*	$I4_1/a$
cryst dimens, mm	0.2 × 0.2 × 0.05	0.3 × 0.3 × 0.2
a, Å	11.996(3)	23.685(6)
b, Å	15.461(3)	23.685(6)
c, Å	30.267(10)	20.355(8)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, $Å^3$	5614(3)	11 419(6)
Z	8	16
μ, cm^{-1}	48.93	48.02
transmission coeff min, max	0.417, 0.888	0.070, 0.102
λ, Å (Mo Kα radiation)	0.710 73	0.710 73
2*θ* range, deg	3−55	3−45
no. of indep rflns	5625	3699
no. of unique data with $I > 2\sigma(I)$	1760	2396
no. of params refined	295	294
goodness of fit[a]	0.771	1.070
ρ_{calcd}, g/cm^3	1.533	1.433
scan type	*ω*	*ω*
R,[b] %	6.48	8.35
R_w,[c] %	13.60	20.78

[a] GOF = $[\Sigma(w(F_o)^2 - (F_c)^2)^2/(n - p)]^{1/2}$, where *n* = number of reflections and *p* = total number of parameters. [b] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [c] $R_w = [\Sigma w((F_o)^2 - (F_c)^2)^2/\Sigma w(F_o)^2]^{1/2}$.

1). Selected bond distances and angles for **3** are shown in Table 2. The geometry around the iridium center is distorted octahedral, with the bicarbonato moiety in a plane perpendicular to the PCP pincer ligand. The hydride and bicarbonate hydrogen could not be reliably located. However, an approximately octahedral geometry around the iridium is completed by assuming the hydride to be located in a position trans to O(1). The pronounced trans effect of the hydride is evident upon comparison of the Ir−O(1) and Ir−O(2) bond distances (2.36(1) vs 2.28(1) Å). The bite angle of the bicarbonato group of 57.1(4)° is quite similar to that found for related bicarbonato complexes.[14]

Table 2. Selected Bond Lengths and Angles for $IrH(\kappa^2\text{-}O_2COH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (3)

	Bond Lengths (Å)		
Ir−P(1)	2.321(5)	C(25)−O(3)	1.27(2)
Ir−P(2)	2.331(5)	P(1)−C(8)	1.83(3)
Ir−C(1)	2.04(2)	P(1)−C(9)	1.88(2)
Ir−O(1)	2.358(12)	P(1)−C(13)	1.84(2)
Ir−O(2)	2.280(13)	P(2)−C(7)	1.82(2)
C(25)−O(1)	1.27(2)	P(2)−C(17)	1.85(2)
C(25)−O(2)	1.31(2)	P(2)−C(21)	1.87(2)
	Bond Angles (deg)		
P(2)−Ir−P(1)	163.0(2)	C(1)−Ir−O(1)	114.7(6)
O(1)−Ir−P(1)	97.1(4)	C(1)−Ir−O(2)	171.6(5)
O(2)−Ir−P(1)	98.6(4)	O(2)−Ir−O(1)	57.1(4)
O(1)−Ir−P(2)	98.0(4)	O(1)−C(25)−O(2)	118.0(14)
O(2)−Ir−P(2)	96.2(4)	O(2)−C(25)−O(3)	120(2)
C(1)−Ir−P(1)	83.6(5)	O(3)−C(25)−O(1)	122(2)
C(1)−Ir−P(2)	82.9(5)		

Reactions with Carbon Monoxide. (a) Reaction of the *μ*-Dinitrogen Complex $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}]_2(\mu\text{-}N_2)$ (1c) with Carbon Monoxide. The treatment of a cyclohexane solution of the dinitrogen complex **1c** under 1 atm of carbon monoxide at 25 °C affords the air-stable yellow-orange carbonyl complex $Ir(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**4**) in nearly quantitative yield within 1 min. The corresponding aliphatic backbone pincer complex $IrH_4\{HC(CH_2CH_2PBu^t{}_2)_2\}$ reacts with carbon monoxide to give a mixture of two isomers of a dihydrido monocarbonyl complex, which were characterized by ^{31}P NMR spectroscopy.[17] However, the rhodium analogue of **1a**, $Rh(H_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$,[18] gives only the corresponding monocarbonyl complex.

