*Revista de la Sociedad Química de México, Vol.* **47***, Núm. 2 (2003) 124-126*

*Investigación*

# Reactivity of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ towards alkene compounds

Valente Gómez-Benítez, Rocío Redón, and David Morales-Morales*

Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, 04510 México D. F. *E-mail: damor@servidor.unam.mx (D. Morales-Morales)

*Dedicated to Dr. Alfonso Romo de Vivar*

Recibido el 22 de noviembre del 2002; aceptado el 20 de marzo del 2003

**Abstract.** The reactions of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ with ethylene and 1-octene have been carried out, products containing the olefin compounds coordinated in a $\eta^2$ fashion have been obtained. Both complexes have been characterized by multinuclear NMR probing unequivocally the proposed formulations. Examination of the thermal stability of both complexes under catalytic conditions shows the 1-octene adduct to be more stable.
**Keywords:** PCP pincer ligands, iridium complexes, olefin complexes, dehydrogenation, catalysis.

**Resumen.** Se llevaron a cabo reacciones del complejo $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ con etileno y 1-octeno, obteniéndose los derivados olefínicos coordinados de forma $\eta^2$. Ambos complejos fueron caracterizados por RMN multinuclear, probando las formulaciones propuestas. El examen de la estabilidad térmica de ambos complejos bajo condiciones catalíticas mostró que el aducto 1-octano es más estable.
**Palabras clave:** ligandos tipo pinza PCP, complejos de iridio, complejos olefínicos, deshidrogenación, catálisis.

## Introduction

Terminal alkenes (alpha-olefins) are a major feedstock for the production of plastics, detergents, and lubricants. Their production through the selective dehydrogenation of linear alkanes would be an attractive alternative to the present commercial processes based on hydrogen, ethylene, and trialkylaluminum catalysts.[1] The iridium PCP pincer complexes: $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PR_2)_2\}$ ($R$ = Bu$^t$, **1**; Pr$^i$, **2**) are extraordinarily active and robust catalysts for aliphatic dehydrogenation reactions.[2-5] Recent studies of this reactivity lead to the discovery of the first efficient catalytic system for the selective dehydrogenation of *n*-alkanes to alpha-olefins [6]. While this system serves to validate the concept of producing alpha-olefins through this method, it suffers from several practical limitations. The concentrations of the dehydrogenated products were found to quickly attain a low (1.5-4.0 %), constant value. Furthermore, the high selectivity for alpha-olefins was found to be short lived as the complexes show secondary catalytic activity for alkene isomerization and the alkene distribution rapidly shifted towards the internal isomers.[6] Finally, the requisite consumption of a stoichiometric amount of a sacrificial hydrogen acceptor used in the reported selective dehydrogenation of *n*-alkanes is economically and environmentally unattractive. Liu and Goldman had previously achieved the thermochemical dehydrogenation of linear alkanes by **2** without the use of a hydrogen acceptor. However, only internal alkenes were produced in their experiments [4].

As a part of our continuous interest in the reaction mechanism ruling in this process we have tried to identify the probable olefin intermediate species during the reaction, although some of these complexes are extremely reactive and short-lived, reactions with simple alkenes might shed light in both the initial stages of the olefin isomerization process and the deactivation of the catalyst by product inhibition reactions which have not yet been explored. Thus, in this paper we wish to present the results obtained from the reactions of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ with ethylene and 1-octene.

## Experimental

### Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware and Young NMR tubes. Solvents were degassed and dried using standard procedures. The $^1$H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent as internal standard (cyclohexane-$d_{12}$, $\delta$ 1.38). $^{13}$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-$d_{12}$, $\delta$ 26.45) and external 85 % $H_3PO_4$ respectively. Elemental analyses were determined on a Perkin-Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 Kv. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 KeV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. The 1-octene was purchased

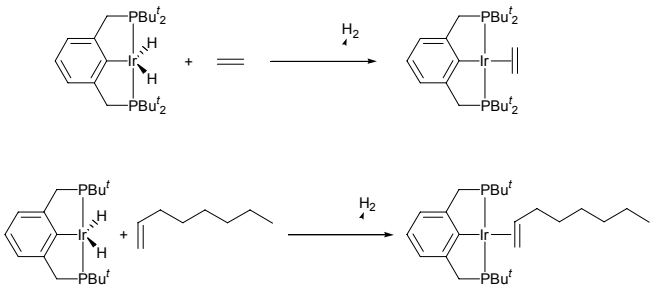
from Aldrich Chemicals Co. and used without further purification. The complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1**) was synthesized by the literature method [2].

