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Mechanistic Features of Iridium Pincer Complex Catalyzed Hydrocarbon Dehydrogenation Reactions: Inhibition upon Formation of a μ-Dinitrogen Complex

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Summary: Deuterium-labeling studies show that vinyl C−H oxidative addition of tert-butylethylene (tbe) to $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ *(**1**) is rapid and reversible, while the stoichiometric hydrogenation of tbe by **1** is slower and irreversible. The dinitrogen complex,* $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}]_2(\mu\text{-}N_2)$ *(**3**), results from the reaction of **1** with excess tbe under 1 atm of nitrogen. A single-crystal X-ray structure determination of **3** reveals a perpendicular arrangement of the P−C−P pincer ligands, which accounts for the surprising stability of **3** and the inhibiting effect of nitrogen on reactions catalyzed by **1**.*

The P−C−P pincer complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**1**) has been found to be a highly active and robust catalyst for the transfer dehydrogenation of cyclooctane to cyclooctene,[1] cycloalkanes to arenes,[2] tetrahydrofuran to furan,[3] and ethylbenzene to styrene.[3] Other iridium and rhodium hydride complexes including $IrH_5(PPr^i{}_3)_2$,[4,5] $IrH_2\{OC(O)CF_3\}(PPr^i{}_3)_2$,[6,7] $RhCl(EMe_3)_2(CO)$ ($E = P$,[8,9] As[10]), $RhCl(PMe_3)_2(PR_3)$,[9] $IrClH_2(PPr^i{}_3)_2$ (**2**),[11] and $Rh\{OC(Ph)CHPPh_2\}(CO)(PAr_3)$[12] also catalyze thermal transfer dehydrogenation of cyclooctane to cyclooctene. Despite the structural resemblance of these complexes, deuterium-labeling studies have revealed they react quite differently with the hydrogen acceptor *tert*-butylethylene (tbe).[11,13,14] Variation has also been found in the mechanism of alkane activation in the catalytic systems. Alkane oxidative addition to 14-electron intermediates arising upon complex dehydrogenation by tbe is thought to occur in several systems.[5,7,9,15] However, we have found evidence for the association of alkanes to the 16-electron neohexyl

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(1) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083.

(2) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.

(3) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1997**, 461.

(4) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279.

(5) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Lin, Y. *Tetrahedron Lett.* **1985**, *26*, 1999.

(6) (a) Burk, M. W.; Crabtree, R. H.; McGrath, D. V. *Chem. Commun.* **1985**, 1829. (b) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294.

(7) Burk, M. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.

(8) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706.

(9) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492.

(10) Miller, J. A.; Knox, L. K. *J. Chem. Soc., Chem. Commun.* **1994**, 1449.

(11) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532.

(12) Braunstein, P; Chauvin, Y.; Nahring, J.; DeChian, A.; Fischer, J.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1996**, *15*, 5551.

(13) Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488.

(14) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.

(15) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088.

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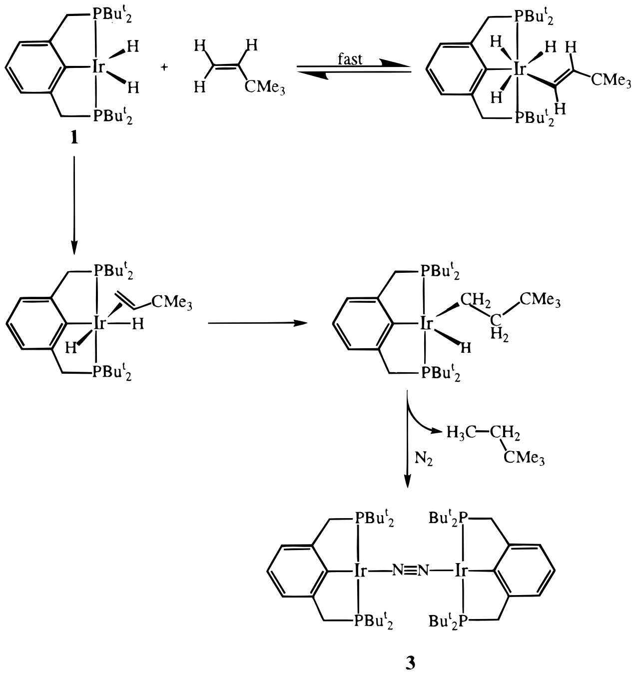
Scheme 1