Carbonyl complex **4** was characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy; this information agrees well with what we have reported previously.[7]

(b) Reaction of the Hydrido Hydroxy Complex $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (1b) with Carbon Monoxide. The treatment of a cyclohexane solution of the hydrido hydroxy complex **1b** under 1 atm of carbon monoxide at 25 °C affords a mixture of two complexes: the air-stable yellow-orange carbonyl complex $Ir(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**4**; 96% yield based on ^{31}P) and the air-sensitive pale yellow carboxyl complex $IrH(C(O)OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**5**; 4% yield based on ^{31}P). The carboxyl complex **5** was characterized by ^1H and ^{31}P NMR and IR spectroscopy. The ^{31}P NMR spectrum of the carboxyl complex **5** shows a single resonance at 61.2 ppm, which is consistent with both phosphorus nuclei being magnetically equivalent. The ^1H NMR spectrum of **5** features the hydride ligand at −9.88 ppm. The infrared spectrum contains an absorption at 2017 (w) cm^{-1} assignable to the presence of a hydride (Ir−H stretch).

The molecular structure of $\mathbf{5}\cdot H_2O$ was elucidated through a single-crystal X-ray structure determination (Figure 2). The crystal structure data and details of the data collection and solution and refinement are summarized in Table 1. Selected bond distances and angles are shown in Table 3. The short bond distance (2.66(2) Å) between O(1a) and O(2b) or O(2a) and O(1b) indicates

(16) (a) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M. McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217. (b) Empsall, H. D.; Johnson, S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 302. (c) Empsall, H. D.; Heys, P. N.; McDonald, W. S.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1119. (d) Empsall, H. D.; Hyde, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1975**, 1690.

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

(18) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1998**, *7*, 13.

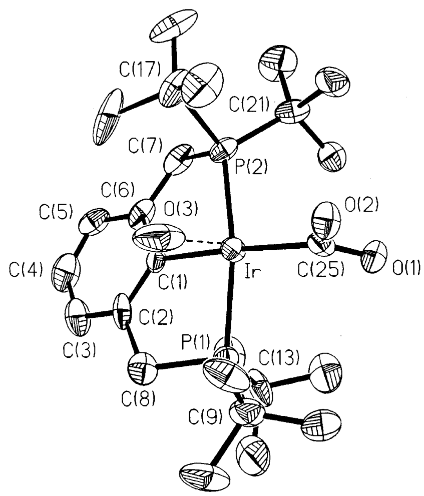


Figure 2. Molecular structure of IrH(C(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}·H_2O (**5**) (50% probability). The hydrogen atoms have been omitted for clarity.

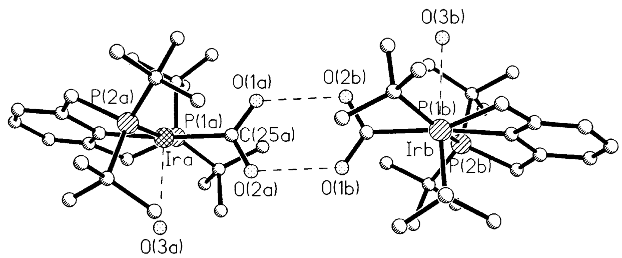


Figure 3. Molecular structure of IrH(C(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}·H_2O (**5**), with hydrogen-bonding interactions indicated by dashed lines. The hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths and Angles for IrH(C(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}·H_2O (5).

