

알칸의 탈수소화반응에서의 촉매독 화합물의 분자구조

이지현 · 전상진 · 권기혁 · 이도원*

서울시립대학교 화학공학과

Molecular Structure of PCP Pincer Complexes: Poisoning Catalyst on the Dehydrogenation of Alkanes

Ji Hyun Lee, Sang Jin Chun, Ki Hyeok Kwon and Do Weon Lee*

Department of Chemical Engineering, University of Seoul,
Jeonnon-Dong, Dongdaemun-Gu, Seoul 130-743, Korea

요 약

알칸화합물(alkanes)에서 탄소-수소결합을 활성화시켜서 더욱 값이 비싸고 더 유용한 알켄화합물(alkenes)로 만들 수 있는 촉매를 만들고자 지난 수 십 년간 많은 화학자들이 연구해왔다. 이러한 목적의 하나로서 두개의 수소를 가지는 이리듐 P-C-P핀서(pincer) 착물 ($\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$)을 성공적으로 합성하였다. 이 착물은 알칸의 탈수소화반응(dehydrogenation)에 아주 효과적인 촉매로 알려졌다. 알칸의 탈수소화반응에 촉매독으로 작용하는 질소, 물, 이산화탄소 및 일산화탄소와 같은 작은 화합물들과 직접 반응시켜서 어떻게 촉매독으로 작용하는지를 알아왔다. 촉매독으로 작용할 수 있는 화합물들을 합성하여 핵자기공명분광법(NMR)과 적외선분광법(IR)으로 확인하였고 분자구조를 알아보기 위해서 단결정 X-ray 회절법을 통하여 확인하였다. 본 논문에서는 촉매 및 촉매독물질의 합성과 분자구조와 각각의 화합물의 반응성과 특이성을 알아보았다.

Abstract

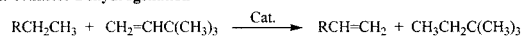
The dihydrido P-C-P pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**1**), was successfully prepared from the reaction of the hydrochloride complex, $\text{IrClH}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$, and super acid (LiBEt_3H) under 1 atm of hydrogen in pentane solution at room temperature and followed by heating at 130°C in vacuo. Jensen recently found that the dihydrido P-C-P pincer complex **1** is a highly active homogeneous catalyst for the transfer dehydrogenation of alkanes with unusual long-term stability at temperatures as high as 200°C. The treatment of dihydrido complex **1** with nitrogen, water, carbon dioxide, and carbon monoxide in presence of *tert*-butylethylene (tbe) at room temperature in an appropriate solution gave the dinitrogen complex, $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}_2(\mu\text{-N}_2)$ (**2**), the hydrido hydroxyl complex, $\text{IrH}(\text{OH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**3**), the carbon dioxide complex, $\text{Ir}(\eta^2\text{-CO}_2)\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (including the bicarbonato complex, $\text{IrH}(\kappa^2\text{-O}_2\text{COH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**4**)), and the carbonyl complex, $\text{Ir}(\text{CO})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**5**) (including the carboxyl complex, $\text{IrH}(\text{C}(\text{O})\text{OH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**6**)), in good yield, respectively. These P-C-P iridium complexes were isolated and characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy. In addition, the complexes (**1-6**) were characterized by a single crystal X-ray crystallography. These complexes account for these small molecules' inhibition of dehydrogenation of alkanes catalyzed by the dihydrido complex **1**.

1. Introduction

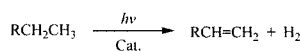
Alkanes (especially methane) are abundant and relatively inexpensive. Therefore, they would be ideal chemical feedstocks. However, alkanes are very poor electron donors and/or acceptors and activation of alkane C-H bonds is difficult. Therefore, the selective functionalization of alkanes is as fundamentally challenging as it is potentially useful. Although alkane C-H bonds are difficult to activate, they are not completely inert. During the past 20 years, many chemists have sought to develop catalysts for the functionalization of saturated hydrocarbons.¹⁻⁵⁾ Pioneering work in this area was carried out in the research groups of Crabtree,⁶⁾ Bergman,⁷⁾ and Graham.⁸⁾ During the past decade there has been a great deal of continued activity focused upon discovering and understanding C-H bond activation by soluble transition metal complexes.¹⁻⁵⁾ The goal of these studies is not simply to find new C-H bond activation reactions, but to gain an understanding of these processes such that catalysts can be developed for the selective transformation of inexpensive alkanes to more valuable compounds. In order to achieve a successful system it has to satisfy at least three requirements: (1) the alkane C-H activation by the metal complex is not just stoichiometric, but catalytic, (2) catalytic activity, often called turnover number, should be higher under mild reaction conditions, and (3) high product selectivity.

Currently, the catalytic dehydrogenation of alkanes to alkenes stands as the greatest practical advance in the use of soluble transition metal complexes for alkane C-H bond activation. Several methods of dehydrogenation of alkanes using transition metal complexes as homogeneous catalysts have been developed. The most common method is transfer dehydrogenation. In this reaction hydrogenation is transferred from alkanes to hydrogen acceptors such as *tert*-butylethylene (tbe) as shown in Scheme 1a.⁹⁻²⁰⁾ The major drawback to transfer dehydrogenation is that the use of a sacrificial hydrogen acceptor is wasteful. Nonetheless, this method is the most common in catalytic dehydrogenation of alkanes because it is usually efficient. "Acceptorless" catalytic dehydrogenation of alkanes has been achieved through

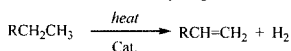
a. Transfer Dehydrogenation



b. Photoirradiation



c. Thermal Evolution of Hydrogen



Scheme 1. Methods of catalytic dehydrogenation of alkanes.

methods involving photoirradiation as shown in Scheme 1b.²¹⁻²⁶⁾ However, such photochemical methods are not applicable to industrial scale operations. Dehydrogenation of alkanes can also be effected by the thermal evolution of hydrogen as shown in Scheme 1c.²⁷⁻³¹⁾ This reaction, however, is very endothermic. Very high temperatures or continuous removal of molecular hydrogen from the system are required to achieve significant levels of conversion to the alkene product.