**Synthesis of $Ir(\eta^2\text{-}CH_2{=}CH_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (3)**

A solution consisting of 5 mg ($8.5 \times 10^{-3}$ mmol) of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1**) and 1 mL of cyclohexane-$d_{12}$, was freeze-pump-thaw degassed 3 times. The solution was then treated with excess of ethylene at room temperature. An immediate change from orange to deep red-brown is observed. Removal of the solvent in vacuo affords $Ir(\eta^2\text{-}CH_2{=}CH_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ as a deep red-brown solid in nearly quantitative yield (based upon $^{31}$P NMR). $^1$H NMR (400.03 MHz, cyclohexane-$d_{12}$) $\delta$ = 1.253 (vt, $J_{HP}$ = 5.8 Hz, 36H, $PC(CH_3)_3$), 3.049 (vt, $J_{HP}$ = 3.2 Hz, 4H, $\mathbf{CH_2}PC(CH_3)_3$), 3.287 (s, 4H, $\mathbf{CH_2}{=}\mathbf{CH_2}$), 6.825 (t, $J_{HH}$ = 7.4 Hz, 1H, arom), 7.026 (d, $J_{HH}$ = 7.2 Hz, 2H, arom); $^{13}$C NMR (100.59 MHz, cyclohexane-$d_{12}$) $\delta$ = 178.28 (s, Ar**C**), 153.84 (vt, $J$ = 9.15 Hz, Ar**C**), 122.81 (s, Ar**C**), 119.77 (vt, $J_{PC}$ = 7.7 Hz, Ar**C**), 40.84 (vt, $J_{PC}$ = 13.53 Hz, $CH_2P$), 37.968 (s, $\mathbf{C}H_2{=}\mathbf{C}H_2$), 36.91 (vt, $J_{PC}$=8.4 Hz, $P\mathbf{C}(CH_3)_2$), 31.02 (s, $PC(\mathbf{C}H_3)_3$); $^{31}$P NMR (161.93 MHz, cyclohexane-$d_{12}$) $\delta$ = 54.68 (s, 1P). Anal calcd for $C_{26}H_{47}P_2Ir_1$ (613.82) C, 50.87 %; H, 7.72 %. Found: C, 50.76 %; H, 7.70 %.

**Synthesis of $Ir(\eta^2\text{-}CH_2{=}CH(CH_2)_5CH_3)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (4)**

$IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBut_2)_2\}$ (**1**) (5 mg, $8.5 \times 10^{-3}$ mmol) was dissolved in 1 mL of 1-octene, an immediate release of hydrogen was observed. A change in color from deep orange to bright yellow was also observed, the reaction was stirred at room temperature for further 5 min after this time the excess of 1-octene is evaporated under vacuo for 36 h to yield a $Ir(\eta^2\text{-}CH_2{=}CH(CH_2)_5CH_3)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ as a bright yellow microcrystalline powder in nearly quantitative yield (based upon $^{31}$P NMR). $^1$H NMR (400.03 MHz, cyclohexane-$d_{12}$) $\delta$ = 0.895 (bs, 10H, -($\mathbf{CH_2}$)$_n$-), 1.30 (bs, 36H, $PC(\mathbf{CH_3})_3$), 1.56 (bs, 3H, -$(CH_2)_n$-$\mathbf{CH_3}$), 2.00 (bs, 4H, $\mathbf{CH_2}PC(CH_3)_3$), 2.18 (bs, 2H, $C\mathbf{H_2}$=CH-R), 2.27 (s, 1H, $CH_2$=C**H**-R), 6.50 (t, $J_{HH}$= 7.3 Hz, 1H, arom), 6.64 (d, $J_{HH}$= 7.2 Hz, 2H, arom); $^{13}$C NMR (100.59 MHz, cyclohexane-$d_{12}$) $\delta$ = 150.0 (bs, Ar**C**), 148.0 (bs, Ar**C**), 122.8 (bs, Ar**C**), 121.0 (bs, Ar**C**), 32.79 (bs, $\mathbf{C}H_2P$), 32.40 (bs, $\mathbf{C}H_2{=}\mathbf{C}H$-R), 32.24 (bs, $P\mathbf{C}(CH_3)_2$), 30.29 (s, $P\mathbf{C}(CH_3)_3$), 23.42 (bs, -($\mathbf{CH_2}$)**n**-), 14.41 (bs, -$(CH_2)_n$-$CH_3$); $^{31}$P NMR (161.93 MHz, cyclohexane-$d_{12}$) $\delta$ = 54.97 (s, 1P). Anal calcd for $C_{32}H_{59}P_2Ir_1$ (697.98) C, 55.07 %; H, 8.52 %. Found: C, 54.94 %; H, 8.47 %.




