Communications to the Editor

Mild, Reversible C–H Oxidative Addition/Reductive Elimination in a Dinuclear Iridium Complex

William D. McGhee and Robert G. Bergman*

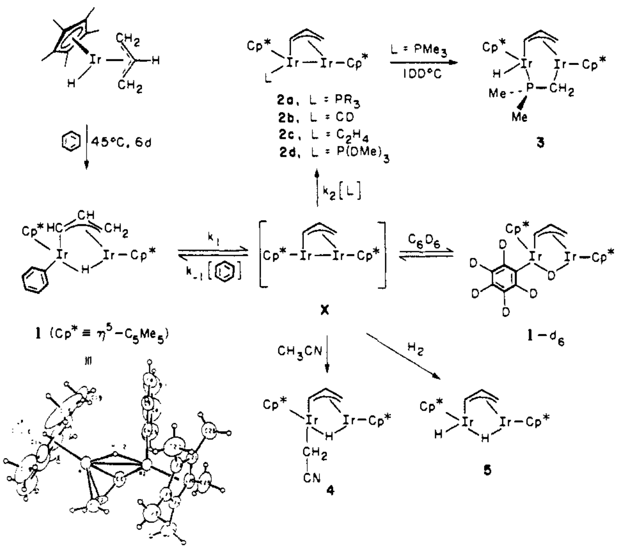
Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Received March 21, 1986

Several mononuclear systems have been found in which single metal centers undergo intermolecular insertion into carbon–hydrogen bonds.[1] Because of the small number of dinuclear analogues, however,[2] little is yet known about the effect of a second, adjacent metal center on the C–H oxidative addition process. The reverse reaction, dinuclear C–H reductive elimination, has also been identified in only a very few cases.[3] We wish to report here a dinuclear complex (iridium complex **1** in Scheme I) which undergoes thermal, *reversible* C–H oxidative addition/reductive elimination. These reactions involve both sp^2- and sp^3-hybridized C–H bonds (H_2 can also be used) and take place under surprisingly mild conditions compared to those which occur in the analogous mononuclear iridium systems.[1g]

Heating a 1 M solution of Cp*(η^3-allyl)hydridoiridium (Cp* = η^5-pentamethylcyclopentadienyl; cf. Scheme I)[4] in benzene for 6 days at 45 °C gave an orange-brown solution. Concentration of this reaction mixture followed by crystallization from hexane[5] gave typically 60% yields of a pure material analyzing properly for $C_{29}H_{40}Ir_2$. In the solid-state infrared spectrum (KBr pellet) no evidence for a terminal hydride appears (2200–1800 cm^{-1}) and in the ^{1}H NMR the hydride resonance appears at −20.5 ppm.[6] This and other spectroscopic information suggested structure **1** for this material, having a hydride ligand bridging the two iridium atoms. To confirm this, a single-crystal X-ray structure determination was performed. An ORTEP diagram of **1** is included in Scheme I; details of the structure are provided as supplementary material.[7] The hydride ligand was located and determined to be in a position bridging the two iridium centers with Ir–H distances of 1.74 (6) and 1.78 (6) Å; the iridium–iridium distance is 2.867 (1) Å. Similar complexes with μ-η^1,η^3-allyl moiety are well-known in the literature and several structure determinations have been carried out.[8] Bridging hydrides that also contain aryl or alkyl ligands, however, are rare.[9]

Scheme I



Complex **1** loses benzene upon the addition of PMe_3, $P(OCH_3)_3$, CO, or ethylene, resulting in the formation of **2**. The material also exchanges benzene reversibly. Heating a C_6D_6 solution of **1** to 45 °C for 2 h resulted in the 60% conversion to **1**-d_6 as shown by ^{1}H NMR, ^{2}H NMR, and mass spectroscopy. Complete exchange occurred in quantitative yield (ferrocene internal standard) after heating to 45 °C for 8.5 h. Analogous reductive elimination of ethylene from dinuclear hydridovinylrhenium complexes upon the addition of dative two-electron ligands has been observed by Brown's group.[2a,b] It was hoped that the unsaturated intermediate generated thermally from **1** would also oxidatively add sp^3-hybridized carbon–hydrogen bonds. Upon heating **1** to 45 °C in pentane for 16 h no reaction occurred and **1** was recovered unchanged. However, heating **1** to 50 °C in a