	Bond Lengths (Å)		
Ir−P(1)	2.323(5)	O(1)−O(2)	2.65(2)
Ir−P(2)	2.291(6)	P(1)−C(8)	1.82(2)
Ir−C(1)	2.07(2)	P(1)−C(9)	1.84(3)
Ir−O(3)	2.69(4)	P(1)−C(13)	1.90(3)
Ir−C(25)	2.10(2)	P(2)−C(7)	1.83(2)
C(25)−O(1)	1.26(2)	P(2)−C(17)	1.96(2)
C(25)−O(2)	1.32(3)	P(2)−C(21)	1.87(3)
	Bond Angles (deg)		
P(2)−Ir−P(1)	159.5(2)	C(7)−P(2)−Ir	103.4(9)
O(3)−Ir−P(1)	93.9(4)	C(1)−Ir−C(25)	173.4(9)
O(3)−Ir−P(2)	96.7(4)	P(2)−Ir−C(25)	100.0(5)
C(1)−Ir−P(1)	80.0(6)	P(1)−Ir−C(25)	96.8(6)
C(1)−Ir−P(2)	82.1(6)	O(3)−Ir−C(25)	93.5(9)
C(1)−Ir−O(3)	92.4(7)	O(1)−C(25)−O(2)	125.4(13)
C(8)−P(1)−Ir	101.6(9)		

the strong hydrogen bonding between the hydrogen and oxygen of the carboxylic groups of the two molecules (Figure 3).

Several possible mechanistic pathways accounting for the formation of **4** and **5** are depicted in Scheme 2. The formation of **4** from **1a** could result from the coordination of CO upon dehydrogenation of **1a** by tbe. Carboxyl complex **5** could result from the insertion of carbon monoxide into the hydrido hydroxy complex **1b**. Decarbonylation of the carbonate group of **5** could give rise to an 18-electron carbonyl hydrido hydroxy complex that could then in turn undergo reductive elimination of water to give **4**. Another possibility is that the reductive elimination of water from **1b** could precede CO coordination.

(c) Reaction of the Bicarbonato Complex IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (3) with Carbon Monoxide. Complex **3** reacts very quickly (∼1 min) with carbon monoxide (Scheme 3) to yield the pale yellow bicarbonato hydrido monocarbonyl complex IrH(CO)(κ^1-OC(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**6**). This complex was characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Resonances for the hydride and bicarbonate hydrogens appear at −7.13 (t, J_{PH} = 15.6 Hz) and 12.33 (broad) ppm, respectively, in the ^1H NMR spectrum. The presence of the carbonyl and bicarbonate ligands is also supported by ^{13}C NMR and infrared spectroscopy. The ^{13}C NMR spectrum features resonances at 184.0 (t, J_{PC} = 5.6 Hz) and 163.9 (s) ppm which can be assigned to the carbonyl and bicarbonato carbons, respectively. The solid-state (KBr) infrared spectrum of **6** shows absorptions at 2620 (m), 2184 (w), 2003 (s), and 1603 (s) cm^{-1} which are assignable to the vibrations of O−H, Ir−H, CO, and OCO, respectively.

Recently, similar reactions have been reported. Esteurelas[15] et al. prepared OsH(κ^1-OC(O)OH)$(CO)_2$-$(PPr^i{}_3)_2$ through the reaction of OsH(κ^2-O_2COH)(CO)-$(PPr^i{}_3)_2$ with CO. Also, *trans*-RhH(κ^1-OC(O)OH)(CO)-$(PPh_3)_2$ has been prepared through the reaction of RhH-(κ^2-O_2CO)$(PPh_3)_2$ with CO.[19]