Jensen and coworkers found that the iridium PCP pincer complexes are highly active robust catalyst for the dehydrogenation of alkanes.^{18,19)} The practical application of the pincer catalyzed reaction is limited by its sensitivity to high concentration of alkene products. It was also found that the reaction must be carried out under an argon atmosphere as even traces of nitrogen, carbon dioxide, and water act as catalyst poisons. In order to design an improved second generation catalyst, it is important to determine the origin of these inhibitive effects as well as catalytic mechanism. Reactions of the iridium PCP pincer complex with N₂, H₂O, CO₂, and CO were carried out. The products were isolated and their molecular structures were determined by a single crystal X-ray diffraction studies. This paper is thus an account of our contribution toward the quest for the "Holy Grail"³⁴⁾ of the development of a transition metal complex catalyst for the selective transformation of alkanes to functionalized organic compounds.

2. Experimental

General Information. All syntheses were carried out under purified argon using standard Schlenk

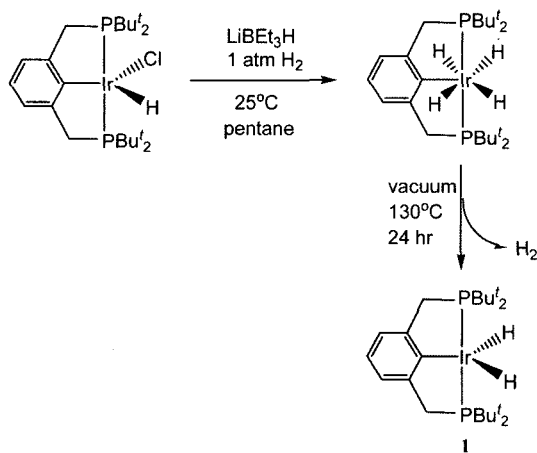
techniques. The pincer ligand $C_6H_3-2,6-(CH_2PBU'_2)_2$ was prepared by the literature method.³²⁾ The complexes $IrClH\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ and $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**) were prepared by cited literature method.¹⁹⁾ The followings were purchased and used without further purification: $IrCl_3 \cdot 3H_2O$ (Johnson Matthey), $LiBEt_3H$ (1.0 M in THF, ACROS Organics). Unless specified, all other reagents were received from commercial sources and used without further purification. All solvents were dried by the standard methods.³³⁾

Characterizations. All prepared compounds were characterized by 1H and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR (Varian Unity Inova 400 MHz FT-NMR Spectrometer) spectroscopy. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) and were referenced to the residual solvents for 1H NMR and to the solvent peaks for $^{13}C\{^1H\}$ NMR. $^{31}P\{^1H\}$ chemical shifts are reported in ppm relative to 85% H_3PO_4 as an external peak.

Syntheses of PCP Pincer Complexes. (1) Synthesis of $[Ir\{C_6H_3-2,6-(CH_2PBU'_2)_2\}_2(\mu-N_2)$ (2**).**³⁴⁾ A pentane (5 mL) solution of $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**) (20 mg, 0.034 mmol) was treated with *tert*-butylethylene (tbe) (66 mL, 0.51 mmol) under 1 atm of nitrogen at 25°C and allowed to stir for 1 hr. Removal of the solvent *in vacuo* gave $[Ir\{C_6H_3-2,6-(CH_2PBU'_2)_2\}_2(\mu-N_2)$ (**2**) as a pale yellow solid in nearly quantitative yield. **(2) Synthesis of $IrH(OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**3**).**³⁵⁾ A pentane (5 mL) solution of $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**) (20 mg, 0.034 mmol) was treated with *tert*-butylethylene (tbe) (66 μ L, 0.51 mmol) under 1 atm of argon at 25°C. After 1 hr of reaction, the resulting red-purple solution was treated with degassed, deionized water (0.1 mL, 5.6 mmol). Removal of the solvent *in vacuo* gave $IrH(OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**3**) as a deep orange solid in nearly quantitative yield. **(3) Syntheses of $Ir(\eta^2-CO_2)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ and $IrH(\kappa^2-O_2COH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**4**).**³⁶⁾ A pentane (5 mL) solution of $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**) (50 mg, 0.085 mmol) was treated with *tert*-butylethylene (tbe) (125 μ L, 1.28 mmol) under 1 atm of carbon dioxide gas at 25°C. Removal of the solvent

in vacuo gave a mixture of the very air- and moisture-sensitive, red-orange η^2 -carbon dioxide complex, $Ir(\eta^2-CO_2)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ and the air-stable pale yellow bicarbonato complex, $IrH(\kappa^2-O_2COH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**4**). **(4) Synthesis of $Ir(CO)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**5**).**³⁷⁾ A cyclohexane (5 mL) solution of $[Ir\{C_6H_3-2,6-(CH_2PBU'_2)_2\}_2(\mu-N_2)$ (**2**) (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 $Ir(CO)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**5**) as an air-stable yellow-orange solid in nearly quantitative yield. **(5) Synthesis of $IrH(C(O)OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**6**).**³⁶⁾ A cyclohexane (5 mL) solution of $IrH(OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**3**) (20 mg, 0.034 mmol) was placed under 1 atm of carbon monoxide at 25°C. Removal of the solvent *in vacuo* gave mixtures of $Ir(CO)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**5**) (>80% yield) and $IrH(C(O)OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**6**) as an air-sensitive yellow solid.

Crystallographic Studies. Crystals of $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**), $[Ir\{C_6H_3-2,6-(CH_2PBU'_2)_2\}_2(\mu-N_2) \cdot (C_6H_{12})_{1.5}$ (**2**· $(C_6H_{12})_{1.5}$), $IrH(OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**3**), $IrH(\kappa^2-O_2COH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**4**), $Ir(CO)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**5**), and $IrH(C(O)OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\} \cdot (H_2O)$ (**6**· (H_2O)) suitable for X-ray diffraction were obtained from concentrated solutions of appropriate solvents. The crystals were mounted on glass fibers with epoxy and centered automatically on a Nicolet P3 Diffractometer using 25 reflections with $15^\circ < 2\theta < 30^\circ$. Three check reflections were monitored every 97 reflections, showing no decrease intensity over the duration of the data collection. The structures were solved by Patterson methods, completed by conventional Fourier Transform techniques, and refined by full-matrix least-squares procedures using SHELXTL-93 computer programs. Semi-empirical ellipsoid absorption corrections from psi-scan were applied to **2**· $(C_6H_{12})_{1.5}$ and **3**. Semi-empirical lamina (0 0 1) absorption correction from psi-scan was applied to **4**. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.