---

(1) For reviews, see: (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (b) Parshall, G. W. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Specialist Periodical Reports, Vol. 1, p 335. (c) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283. (d) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (e) Shilov, A. E. *Activation of Saturated Hydrocarbons Using Transition Metal Complexes*; D. Riedel: Dordrecht, 1984. (f) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (g) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902.

(2) See, for example: (a) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (c) *Ibid.* **1984**, *106*, 644. (d) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185 and references cited there.

(3) For recent examples, see: (a) Kellenberger, B.; Young, S. J; Stille, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6105. (b) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(4) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388.

(5) Complexes **1**, **2a–d**, and **3–5** have been characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR (where applicable), IR, mass spectroscopy, UV spectroscopy, and microanalysis. Details are provided as supplementary information.

(6) For (η^5-pentamethylcyclopentadienyl)(η^3-allyl)iridium hydride: ^{1}H NMR (Ir–H) δ −16.7; IR (Ir–H) 2095 cm^{-1}.

(7) The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of most of the hydrogen atoms were found. The hydride hydrogens and those on the allyl moiety were included in subsequent refinements with isotropic thermal parameters. Crystal data for **1** at −45 °C: space group $P\bar{1}$; a = 11.3383 (27) Å, b = 14.3940 (20) Å, c = 16.7212 (27) Å; α = 92.668 (12)°, β = 92.351 (17)°, γ = 105.783 (16)°, V = 2619.1 (17) A^3; Z = 4; d_c = 1.96 g cm^{-1}; μ_{calcd} = 101.3 cm^{-1}. A total of 6811 unique reflections were collected, the final residuals for which 600 variables refined against 5177 data for which $F^2 > 3\sigma F^2$ were R = 2.48%, R_w = 3.37%, and GOF = 1.589.

(8) (a) Barker, G.; Carroll, W. D.; Green, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1071. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *Ibid.* **1980**, 803. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *Ibid.* **1980**, 547. (d) Levisalles, J.; Rudler, H.; Dahan, F.; Jeannin, Y. *J. Organomet. Chem.* **1980**, *188*, 803. (e) Levisalles, J.; Rose-Munch, F.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1981**, 152. (f) Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Rove, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *Ibid.* **1981**, 537. (g) Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J.; Dromzee, Y.; Jeannin, Y.; Ades, D.; Fontanille, M. *Ibid.* **1981**, 1055. (h) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269. (i) Muller, J.; Passon, B.; Pickardt, J. *J. Organomet. Chem.* **1982**, *236*, C11. (j) Colborn, R. E.; Dyke, A. F.; Knox. S. A. R.; MacPherson, K. A.; Orpen, A. G. *Ibid.* **1982**, *239*, C15. (k) Rudler, H.; Rose, F.; Rudler, M.; Alvarez, C. *J. Mol. Catal.* **1982**, *15*, 81. (l) Adams, P. Q.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 222. (m) Bott, S. G.; Connelly, N. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Paxton, J. F.; Schaverien, C. J. *Ibid.* **1983**, 378. (n) Green, M.; Orpen, A. G.; Schaverien, C. J.; Williams, I. D. *Ibid.* **1983**, 1399. (o) King, J. A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846. (p) Green, M.; Orpen, A. G.; Schaverien, C. J.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 583. (q) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans* **1984**, 1563. (r) Jeffery, J. C.; Moore, I.; Stone, F. G. A. *Ibid.* **1984**, 1571. (s) Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. *Ibid.* **1984**, 1581.