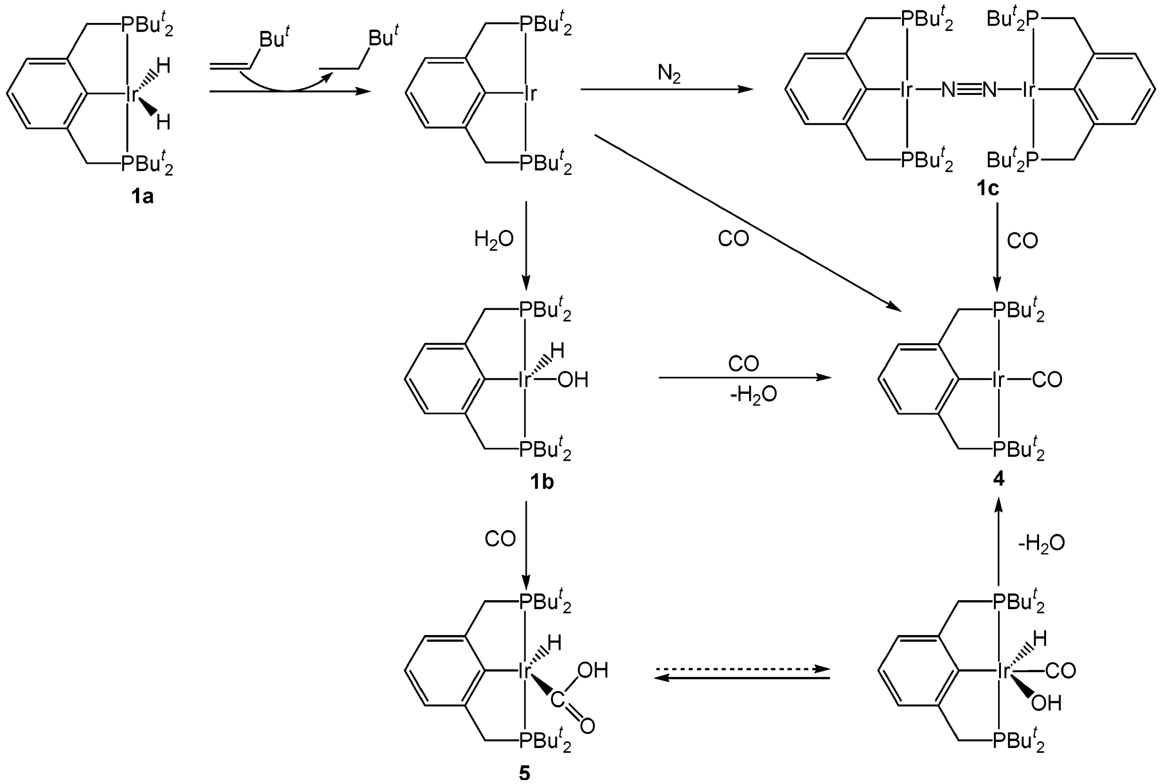
We have shown that CO_2 and CO are activated and, in the presence of water, hydroxylated at the PCP iridium reaction center. Our findings may point to advanced versions of the much studied catalytic system of dehydrogenation of alkanes by $PCPIrH_2$ complexes. For example, a tandem process of alkane and CO_2 activation can be envisioned in which the initial formation of α-olefin is followed in a second step by the formation of carbonylic compounds, thus avoiding the problem of product inhibition that plagues the original catalytic system. One can also envision the application of some of these species to organic synthesis.[22] Efforts aimed at exploring these possibilities are currently under study in our laboratories.

Experimental Section

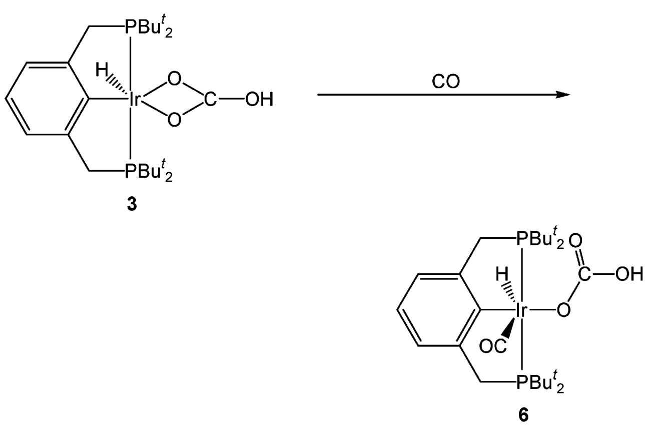
All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures. The carbon dioxide gas (99.99%) and carbon monoxide (99.99%) were purchased from Air Liquide and Matheson, respectively, and used without further purification. The complexes IrH_2{C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**1a**), IrH(OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**1b**), and [Ir{C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}]$_2$(μ-N_2) (**1c**) were synthesized by the literature methods.[20] The ^1H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm downfield of TMS using the solvent as internal standard (cyclohexane-d_{12}, δ 1.38; toluene-d_8, δ 2.09). ^{13}C and ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with solvent as internal standard (cyclohexane-d_{12}, δ 26.45; toluene-d_8, δ 20.4) and external 85% H_3PO_4, respectively.