intermediate resulting upon hydride migration to tbe coordinated to **2**.[11] It was, therefore, of interest to examine the reactivity of **1** with tbe. All of the dehydrogenation reactions catalyzed by **1** are inhibited by even traces of nitrogen gas.[1−3] In order to better understand this unusual nitrogen inhibition, we have examined the reaction of **1** with tbe both in the presence and absence of nitrogen. We report here the mechanistic details of the reaction of **1** with tbe as revealed by deuterium-labeling studies and the results of an X-ray crystal structure determination of $[\mathrm{Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}]_2(\mu\text{-}\mathrm{N_2})$ (**3**).

We have observed that **1** undergoes a number of reactions with tbe. The most facile process is the reversible oxidative addition of tbe vinyl C−H bonds, as shown in Scheme 1. This reaction was detected by dissolving $\mathrm{IrD_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}$ (**1**-d_2)[16] in neat tbe at 25 °C under an atmosphere of argon. The deuterium label was observed by ^{2}H NMR spectroscopy to be completely transferred to the trans α position of tbe within 10 min. The deuterium scrambling apparently results from the reversible oxidative addition of the α-vinyl C−H bonds of tbe to form a vinyl hydride. Deuterium incorporation exclusively into the α position of tbe from $\mathrm{IrH_5(PPr^i{}_3)_2/C_6D_6}$ was previously shown to involve the reversible oxidative addition of α-vinyl C−H bonds.[13] It is unclear whether these oxidative additions of the vinyl C-H bonds proceed through a π-alkene intermediate or an alternative mechanism, as observed for the oxidative addition of the vinyl C−H bonds of ethylene to $\mathrm{(C_5Me_5)Ir(PMe_3)}$.[17]

At longer reaction times (>1 h), **1** reacts with neat tbe at 25 °C under argon gas to give a stoichiometric amount of *tert*-butylethane (tba).[18] While coordination of tbe and subsequent hydride migration are also facile with the chloro complex **2**, the reductive elimination of tba from the resulting alkyl hydride complex requires the addition of an alkane and heating to 150 °C.[11] The high barrier to elimination of tba in the case of **2** renders the hydride migration step reversible, as demonstrated by the transfer of deuterium from $\mathrm{IrClD_2(PPr^i{}_3)_2}$ (**2**-d_2) to the β position of tbe.[11] No deuterium transfer is observed when **1** is dissolved in neat $\mathrm{H_2C{=}CDCMe_3}$, and exclusively β-labeled tba is produced.[19] Thus, hydride migration to coordinated tbe is irreversible. The subsequent elimination of tba is clearly a monomolecular process as no effect on the rate of tba production was found upon 4-fold dilution. It is possible that an agostic interaction with the *tert*-butyl methyl groups triggers tba elimination from the pincer complex. This hypothesis is supported by the observation of deuterium scrambling in the dideuterio complex, **1**-d_2. The exchange between the deuteride and *tert*-butyl methyl groups of the pincer ligand was apparent within 2 h of dissolving **1**-d_2 in cyclohexane at 25 °C.[19] In contrast, heating the dideuterio complex **2**-d_2 in toluene solution at 150 °C for 24 h does not result in transfer of the deuterium label to the isopropyl methyl groups of the phosphine ligands.[20] The ability of the phosphine alkyl groups of **1** to interact with the iridium center may eliminate the requirement of alkane association for tba elimination found for **2**[11] and partially account for **1** having a much higher activity for the catalytic transfer dehydrogenation of alkanes than **2**.