Scheme 2. Synthesis of dihydrido iridium PCP pincer complex (1).

3. Results and Discussion

Synthesis of $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (1).¹⁹⁾

As seen in Scheme 2, treatment of a pentane solution of the hydrochloride complex, $\text{IrHCl}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$, under 1 atm of hydrogen with super acid (LiBEt_3H) at 25°C produces the white tetrahydrido complex, $\text{IrH}_4\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$, in 85% yield. The brown dihydrido complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (1), is obtained quantitatively upon heating finely powdered tetrahydrido complex to 130°C *in vacuo*. The complex 1 was characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy. An X-ray structure determination was carried out on a single crystal of 1 in order to verify the structural composition. Details relating to the crystal data, the

Table 1. Summary of crystal data for iridium PCP pincer complexes

	1	2·(C ₆ H ₁₂) _{1.5}	3	4	5	6·H ₂ O
Formula	IrC ₂₄ P ₂ H ₄₅	C ₅₇ H ₁₀₄ Ir ₂ N ₂ P ₄	C ₂₄ H ₄₅ IrOP ₂	C ₂₅ H ₄₅ IrO ₃ P ₂	C ₂₅ H ₄₃ IrOP ₂	C ₂₅ H ₄₇ IrO ₃ P ₂
Formula weight	587.74	1325.70	603.74	647.75	613.73	649.77
Crystal system	Tetragonal	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Tetragonal
Space group	P4 ₂	P1	Pbca	Pbca	P2 ₁ /n	I4(1)/a
Color of crystal	Orange	Orange	Yellow	Yellow	Yellowish Orange	Pale Yellow
Crystal dimensions, mm	0.5 × 0.4 × 0.2	0.5 × 0.5 × 0.5	0.5 × 0.3 × 0.2	0.2 × 0.2 × 0.5	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.2
a, Å	11.710(4)	14.428(10)	11.520(7)	11.996(3)	15.443(4)	23.685(6)
b, Å	11.710(4)	14.639(5)	16.094(10)	15.461(3)	11.619(3)	23.685(6)
c, Å	9.701(5)	16.702(11)	28.53(2)	30.267(10)	30.608(8)	20.355(8)
α, deg	90	71.780(10)	90	90	90	90
β, deg	90	75.590(10)	90	90	93.22	90
γ, deg	90	68.599(10)	90	90	90	90
V, Å ³	1330.2(9)	3090(3)	5291(6)	5614(3)	5483(3)	11419(6)
Z	2	2	8	8	8	18
μ, cm ⁻¹	51.46	44.40	51.80	48.93	49.99	54.12
Transmission Coeff. min	0.631, 0.970	0.001, 0.008	0.055, 0.127	0.417, 0.888	0.389, 1.000	0.070, 0.102
max						
T, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ, Å (MoKα radiation)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range, deg	3-45	3-40	3-40	3-55	3-45	3-45
Independent reflections	1766	5744	2429	5625	7143	3699
Unique data with I > 2σ(I)	1744	4803	1547	1760	1980	2396
Parameters refined	137	614	272	295	526	283
Goodness of fit ^a	0.920	1.0731	0.920	0.771	0.986	1.109
ρ _{calc} , g/cm ³	1.467	1.425	1.516	1.533	1.487	1.701
Scan type	2θ	ω	ω	ω	ω	ω
R ^b , %	3.05	4.85	4.42	6.48	3.78	8.30
R _w ^c , %	6.21	11.88	9.78	13.60	8.87	20.54

^aGOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$. ^bR = $\sum |F_o| - |F_c| / \sum F_o$. ^cR_w = $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

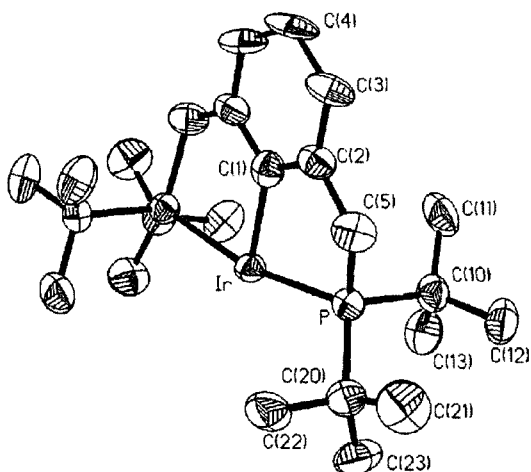


Fig. 1. Projection of $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}_2]$ (**1**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir-C(1), 2.12(1); Ir-P, 2.308(2); P-Ir-C(1), 82.41(6); P-Ir-P(a), 164.8(1). The hydrogen atoms are omitted for clarity.¹⁹⁾

data collection, and solution and refinement are summarized in Table 1. A projection of the structure **1** is seen in Fig. 1. The hydride could not be reliably located. The angle P-Ir-P(a) is 164.8(1)°.

Jensen and coworkers found that the iridium P-C-P pincer complex **1** is a highly active homogeneous catalyst for the transfer dehydrogenation of cyclooctane with unusual long-term stability at temperatures as high as 200°C.¹⁸⁻²⁰⁾

Synthesis of $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}_2](\mu\text{-N}_2)$ (2**).**³⁴⁾ As seen in Scheme 3, treatment of a pentane solution of **1** with a 15 fold excess of *tert*-butylethylene (tbe) under 1 atm of nitrogen at 25°C gives the dinitrogen complex, $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}_2](\mu\text{-N}_2)$ (**2**) in nearly quantitatively yield within 1 hr. The formation of **2** is evidently initiated by the reaction of nitrogen with the intermediate, $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}]$, which results from the dehydrogenation of **1** by tbe, as nearly one equivalent of *tert*-butylethane (tba) is produced in the reaction. The dinitrogen complex **2** is rapidly converted back to **1** upon exposure to 1 atm of H₂ at 25°C.