(19) Hossain, S. F.; Nicholas, K. M.; Teas, C. L.; Davis, R. E. *J. Chem. Soc., Chem. Commun.* **1981**, 268.
(20) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
(21) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.
(22) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

Scheme 2. PCP Pincer Complexes: Reactivity with CO



Scheme 3



Infrared spectra were recorded on a Perkin-Elmer Paragon FT-IR spectrometer as Nujol mulls on KBr plates.

Synthesis of Ir(η^2-CO_2){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (2) and IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (3) (Mixture). A pentane (5 mL) solution of IrH_2{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (50 mg, 0.085 mmol) was treated with *tert*-butylethylene (125 μL, 1.28 mmol) under 1 atm of carbon dioxide gas at 25 °C. Removal of the solvent in vacuo yielded a mixture of the air- and moisture-sensitive red-orange η^2-carbon dioxide complex Ir(η^2-CO_2)-{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**2**) and the air-stable pale yellow bicarbonato complex IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**3**). Data for **2** are as follows. ^{31}P NMR (161.90 MHz, benzene-d_6): δ 63.3 (s). IR (KBr) ν_{IrCO_2} 1757 (vs), 1149 (vs) cm^{-1}. Data for **3** are as follows. ^{1}H NMR (400.00 MHz, cyclohexane-d_{12}, under 1 atm of CO_2): δ 6.65 (d, J_{HH} = 7.3 Hz, 2H, *m*-H), 6.50 (t, J_{HH} = 7.3 Hz, 1H, *p*-H), 3.21, 2.96 (d of t, J_{HH} = 16.5 Hz, J_{PH} = 3.7 Hz, 2H, CH_2), 1.34, 1.27 (t, J_{PH} = 6.4 Hz, 18H, C(CH_3)$_3$), −30.41 (t, J_{PH} = 13.7 Hz, Ir−*H*), 11.62 (brs, 1H, Ir−CO_3H). ^{13}C NMR (100.60 MHz, cyclohexane-d_{12}): δ 162.2 (s, *C*O_3), 147.3 (t, J_{PC} = 8.6 Hz, *o-C*), 132.9 (s, *C-1*), 121.1 (s, *p-C*), 119.7 (t, J_{PC} = 7.4 Hz, *m-C*), 34.0 (t, J_{PC} = 13.9 Hz, *C*H_2P), 36.2 (t, J_{PC} = 9.0 Hz, *C*(CH_3)$_3$), 34.6 (t, J_{PC} = 11.6 Hz, *C*(CH_3)$_3$), 29.9, 29.8 (s, C(*C*H_3)$_3$). ^{31}P NMR (161.90 MHz, cyclohexane-d_{12}): δ 59.5 (s). IR (KBr): ν_{OH} 2650 (m), ν_{OCO} 1580 (vs), ν_{OHO} 1482 (vs) cm^{-1}. Anal. Calcd for $C_{25}H_{45}O_3P_2Ir$ (647.80): C, 46.35; H, 7.00. Found: C, 46.43; H, 7.07.

Synthesis of IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (3) from IrH(OH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (1b) and CO_2. A cyclohexane (5 mL) solution of IrH(OH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**1b**; 10 mg, 0.017 mmol) was placed under 1 atm of carbon dioxide at 25 °C for 1 min. Removal of the solvent in vacuo afforded IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**3**) as a pale yellow solid in nearly quantitative yield (based on ^{31}P NMR).