We have characterized the intermediate arising upon elimination of tba by ^{1}H and ^{31}P NMR spectroscopy.[21] The intermediate clearly contains the pincer ligand and no hydride. However, it is not possible to ascertain on the basis of this data whether the intermediate complex contains the only the pincer ligand (with or without a highly fluxional agostic interaction) or if it also contains rapidly exchanging tbe and/or solvent ligands. The intermediate is highly reactive, and all attempts to isolate it as a crystalline solid gave rise to a complicated mixture of unidentified products. Similar, highly reactive intermediates have recently been reported to result from the dehydrogenation of $\mathrm{IrFH_2(PBu^t{}_2Ph)_2}$ by ethylene.[22]

As seen in Scheme 1, a tractable product is obtained upon treatment of a cyclohexane solution **1** with a 15-fold excess of tbe under 1 atm of **nitrogen** at 25 °C. The dinitrogen complex $[\mathrm{Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}]_2(\mu\text{-}\mathrm{N_2})$ (**3**)[23] is produced in nearly quantitative yield within 1 h. The formation of **3** is evidently initiated by the reaction of nitrogen to the intermediate resulting upon the dehydrogenation of **1** by tbe as nearly 1 equiv of tba is produced in the reaction.[18] The molecular structure

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[16] The tetradeuterio complex $\mathrm{IrD_4\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}$ was prepared by allowing a pentane solution of $\mathrm{IrH_4\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}$[2] to stir for 1 h under 1 atm of deuterium gas. The dideuterio complex $\mathrm{IrD_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}}$ (**1**-d_2) was obtained by allowing the tetradeuterio complex to stand *in vacuo* for 48 h. The level of hydride deuteration was over 95% based on ^{1}H NMR.

[17] Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

[18] *tert*-Butylethane (tba) was identified and quantified by GC analyses performed on a temperature-programmed (45 °C isothermal for 1 min, 5 °C/min to 75 °C) Hewlett-Packard 5890 gas chromatograph using a 250 μm × 25 m OV-1 capillary column.

[19] The results of the deuterium-labeling experiments are based on ^{2}H NMR (60.4 MHz) spectroscopic analysis of the reaction mixtures.

[20] Belli, J. Ph.D. Thesis, University of Hawaii, 1997.

[21] ^{1}H NMR (400.032 MHz, cyclohexane-d_{12}) δ 6.94 (d, $J_{\mathrm{HH}} = 7.6$ Hz, 2H, *m*-H), 6.63 (t, $J_{\mathrm{HH}} = 7.6$ Hz, 1H, *p*-H), 3.39 (vt, $J_{\mathrm{PH}} = 4.8$ Hz, 4H,$\mathrm{C}H_2$), 1.27 (vt, $J_{\mathrm{PH}} = 6.0$ Hz, 36H, $\mathrm{C(C}H_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.9 MHz, cyclohexane-d_{12}) δ 70.6 (s).

[22] Cooper, A. C.; Folting, K.; Huffman, J. C.; Caulton, K. C. *Organometallics* **1997**, *16*, 505.

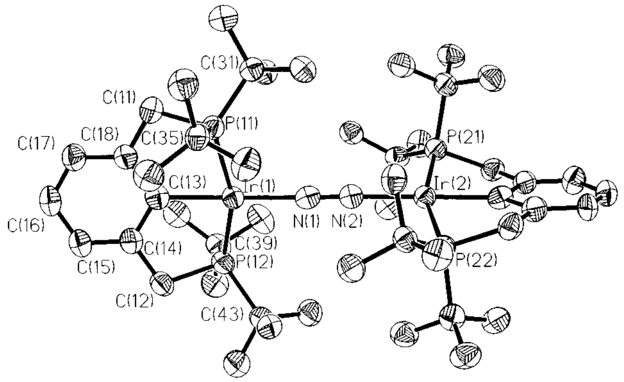

Figure 1. Projection of $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}]_2(\mu\text{-}N_2)$ (**3**) with the thermal ellipsoids at 25% probability. Selected bond distances (Å) and angles (deg): Ir(1)−C(13), 2.053(12); Ir(1)−P(11), 2.312(3); Ir(1)−N(1), 2.007(11); N(1)−N(2), 1.176(13); C(13)−Ir(1)−P(11), 78.6(3); P(11)−Ir(1)−P(12), 160.22(10); Ir(1)−N(1)−N(2), 178.7(9). The hydrogen atoms are omitted for clarity.