The dinitrogen complex **2** was characterized by ¹H, ¹³C, ³¹P NMR, and IR spectroscopy. The nitrogen-nitrogen stretching frequency in IR spectrum appeared at 2078 cm⁻¹, which is in usual metal-hydride region. The elemental analysis data for C, H, and N are in accordance with the calculated

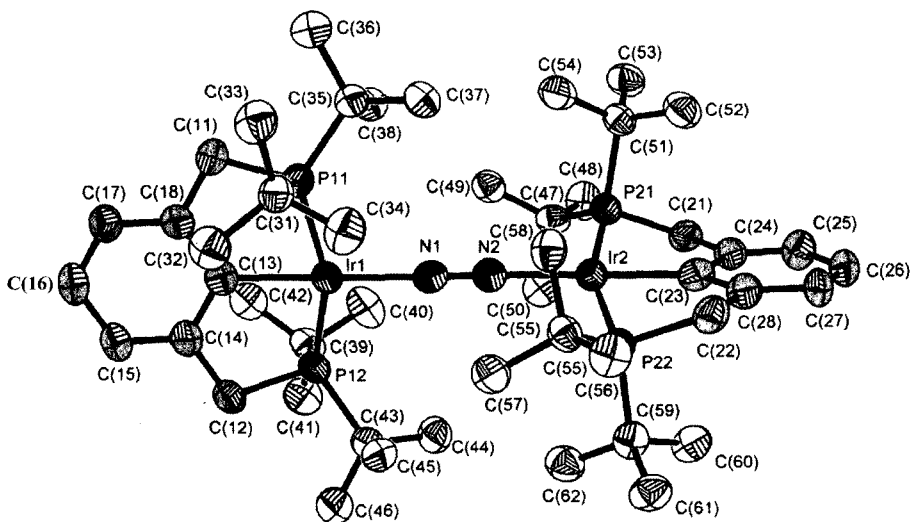
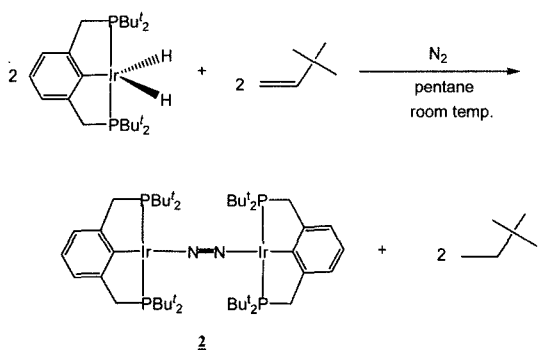


Fig. 2. Projection of $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}_2](\mu\text{-N}_2)$ (**2**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir(1)-C(13), 2.053(12); Ir(1)-P(11), 2.312(3); Ir(1)-N(1), 2.007(11); Ir(2)-N(2), 1.987(11); N(1)-N(2), 1.176(13); P(11)-Ir(1)-P(12), 160.22(10); N(1)-Ir(1)-C(13), 179.6(4); N(1)-Ir(1)-P(12), 98.6(2); Ir(1)-N(1)-N(2), 178.7(9). The hydrogen atoms are omitted for clarity.³⁴⁾



Scheme 3. Synthesis of dinitrogen PCP pincer complex (**2**).

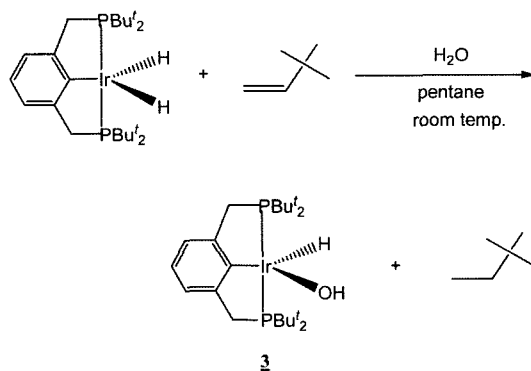
data. The molecular structure of **2** was elucidated through a single crystal X-ray structure determination. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table 1. A projection of the structure is seen in Fig. 2. The inclusion of a cyclohexane solvate is unusual. Recrystallization from methylcyclohexane also produces crystals containing a methylcyclohexane solvate. Solvate free material can be obtained by recrystallization from pentane solution. The dinitrogen ligand is bonded in linear, $\mu\text{-}\eta^1\text{:}\eta^1$ coordination mode. While not as common as the terminal, end-on coordination mode of dinitrogen, it is quite common for Group 4 and 5 metals.³⁸⁾ The nitrogen-nitrogen bond distance is 1.176(13) Å. This is significantly longer than the 1.0976(2) Å distance found in free N_2 ³³⁾ or the 1.134(5) Å N-N distance in the closely related Rh(I) dinitrogen complex, $[\text{RhH}(\text{PPr}'_3)_2](\mu\text{-N}_2)$.³⁹⁾ While this signifies a weakening of the nitrogen-nitrogen interaction, it is within the 1.12–1.20 Å range of dinitrogen (N_2)⁰ ligands rather than the 1.25–1.34 Å range of hydrazido (N_2)⁴⁻ ligands.^{38,40)} The dihedral angle between the planes defined by Ir(1), P(11), P(12) and Ir(2), P(21), P(22) is 89.5°.

Dinitrogen is typically a very weak binding ligand.⁴⁰⁻⁴²⁾ Several studies of alkane dehydrogenation using rhodium and iridium complexes as catalysts have been carried out a nitrogen atmosphere.^{6,23,24,28)} Thus, observations that even trace of nitrogen poisons all catalytic dehydrogenation activity of **1** even at 200°C were quite unexpected.¹⁸⁻²⁰⁾ The dinitrogen complex

2 was found to be completely inactive as a catalyst for alkane dehydrogenation. Thus the reaction of **1** with nitrogen to give **2** is apparently responsible for the suppression of catalytic activity. *A priori* it seems unlikely that a dinitrogen complex could have sufficient stability at 200°C to act as a thermodynamic sink. However, an explanation of this effect may be provided by the molecular structure which has been determined for **2**. The bridging nitrogen ligand is essentially encapsulated by nearly perpendicular pincer ligands. It is likely that this arrangement provides a kinetic stabilization of the dinitrogen ligand while preventing substrates from coordinating to the iridium centers. Thus, upon formation of **2** the iridium center is rendered unreactive with cycloalkanes and catalytically inactive.