Synthesis of IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (3) from [Ir{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$}]$_2$(μ-N_2) (1c) and CO_2/H_2O. A cyclohexane (5 mL) solution of [Ir{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$}]$_2$-(μ-N_2) (**1c**; 10 mg, 0.0083 mmol) was placed under 1 atm of carbon dioxide/water at 25 °C for 1 min. Removal of the solvent in vacuo afforded IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**3**) as a pale yellow solid in nearly quantitative yield (based on ^{31}P NMR).

Reaction of [Ir{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$}]$_2$(μ-N_2) (1c) with CO. A cyclohexane (5 mL) solution of [Ir{C_6H_3-2,6-(CH_2-PBu^t_2)$_2$}]$_2$(μ-N_2) (**1c**; 20 mg, 0.017 mmol) was placed under 1 atm of carbon monoxide at 25 °C for 1 min. Removal of the solvent in vacuo gave Ir(CO){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (**4**) in nearly quantitative yield (based on ^{31}P NMR) as an air-stable yellow-orange solid. ^{1}H NMR (400.00 MHz, cyclohexane-d_{12}): δ 6.93 (d, J_{HH} = 7.3 Hz, 2H, *m*-H), 6.67 (t, J_{HH} = 7.3 Hz, 1H, *p*-H), 3.42 (t, J_{HH} = 3.0 Hz, 4H, CH_2), 1.28 (t, J_{PH} = 7.3 Hz, 36H, C(CH_3)$_3$). ^{13}C NMR (100.60 MHz, cyclohexane-d_{12}): δ 197.6 (s, Ir−*C*O), 168.8 (s, *C-1*), 155.3 (t, J_{PC} = 12.0 Hz, *o-C*), 125.9 (s, *p-C*), 120.3 (t, J_{PC} = 9.1 Hz, *m-C*), 39.6 (t, J_{PC} = 13.9 Hz, *C*H_2P), 36.5 (t, J_{PC} = 10.7 Hz, *C*(CH_3)$_3$), 30.1 (s, C(*C*H_3)$_3$). ^{31}P NMR (161.90 MHz, cyclohexane-d_{12}): δ 82.8 (s). IR (KBr) ν_{IrCO} 1913 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{43}OP_2Ir$ (613.77): C, 48.92; H, 7.06. Found: C, 48.96; H, 7.01.

Reaction of IrH(OH){C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} (1b) with CO. A cyclohexane (5 mL) solution of IrH(OH){C_6H_3-2,6-(CH_2-PBu^t_2)$_2$} (**1b**; 20 mg, 0.034 mmol) was placed under 1 atm of carbon monoxide at 25 °C. Removal of the solvent in vacuo yielded a mixture of Ir(CO){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (**4**; 96% yield based on ^{31}P NMR) and IrH(C(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (**5**; 4% yield based on ^{31}P NMR) as an air-sensitive pale yellow solid. Data for **5** are as follows. ^{1}H NMR (400.00 MHz, cyclohexane-d_{12}): δ 6.82 (d, J_{HH} = 7.3 Hz, 2H, *m*-H), 6.69 (t, J_{HH} = 7.3 Hz, 1H, *p*-H), 3.44 (d of t, J_{HH} = 22.0, J_{PH} = 4.6 Hz, 2H, CH_2), 3.36 (d of t, J_{HH} = 16.5, J_{PH} = 3.7 Hz, 2H, CH_2), 1.42 (t, J_{PH} = 6.4 Hz, 18H, C(CH_3)$_3$), 1.26 (t, J_{PH} = 6.4 Hz, 18H, C(CH_3)$_3$), −9.88 (t, J_{PH} = 16.5 Hz, 2H, Ir−H). ^{31}P NMR (161.90 MHz, cyclohexane-d_{12}): δ 61.2 (s). IR (KBr): ν_{IrH} 2202 (w), 2017 (s), 1987 (w) cm^{-1}.