**Scheme 1**

## Results and discussion

**Synthesis and characterization of $Ir(\eta^2\text{-}CH_2{=}CH_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (3) and $Ir(\eta^2\text{-}CH_2{=}CH(CH_2)5CH_3)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (4)**

The reaction of the PCP pincer complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**1**) with excess of ethylene or 1-octene affords complexes $Ir(\eta^2\text{-}CH_2{=}CH_2)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**3**) and $Ir(\eta^2\text{-}CH_2{=}CH(CH_2)_5CH_3)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ (**4**) as unique products (Scheme 1) in quantitative yields as red brown or bright yellow powders respectively. The $^1$H NMR spectrum of **3** clearly shows a singlet at 3.29 ppm corresponding to the ethylene molecule coordinated in a $\eta^2$ fashion to the metal center, moreover the fact that only one signal is observed for this molecule implies that is placed in a highly symmetrical environment. Besides the presence of the coordination of the ethylene, the signals corresponding to the presence of the PCP pincer ligand can also be clearly identified. Thus, a signal corresponding to the methyl groups in the $PC(\mathbf{CH_3})_3$ can be observed at 1.25 ppm. A virtual triplet due to the $CH_2$ group can be observed at 3.5 ppm, the multiplicity of the signal being due to the coupling of the protons on the $CH_2$ group with the phosphorous nuclei in $\mathbf{CH_2}PC(CH_3)_3$). A signal corresponding to the aromatic proton 4-H can be observed as a triplet centered at 6.83 ppm, while that corresponding to the aromatic protons 3,5-H is located at 7.03 ppm, no signals corresponding to the presence of metal-hydrides where detected at higher field. Analogously, signals in the $^1$H NMR spectrum of **4** corresponding to the presence of the 1-octene coordinated in a $\eta^2$ fashion can be observed as broad singlets in 2.18 and 2.27 ppm, other signals corresponding to the rest of the coordinated 1-octene molecule can be observed at 0.9 ppm for the -($\mathbf{CH_2}$)$_n$- groups and a broad singlet at 1.56 ppm which can be assigned to the terminal -$(CH_2)n$-$\mathbf{CH_3}$, signals due to the presence of the PCP pincer ligand can be observed at similar chemical shifts as those observed for the analogous complex with ethylene. As is the case for **3**, no signals for the presence of hydride ligands were detected at higher field.

The $^{13}$C NMR spectrum of **3** exhibits all the signals expected for the proposed formulation, it is noteworthy that the signal at 37.97 ppm corresponding to the coordinated ethylene is a singlet, thus the same conclusion regarding the molecule to be in a highly symmetrical environment can be deducted. The $^{13}$C NMR spectrum of **4** exhibits signals corresponding to the presence of the aliphatic moiety and the *tert*-butyl groups in the PCP pincer ligand as well as those for the

$CH_2$ directly coordinated to the P centers. It is noteworthy the presence of a signal at 32.40 ppm which evidences the presence of the coordinated olefin, the shift to higher field of this particular signal clearly illustrates the protecting effects of the aliphatic chain moiety in the case of the 1-octene adduct **4**.

In both cases, the $^{31}P$ NMR spectra shows a unique signal at 54.7 and 54.97 ppm for **3** and **4** respectively which is consistent with a *trans* configuration for both phosphorus nuclei in the two molecules. Elemental analysis are also consistent with the proposed formulations. The $FAB^+$-Mass spectra of **3** exhibits a peak at 585 M/z [$M^+$-$H_2C$=$CH_2$] corresponding to the loss of the ethylene molecule while that of **4** shows the molecular ion at [$M^+$ = 698 M/z].

Both complexes have been exposed to catalytic conditions where the reaction temperature reaches 200 °C, at this temperature the complex containing ethylene, releases the ethylene molecule which makes this complex an excellent candidate for further studies oriented to the possible functionalization of this molecule, however the complex containing the 1-octene it is resistant even at this temperatures, therefore it can be conclude that it is precisely this stability the problem (product inhibition) we have to go against in order to optimize the present system for the dehydrogenation process, other alternatives will involve the design of new ligands where electronic and steric factors could be tuned in such way that the elimination of the alkene molecule could be carried out easier and faster. Efforts aimed to achieve this goals are currently under investigation in our laboratory.

## Acknowledgements

V. G.-B. would like to thank CONACyT and DGAPA for financial support. We would like to thank Chem. Eng. Luis Velasco Ibarra and M. Sc. Francisco Javier Perez Flores for their invaluable help in the running of the FAB-Mass Spectra. The support of this research by CONACyT (J41206-Q) and DGAPA-UNAM (IN116001) is gratefully acknowledged.

## References

1. Behr, A. *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edn.; Elvers, B.,Hawkins, S., Russey, W., Eds.; VCH Verlagsgesellschaft: Weinheim, **1994**, pp 242-249.
2. (a) Gupta, M.; Hagen, C.; Kaska, W. C.; Flesher, R.; Jensen, C. M. *Chem. Commun.*, **1996**, 2083-2084. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, V.; Jensen, C. M. *J. Am. Chem. Soc.*, **1997**, *119*, 840-841. (c) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.*, **1997**, 461-462.
3. Xu, W. -W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C. Krough-Jespersen, K.; Goldman, A. S. *Chem. Commun.*, **1997**, 2273-2274.
4. Liu, F.; Goldman, A. S. *Chem. Commun.*, **1999**, 655-656.
5. Jensen, C. M. *Chem. Commun.*, **1999**, 2443-2449.
6. Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086-4087.