Synthesis of $\text{IrH}(\text{OH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}'_2)\}$ (3**).**³⁵⁾ A red-purple pentane solution of the intermediate, $[\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}'_2)\}_2]$, becomes deep orange within a few minutes upon treatment with excess deoxygenated water under 1 atm of argon at 25°C as seen in Scheme 4. Deep orange crystals of the hydrido hydroxyl complex, $\text{IrH}(\text{OH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}'_2)\}$ (**3**), are obtained in nearly quantitative yield upon removal of solvent.

Complex **3** was characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy and its molecular structure was elucidated through a single crystal X-ray structure determination. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table 1. A projection of



Scheme 4. Synthesis of hydrido hydroxy PCP pincer complex (**3**).

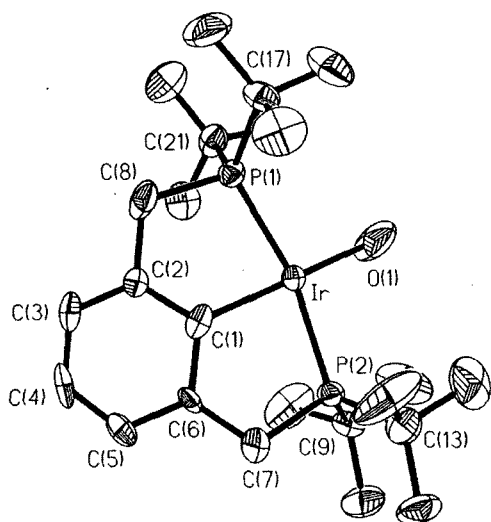


Fig. 3. Projection of $\text{IrH(OH)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (**3**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir-C(1), 2.01(2); Ir-O(1), 2.00(3); Ir-P(1), 2.304(4); P(1)-Ir-P(2), 166.9(2); C(1)-Ir-P(2), 83.9(5); O(1)-Ir-P(2), 95.3(7). The hydrogen atoms are omitted for clarity.³⁵⁾

the structure is seen in Fig. 3. The hydride ligand and the hydroxyl hydrogen could not be reliably located. The most intriguing structural feature is the Ir-O bond distance of 2.00(3) Å. This distance is significantly shorter than that found for the 18-electron iridium complex *cis*- $\text{IrH(OH)(PMe}_3\text{)}_4^+\text{PF}_6^-$ (2.119(5) Å).⁴³⁾ Similar variation in Ir-O bond distances has been noted for a pair of formally 16- and 18-electron iridium(III) alkoxide complexes (2.032 vs. 2.169 Å).⁴⁴⁾ Caulton has explained these differences in terms of $\text{O}\rightarrow\text{Ir}$ π -donation in the formally unsaturated complex. The molecular structure determined for **3** also provides evidence that such π -donation extends to late transition metal hydroxide complexes.

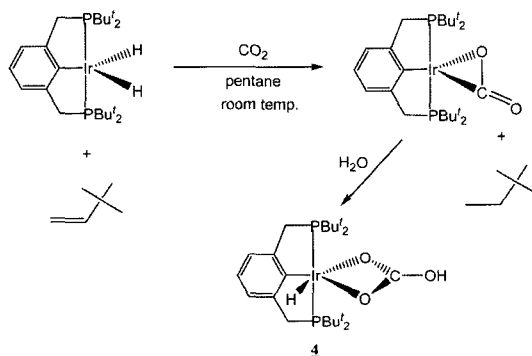
To our knowledge, complex **3** is the first example of a structurally characterized 16-electron transition metal hydrido hydroxyl complex. The spectroscopic data obtained for **3** are in accordance with the structure determined by X-ray diffraction and that reported for the closely related $\text{OsH(OH)(CO)(PPr}_3\text{)}_2$.⁴⁵⁾ Another interesting variation is provided by $\text{RhH(OH)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$, the rhodium analog of **3**. The

rhodium complex was prepared by the reaction of $\text{RhHCl}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ with NaOH rather than the oxidative addition of water as in this case of **3**. The presence of a hydroxide ligand in the resulting complex was inferred from the observations of an absorption in the infrared spectrum at 3300 cm^{-1} .

Syntheses of $\text{Ir}(\eta^2\text{-CO}_2)\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ and $\text{IrH}(\kappa^2\text{-O}_2\text{COH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (**4**).³⁶⁾

Treatment of a pentane solution of **1** with a 15 fold excess of the under 1 atm of carbon dioxide at 25°C yields a mixture of two complexes: the very air- and moisture-sensitive red-orange carbon dioxide complex, $\text{Ir}(\eta^2\text{-CO}_2)\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$, and the relatively air-stable pale yellow bicarbonato complex, $\text{IrH}(\kappa^2\text{-O}_2\text{COH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (**4**) as seen in Scheme 5. The product ratio is dependent upon the amount of water vapor present in the carbon dioxide. The initial product of this reaction is the $\eta^2\text{-CO}_2$ complex, $\text{Ir}(\eta^2\text{-CO}_2)\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$, which reacts with water to produce the bicarbonato complex **4**. Complex **4** is also obtained in good yield from the reaction of the hydrido hydroxyl complex **3** with carbon dioxide. Thus bicarbonato product is obtained regardless of the order of the carbon dioxide and water reaction sequence.

The $\eta^2\text{-CO}_2$ complex was characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy. Evidence for the presence of coordinated CO_2 is provided by the solid state infrared spectrum. Very strong absorptions are observed at 1756 and 1149 cm^{-1} , which



Scheme 5. Synthesis of bicarbonato PCP pincer complex (**4**).