(9) For a diplatinum complex see: Bracher, G.; Grove, D. M.; Venanzi, L. M; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778.

0002-7863/86/1508-5621$01.50/0

1:10 mixture of acetonitrile/THF resulted in the clean formation of **4** in 64% isolated yield. Heating **1** to 50 °C under 600 torr of dihydrogen in pentane for 16 h gave dinuclear dihydride **5** in 80% isolated yield.

The isolation of **2a–c** enabled us to explore the possibility of regenerating the C–H activating intermediate (presumably complex X shown in Scheme I) by dissociation of a dative ligand from a dinuclear complex. In hopes of converting **2a** to X, the trimethylphosphine adduct was heated to 100 °C for 11.5 h in benzene. However, conversion back to **1** was not observed. Instead, intramolecular C–H insertion occurred, giving a mixture of two new organometallic complexes in a ratio of 10:1. The major product obtained was isolated in 52% yield, analytically pure after two crystallizations from toluene/hexane.[10] On the basis of spectral and analytical data[5] the new product is formulated as the diiridium complex **3** having a terminal hydride and bridging (CH_2PMe_2) ligand. Complex **3** arises from formal intramolecular oxidative addition of the C–H bond of the bound trimethylphosphine across the Ir–Ir bond; complexes having a μ-CH_2PMe_2 ligand are rare.[11]

Because of the intramolecular reaction observed with **2a**, generation of X from carbonyl complex **2b** was investigated. Heating to 165 °C gave no reaction in C_6D_6, but irradiation of **2b** in benzene-d_6 resulted in the generation of **1**-d_6 in 53–60% yield by ^{1}H NMR (ferrocene internal standard). Surprisingly (especially in view of the behavior of Brown's rhenium system[2a,b]), **2c** exhibits chemistry paralleling that of **2b**, with no addition to the C–H bonds of ethylene observed. Irradiation of **2c** in benzene-d_6 gave **1**-d_6 in 40–53% yields (ferrocene internal standard) along with several unidentified minor compounds.

Preliminary mechanistic information on the elimination of benzene from **1** has been obtained from crossover isotope labeling and kinetic studies. The crossover experiment was carried out by heating a 1:1 mixture of **1** and **1**-d_{10} (phenyl and allyl groups completely deuterated; prepared as described above using C_6D_6 in place of C_6H_6)[12] to 50 °C in pentane with added ethylene for 2.25 h. Only C_6D_6 and C_6H_6 were obtained from the volatile materials as determined by GC/mass spectroscopy, demonstrating that the benzene C–H reductive elimination reaction (and therefore, by the principle of miroscopic reversibility, the corresponding oxidative addition reaction) is cleanly intramolecular. Kinetic studies were carried out by following reactions of **1** in the presence of various ligands by ^{1}H NMR and UV spectroscopy. Clean pseudo-first-order kinetics were observed, providing the following data at 45 °C: $k_{obsd}(C_6D_6) = 1.50 \times 10^{-4}\ s^{-1}$; k_{obsd} (PMe_3, *n*-hexane) $= 2.41 \times 10^{-4}\ s^{-1}$; no dependence on [$PMe_3$]; $k_{obsd}(P(OCH_3)_3; C_6D_{12}) = 1.65 \times 10^{-4}\ s^{-1}$. The isotope data and minimal influence of concentration or identity of entering ligand on k_{obsd} require intramolecular, rate-determining elimination of benzene to form an intermediate (presumably X in Scheme I). This is then followed by attack of ligand in a subsequent step.[13]

Complex **1** can be related conceptually to the analogous mononuclear hydrido phenyl complex, $Cp^*(PMe_3)Ir(Ph)(H)$, by replacing the phosphine group with a second iridium moiety and allowing the hydride to bridge both metal centers. Perhaps the most striking feature of the binuclear system is the fact that the temperature for reductive elimination of benzene from **1** is *at least* 150 °C lower than that required for the corresponding reductive elimination from the mononuclear complex, which is stable to nearly 200 °C.[14] We do not yet know whether the primary reaction step involves interaction of the C–H bond with one or two metal centers. Whatever the precise reaction mechanism, however, our results make it clear that a second metal attached to a center capable of C–H activation can have a profound effect on the energetics of the insertion process. On the basis of the results described here it seems reasonable to expect that attachment of other metals will retain this energetic effect but also return the ability of the iridium center to react with alkanes. We hope to be able to test this hypothesis in the near future.