Reaction of IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (3) with CO. A toluene-d_8 solution (0.7 mL) of IrH(κ^2-O_2COH)-{C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (10 mg, 0.015 mmol) was placed under 1 atm of carbon monoxide gas at 25 °C. Removal of the solvent in vacuo gave IrH(CO)(κ^1-OC(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (**6**) as an air-stable pale yellow solid in nearly quantitative yield (based on ^{31}P NMR). ^{1}H NMR (400.00 MHz, toluene-d_8, under 1 atm of CO): δ 6.75 (d, J_{HH} = 7.3 Hz, 2H, *m*-H), 6.83 (t, J_{HH} = 7.3 Hz, 1H, *p*-H), 2.89 (t, J_{PH} = 3.7 Hz, 4H, CH_2), 1.31 (t, J_{PH} = 7.3 Hz, 18H, C(CH_3)$_3$), 1.16 (t, J_{PH} = 6.4 Hz, 18H, C(CH_3)$_3$), −7.13 (t, J_{PH} = 15.6 Hz, Ir−*H*), 12.33 (br s, 1H, Ir−CO_3H). ^{13}C NMR (100.60 MHz, toluene-d_8): δ 184.0 (t, J_{PC} = 5.6 Hz, *C*O), 163.9 (s, *C*O_3), 146.9 (t, J_{PC} = 6.4 Hz, *o-C*), 134.1 (s, *C-1*), 123.6 (s, *p-C*), 121.5 (t, J_{PC} = 6.4 Hz, *m-C*), 36.9 (t, J_{PC} = 13.9 Hz, *C*H_2P), 36.1 (t, J_{PC} = 12.8 Hz, *C*(CH_3)$_3$), 35.9 (t, J_{PC} = 10.7 Hz, *C*(CH_3)$_3$), 29.7, 29.1 (s, C(*C*H_3)$_3$). ^{31}P NMR (161.90 MHz, toluene-d_8): δ 59.3 (s). IR (KBr): ν_{OH} 2620 (m), ν_{Ir-H} 2184 (w), ν_{CO} 2003 (vs), ν_{OCO} 1603 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{45}O_4P_2Ir$ (675.80): C, 46.21; H, 6.71. Found: C, 46.18; H, 6.68.

Single-Crystal X-ray Structure Determination of IrH-(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (3) and IrH(C(O)OH)-{C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$}·H_2O (5). Suitable crystals of IrH(κ^2-O_2COH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$} (**3**) and IrH(C(O)OH){C_6H_3-2,6-($CH_2PBu^t{}_2$)$_2$}·H_2O (**5**) grown from pentane/methylcyclohexane solvent systems were glued to glass fibers. Intensity data were measured at room temperature using a Nicolet P3 diffractometer, equipped with a graphite monochromator (λ = 0.710 73 Å, Mo Kα). The unit cells were determined from the angular coordinates of 25 reflections with 2θ values between 15 and 30°. The diffractometer autoindexing routine found orthorhombic and tetragonal unit cells, respectively, which were in both cases confirmed by axial photographs.

Three check reflections, monitored every 100 reflections, showed no significant decay. The data were processed using the SHELXTL program package, and an absorption correction was applied based upon ψ scans of 5 reflections. The structures were solved by Patterson methods. The remainder of the structures were easily developed via a few cycles of least-squares refinement and difference Fourier maps. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Two groups of thermal parameters were refined for hydrogen atoms, one each for methylene and methyl protons. The final cycles of refinement were carried out on all nonzero data using SHELXL-97[21] and anisotropic thermal parameters for all non-hydrogen atoms. Crystal data are collected in Table 1.

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Supporting Information Available: Tables of crystallographic parameters, atomic coordinates, all bond distances and angles, anisotropic displacement coefficients, and coordinates of hydrogen atoms for complexes **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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