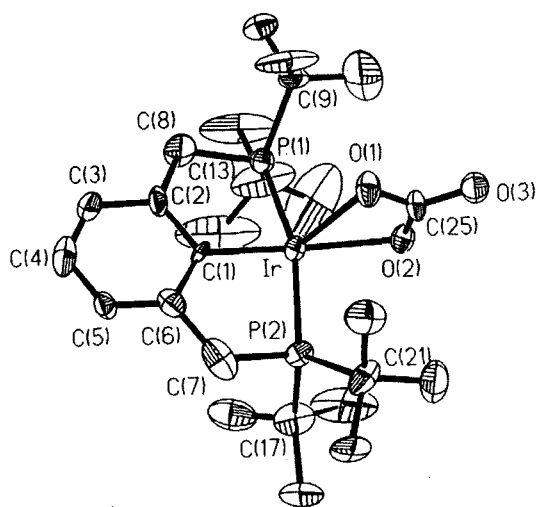
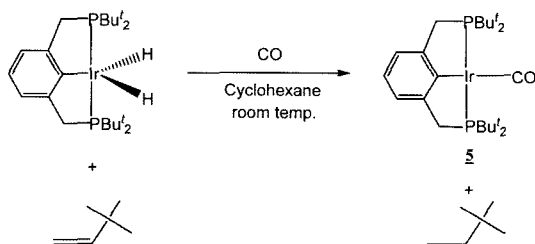


Fig. 4. Projection of $\text{IrH}(\kappa^2\text{-O}_2\text{COH})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**4**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir-C(1), 2.04(2); Ir-O(1), 2.358(12); Ir-O(2), 2.280(13); O(1)-C(25), 1.27(2); O(2)-C(25), 1.31(2); O(3)-C(25), 1.27(2); Ir-P(1), 2.321(5); Ir-P(2), 2.331(5); P(1)-Ir-P(2), 163.0(2); C(1)-Ir-P(1), 83.6(5); O(1)-Ir-O(2), 57.1(4); O(1)-C(25)-O(2), 118.0(14). The hydrogen atoms are omitted for clarity.³⁶⁾

correspond respectively to asymmetric and symmetric stretches of the carbonyl group. As seen in Scheme 4, the $\eta^2\text{-CO}_2$ complex reacts with water to give bicarbonato complex **4** which was characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy. The presence of bicarbonato ligand in **4** is supported by NMR and IR spectroscopic data. The resonance for the bicarbonate carbon is observed at 162.2 ppm in the ^{13}C NMR spectrum.

The molecular structure of **4** was elucidated through a single crystal X-ray structure determination as seen in Fig. 4. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table 1. The geometry around the iridium shows a distorted octahedron with a bicarbonato moiety in a plane perpendicular to the P-C-P 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 at the *trans* position to O(1). The pronounced *trans* influence of hydride is evi-



Scheme 6. Synthesis of carbonyl PCP pincer complex (**5**).

dent upon comparison of the Ir-O(1) and Ir-O(2) bond distance (2.36(1) vs. 2.28(1) Å). The bite angle of the bicarbonato group is 57.1(4)°, quite similar to that which has been found for related bicarbonato complexes.⁴⁶⁾

Synthesis of $\text{Ir}(\text{CO})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**5**).³⁷⁾

The treatment of a cyclohexane solution of dinitrogen complex **2** under 1 atm of carbon monoxide at 25°C gives the air-stable yellow-orange carbonyl complex, $\text{Ir}(\text{CO})\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ (**5**) in nearly quantitative yield within a minute as seen in Scheme 6. The corresponding aliphatic backbone pincer complex $\text{IrH}_4\{\text{HC}(\text{CH}_2\text{CH}_2\text{PBU}'_2)_2\}$ reacts with carbon monoxide to give a mixture of two isomers of a dihydrido monocarbonyl complex and dicarbonyl complex which were characterized by ^{31}P NMR spectroscopy.⁴⁷⁾ However, the rhodium analog of **1**, $\text{Rh}(\text{H}_2)\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2)_2\}$ gives only the corresponding monocarbonyl complex.⁴⁸⁾

The carbonyl complex **5** was characterized by ^1H , ^{13}C , ^{31}P NMR, and IR spectroscopy. A resonance for the carbonyl carbon appears at 197.6 ppm in the ^{13}C NMR spectrum. The infrared spectrum of **5** shows a carbonyl stretch at 1923 cm^{-1} . No hydride peak was observed in the ^1H NMR spectrum of **5**. The elemental analysis data for C and H are in accordance with calculated data.

The molecular structure of **5** was elucidated through a single crystal X-ray structure determination as seen in Fig. 5. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table 1. The geometry around the iridium metal is a slightly square plane. The carbon-oxygen bond distance (even though this showed

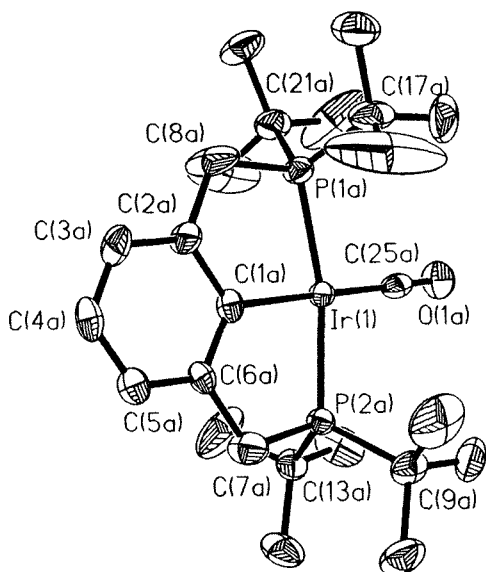
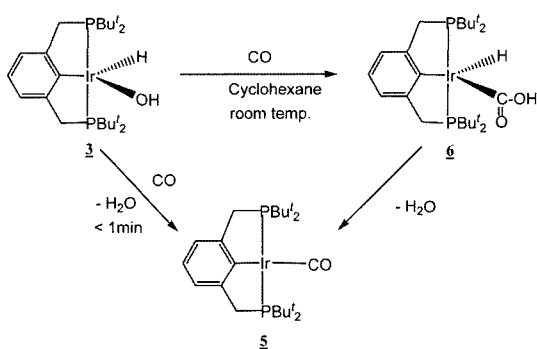


Fig. 5. Projection of $\text{IrH(CO)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (**5**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir(1)-C(1a), 2.102(8); Ir(1)-C(25a), 1.873(10); Ir(1)-P(1a), 2.298(2); Ir(1)-P(2a), 2.291(2); O(1a)-C(25a), 1.167(10); P(1a)-Ir(1)-P(2a), 164.51(8); C(1)-Ir-P(1), 83.6(5); C(1a)-Ir(1)-P(1a), 82.9(2); C(1a)-Ir(1)-C(25a), 178.1(3); Ir(1)-C(25a)-O(1a), 176.8(8). The hydrogen atoms are omitted for clarity.³⁷⁾

two different bond distances) is between triple (1.128 Å) and double (1.26(1) Å) bond distance.³³⁾ The bond distance (1.87(1) Å) between iridium and the carbon of carbonyl group is significantly short compared to that (2.10(1) Å) between iridium and carbon of aromatic ring. The bond C(1)-Ir-C(25)-O(1) is almost linear. There are two molecules containing some different orientations, which are responsible for the monoclinic (space group P2(1)/n) instead of the usual orthorhombic (space group Pbcu).