Acknowledgment. This work was carried out under the auspices of a collaborative Lawrence Berkeley Laboratory/Industrial research project supported by the Chevron Research Co., Richmond, CA, and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. W.D.M. acknowledges the Organic Division of the American Chemical Society for a predoctoral fellowship. We are also grateful for a generous loan of $IrCl_3 \cdot nH_2O$ from Johnson-Matthey, Inc. The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at UC Berkeley X-ray crystallographic facility (CHEXRAY).

Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **1**-d_{10}, **2a–c**, and **3–5** and details of the structure determination of complex **1**, including experimental description, ORTEP drawings showing full atomic numbering scheme, crystal and data collection parameters, general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and intramolecular distances and angles (23 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

---

(10) The minor product was also isolated and characterized as $Cp^*(\eta^2$-$Me_2P{=}CH_2)Ir(\mu$-$CH{=}CHMe)IrCp^*$. Its formation will be discussed in a full account of this work.

(11) (a) See, for example: Graimann, C. E.; Green, M. L. H. *J. Organomet. Chem.* **1984**, *275*, C12. (b) Klein, H.-F.; Wemninger, J.; Schubert, J. *Z. Naturforsch, B* **1979**, *34B*, 1391. (c) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601. As pointed out by a referee, the formation of **3** suggests that both iridium atoms may be independently capable of C–H oxidative addition.

(12) **1**-d_{10} was characterized by ^{1}H NMR, ^{2}H NMR, and mass spectrometry.

(13) Preliminary isotope effect data suggest that a second intermediate (possibly an η^2-arene complex; cf.: Feher, F. J.; Jones, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1650) may intervene between **1** and X. This possibility will be discussed in a full paper.

(14) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *Ibid.* **1986**, *108*, 1537.

Rapid Measurement of Less Abundant and Low-γ Spin-$^1/_2$ Nuclei: $\delta(^{57}Fe)$, $^1J(^{57}Fe,^1H)$, and $^1J(^{57}Fe,^{31}P)$ from Reverse 2D $^1H\{^{57}Fe\}$ Spectroscopy

Reinhard Benn*

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-4330 Mülheim a. d. Ruhr, West Germany

Christian Brevard*

Laboratoire d'Applications, Bruker Spectrospin
F-67160 Wissembourg, France

Received March 31, 1986

Beside ^{187}Os the ^{57}Fe isotope is the most insensitive spin-$^1/_2$ nucleus in NMR spectroscopy,[1] and despite the extensive chemistry involving iron,[2] ^{57}Fe NMR studies of iron complexes are still rare.[1] Among the approaches made to improve the NMR detection of ^{57}Fe NMR parameters are isotopic enrichment of ^{57}Fe,[3] the application of steady-state techniques,[4] and the use of high magnetic

---

(1) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981. Benn, R.; Rufińska, A. *Angew. Chem.*, in press, and references cited. While the ^{3}He nucleus is even more insensitive, this isotope has received no attention in chemistry.

(2) Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. 1, 1981; Vol. 2.

(3) Koridze, A. A.; Petrovskii, P. V.; Gubin, S. P.; Fedin, E. I. *J. Organom. Chem.* **1975**, *93*, C26. Koridze, A. A.; Astakhava, N. M.; Petrovskii, P. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1982**, 956; **1982**, 957.

0002-7863/86/1508-5622$01.50/0