of **3** was elucidated through a single-crystal X-ray structure determination.[24] A projection of the structure and selected bond distances and angles are presented in Figure 1. The linear, μ-η^1: η^1 coordination mode of the dinitrogen is well-known, although more common for group 4 and 5 metals.[25] 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[26] or the 1.134(5) Å N−N distance in the closely related Rh(I) dinitrogen complex $[RhH(PPr^i_3)_2]_2(\mu\text{-}N_2)$.[27] 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.[25,28] The dihedral angle between the planes defined by Ir(1), P(11), P(12) and Ir(2), P(21), P(22) is 89.5°. This nearly perpendicular arrangement results in the encapsulation of the nitrogen ligand and is apparently responsible for the surprising stability of **3** and the pronounced inhibiting effect of nitrogen on the catalytic reactions.

We have found that the unusual N_2 inhibition of the catalytic activity of **1** is due to the formation of a dinitrogen complex which is stabilized by encapsulation in the bis(P−C−P pincer) complex. Our results suggest that the high activity of **1** as a hydrocarbon dehydrogenation catalyst may be in part due to “agostic promotion” by the pendent *tert*-butyl methyl groups.

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Supporting Information Available: Tables of crystal data, thermal parameters, bond distances, bond angles, and atomic coordinates for complex **3** (9 pages). Ordering information is given on any current masthead page.

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[23] For **3**: ^{1}H NMR (400.032 MHz, methylcyclohexane-d_{14}) δ 6.75 (d, J_{HH} = 8.8 Hz, 2H, *m*-H), 6.49 (t, J_{HH} = 7.3 Hz, 1H, *p*-H), 3.13 (vt, J_{PH} = 3.7 Hz, 4H, CH_2), 1.27 (vt, J_{PH} = 5.9 Hz, 36H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.595 MHz, cyclohexane-d_{12}) δ 166.65 (s, C-1), 154.33 (vt, J_{PC} = 11.9 Hz, *o*-C), 124.12 (s, *p*-C), 120.31 (vt, J_{PC} = 9.15 Hz, *m*-C), 37.48 (vt, J_{PC} = 13.7 Hz, CH_2), 36.70 (vt, J_{PC} = 10.1 Hz, $C(CH_3)_3$), 30.08 (two vt, J_{PC} = 20.1 Hz, $C(CH_3)_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, cyclohexane-d_{12}) δ 72.9 (s); IR(KBr) ν_{NN} = 2078 cm^{-1}. Anal. Calcd for $C_{48}H_{86}Ir_2N_2P_4$: C, 48.07; H, 7.23; N, 2.33. Found: C, 47.95; H, 7.33; N, 2.40.

[24] Orange crystals of $\mathbf{3}\cdot(C_6H_{12})_{1.5}$ were obtained from slow evaporation of 1:1 cyclohexane: methylcyclohexane: triclinic $P1$, $Z = 2$, $a =$ 14.428(10) Å, $b =$ 14.639(5) Å, $c =$ 16.702(11) Å, $\alpha =$ 71.780(10)°, $\beta =$ 75.590(10)°, $\gamma =$ 68.950(10)°, $V =$ 3090(3) Å^3; 614 parameters were refined on 4803 reflections having $I > 2\sigma(I)$; R (R_w) = 4.85% (11.88%), GOF = 1.073. The finding of the unusual cyclohexane solvate in the crystals was unexpected and noteworthy.

[25] Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

[26] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, **1972**; p 107.

[27] Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183.

[28] Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.