Synthesis of $\text{IrH(C(O)OH)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (6**).**³⁶⁾ The treatment of a cyclohexane solution of hydrido hydroxyl complex **3** under 1 atm of carbon monoxide at 25°C gives a mixture of two complexes: an air-stable yellow-orange carbonyl complex **5** (>80% yield) and an air-sensitive pale yellow carboxyl complex, $\text{IrH(C(O)OH)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\}$ (**6**) (<5% yield) as seen in Scheme 7. Hydrogen bonding and water interaction with **6** result in *trans*



Scheme 7. Reaction of hydrido hydroxy PCP pin-cer complex with CO.

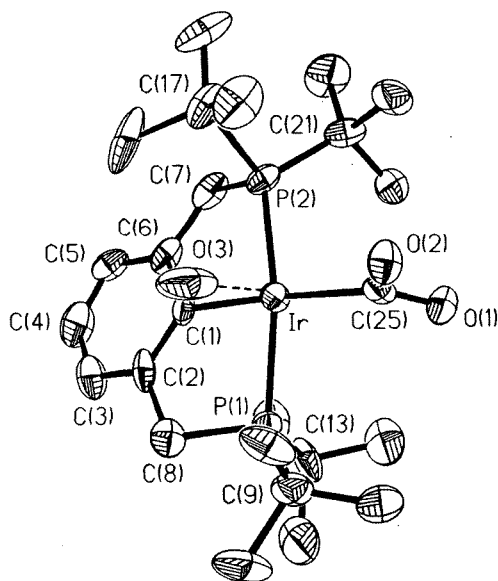


Fig. 6. Projection of $\text{IrH(C(O)OH)\{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}'_2\text{)}_2\} \cdot \text{H}_2\text{O}$ (**6·H}_2\text{O}**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir-C(1), 2.07(2); Ir-C(25), 2.10(2); Ir-P(1), 2.323(5); Ir-P(2), 2.291(6); Ir-O(3), 2.69(4); C(25)-O(1), 1.26(3); C(25)-O(2), 1.32(3); O(1)-O(2), 2.65(2); P(1)-Ir-P(2), 159.5(2); C(1)-Ir-C(25), 173.4(9); O(1)-C(25)-O(2), 116(2). The hydrogen atoms are omitted for clarity.³⁶⁾

and *cis* geometric isomers.

The carboxyl complex **6** was characterized by ¹H, ¹³C, ³¹P NMR, and IR spectroscopy. The carboxyl complex **6** shows resonances at 61.2 (major) and 65.1 (minor) ppm on the ³¹P NMR spectrum which correspond to the two geometric isomers. The molec-

ular structure of $6 \cdot H_2O$ was elucidated through a single crystal X-ray structure determination as seen in Fig. 6. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table 1. The short bond distance (2.66(2) Å) and between O(1a) and O(2b) or O(2a) and O(1b) indicates the strong hydrogen-bonding between hydrogen and oxygen of carboxylic groups of two molecules. The formation of **5** from **1** could result from the coordination of CO upon dehydrogenation of **1** by tbe. The carboxyl complex **6** could result from the insertion of carbon monoxide into hydrido hydroxyl complex **3**. Decarbonylation of the carboxyl group of **6** could give rise to an 18-electron carbonyl hydrido hydroxyl complex that could then undergo reductive elimination of water to give **5**. Another possibility is that the reductive elimination of water from **3** could precede CO coordination.

4. Summary

Jensen and coworkers found that the iridium PCP pincer complex, $IrH_2\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**1**), is highly active robust catalyst for the dehydrogenation of alkanes.^{18,19)} It was found that the reaction must be carried out under an argon atmosphere as even traces of nitrogen, carbon dioxide, and water act as catalyst poisons. In order to design an improved second generation catalyst, it was important to determine the origin of these inhibitive effects as well as catalytic mechanism. Reactions of the iridium PCP pincer complex with N_2 , H_2O , CO_2 , and CO were carried out. The products were isolated and their molecular structures were determined by a single crystal X-ray diffraction studies. The formations of the dinitrogen complex, $[Ir\{C_6H_3-2,6-(CH_2PBU'_2)_2\}]_2$ ($\mu-N_2$) (**2**), the hydrido hydroxyl complex, $IrH(OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**3**), the carbon dioxide complex, $Ir(\eta^2-CO_2)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (including the bicarbonato complex, $IrH(\kappa^2-O_2COH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**4**)), and the carbonyl complex, $Ir(CO)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**5**) (including the carboxyl complex, $IrH(C(O)OH)\{C_6H_3-2,6-(CH_2PBU'_2)_2\}$ (**6**)), are clearly responsible for the poisoning effects of nitrogen, water, carbon dioxide, and carbon mon-

oxide on the catalytic dehydrogenation activity of the dihydrido P-C-P pincer iridium complex **1**. The ability to isolate such species also foreshadows the development of new catalytic processes. This paper is thus an account of our contribution toward the quest for the "Holy Grail"⁴⁾ of the development of a transition metal complex catalyst for the selective transformation of alkanes to functionalized organic compounds.

References

- Hill, C. L., *Activation and Functionalization of Alkanes*, John Wiley, New York (1989).
- Shilov, A. E., *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Boston (1984).
- Davies, J. A., Watson, P. L., Leibman, J. F. and Greenberg, A., *Selective Hydrocarbon Activation*, VCH, Toledo (1990).
- Arndtsen, B. A., Bergman, R. G., Mobley, T. A. and Peterson, T. H., *Acc. Chem. Res.*, **28**, 154 (1995).
- All publications in *J. Organomet. Chem.*, **504**, 1-155 (1995).
- (a) Crabtree, R. H., Mihelcic, J. M. and Quirk, J. M., *J. Am. Chem. Soc.*, **101**, 7738 (1979). (b) Crabtree, R. H., Mellea, M. F., Mihelcic, J. M. and Quirk, J. M., *J. Am. Chem. Soc.*, **104**, 107 (1982).
- Janowicz, A. H. and Bergman, R. G., *J. Am. Chem. Soc.*, **104**, 352 (1982).
- Hoyano, J. K., McMaster, A. D. and Graham, W. A. G., *J. Am. Chem. Soc.*, **105**, 7190 (1983).
- Baudry, D., Ephritikhine, M. and Felkin, H., *Chem. Commun.*, 1243 (1980); 606 (1982); 788 (1983).
- Felkin, H., Fillebeen-Khan, T., Holmes-Smith, R. and Zakrzewski, J., *Tetrahedron Lett.*, **25**, 1279 (1984).
- Burk, M. W., Crabtree, R. H., Parnell, C. P. and Uriarte, R. J., *Organometallics*, **3**, 816 (1984).
- Felkin, H., Fillebeen-Khan, T., Holmes-Smith, R. and Lin, Y., *Tetrahedron Lett.*, **26**, 1999 (1985).
- Maguire, J. A. and Goldman, A. S., *J. Am. Chem. Soc.*, **113**, 6706 (1991).
- Maguire, J. A., Petrillo, A. and Goldman, A. S., *J. Am. Chem. Soc.*, **114**, 9492 (1992).

- 15) Miller, J. A. and Knox, L. K., *Chem. Commun.*, 1449 (1994).
- 16) Belli, J. and Jensen, C. M., *Organometallics*, **15**, 5551 (1996).
- 17) Braunstein, P., Chauvin, Y., Nahring, J., DeChian, A., Fischer, J., Tiripicchio, A. and Ugozzoli, F., *Organometallics*, **3**, 816 (1984).
- 18) (a) Gupta, M., Hagen, C., Flesher, R. J., Kaska, W. C. and Jensen, C. M., *Chem. Commun.*, 2083 (1996). (b) Jensen, C. M., *Chem. Commun.*, 2443 (1999).
- 19) (a) Gupta, M., Hagen, C., Kaska, W. C., Cramer, R. E. and Jensen, C. M., *J. Am. Chem. Soc.*, **119**, 840 (1997). (b) Liu, F., Pak, E. B., Singh, B., Jensen, C. M. and Goldman, A. S., *J. Am. Chem. Soc.*, **121**, 4086 (1999).
- 20) Gupta, M., Kaska, W. C. and Jensen, C. M., *Chem. Commun.*, 461 (1997).
- 21) Burk, M. W., Crabtree, R. H. and McGrath, D. V., *Chem. Commun.*, 1829 (1985).
- 22) Burk, M. W. and Crabtree, R. H., *J. Am. Chem. Soc.*, **109**, 8025 (1987).
- 23) Nomura, K. and Saito, Y., *Chem. Commun.*, 161 (1988); *J. Mol. Catal.*, **54**, 57 (1989).
- 24) Sakakura, T., Sodeyama, T. and Tanaka, M., *New J. Chem.*, **13**, 737 (1989).
- 25) Maguire, J. A., Boese, W. T. and Goldman, A. S., *J. Am. Chem. Soc.*, **111**, 7088 (1989).
- 26) Sakakura, T., Sodeyama, T., Abe, F. and Tanaka, M., *Chem. Lett.*, 297 (1991).
- 27) Fujii, T. and Satio, Y., *Chem. Commun.*, 757 (1990).
- 28) Fujii, T., Higashino, Y. and Satio, Y., *J. Chem. Soc., Dalton Trans.*, 517 (1993).
- 29) Aoki, T. and Crabtree, R. H., *Organometallics*, **12**, 294 (1993).
- 30) Xu, W.-W., Risini, G. P., Gupta, M., Jensen, C. M., Kaska, W. C., Krogh-Jespersen, K. J. and Goldman, A. S., *Chem. Commun.*, 2273 (1997).
- 31) Jacobs, M. Ed., *Chem. Eng. News*, **75**, 25 (1997).
- 32) Moulton, C. J. and Shaw, B. L., *J. Chem. Soc., Dalton Trans.*, 1020 (1976).
- 33) Gordon, A. J. and Ford, R. A., *Chemist's Companion*, John Wiley & Sons, New York (1972).
- 34) Lee, D. W., Kaska, W. C. and Jensen, C. M., *Organometallics*, **17**, 1 (1998).
- 35) Morales-Morales, D., Lee, D. W., Jensen, C. M. and Wang, Z., *Organometallics*, **20**, 1144 (2001).
- 36) Lee, D. W., Jensen, C. M. and Morales-Morales, D., *Organometallics*, **22**, 4744 (2003).
- 37) Morales-Morales, D., Redon, R., Wang, Z., Lee, D. W., Yung, C., Magnuson, K. and Jensen, C. M., *Can. J. Chem.*, **79**, 823 (2001).
- 38) (a) Hidai, M. and Mizobe, Y., *Chem. Rev.*, **95**, 1115 (1995). (b) Fryzuk, M. D., Love, J. B., Rettig, S. J. and Young, V. G., *Science*, **275**, 1445 (1997).
- 39) Yoshida, T., Okano, T., Thorn, D. L., Tulip, T. H., Otsuka, S. and Ibers, J. A., *J. Organomet. Chem.*, **181**, 183 (1979).
- 40) Chatt, J., Dilworth, J. R. and Richards, R. L., *Chem. Rev.*, **78**, 589 (1978).
- 41) Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G., *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, pp. 190-192 (1987).
- 42) Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*, 4th Ed., John Wiley & Sons, New York, pp. 440-446 (1994).
- 43) Milstein, D., Calabrese, J. C. and Williams, I. D., *J. Am. Chem. Soc.*, **108**, 6387 (1986).
- 44) Lunder, D. M., Lobkovsky, E. B., Streib, W. E. and Caulton, K. G., *J. Am. Chem. Soc.*, **113**, 1837 (1991).
- 45) Edwards, A. J., Elipe, S., Esteruelas, M. A., Lahoz, F. J., Oro, L. A. and Valero, C., *Organometallics*, **16**, 3828 (1997).
- 46) Yoshida, T., Thorn, D. L., Okano, T., Ibers, J. A. and Otsuka, S., *J. Am. Chem. Soc.*, **101**, 4212 (1979).
- 47) Errington, R. J. and Shaw, B. L., *J. Organomet. Chem.*, **238**, 319 (1982).