Å, and 143.3°, respectively. The equivalent distances and angle in the tetrahydrofuran complex are 2.663 ± 0.011 Å, 2.37 Å, and 143.5°, respectively. The C(1)C(2) and averaged C–C(Me) distances in the complex are 1.154 (6) and 1.468 ± 0.005 Å, respectively. The equivalent distances in free 2-butyne (−50 °C) are 1.21 (2) and 1.46 (1) Å, respectively.[10] The averaged C–C–C(Me) angle in the complex is 177.4 ± 0.7° and the equivalent angle in the free ligand is linear. Comparison of the C–C distance and the C–C–C(Me) angle in $(Me_5C_5)_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$ with the equivalent bond parameters in *trans*-$[MePt(PMe_2Ph)_2(\eta^2\text{-}MeC{\equiv}CMe)]PF_6$[11a] and $(Ph_3P)_2Pt(\eta^2\text{-}MeC{\equiv}CPh)$[11b] in which the C–C distance is 1.22 (3) and 1.28 (3) Å and the C–C–C(Me) angle is 168 ± 2° and 141.8(1.8)°, respectively, shows that little or no π-back-bonding is involved in the ytterbium–acetylene bond. The averaged Yb–C(1,2) distance is 2.850 ± 0.010 Å and the C(1)–Yb–C(2) angle is 23.4 (1)°. The dihedral angle formed by intersection of the plane defined by C(1,2,3,4) and Yb with the plane defined by the Me_5C_5 ring centroid–Yb–Me_5C_5 ring centroid is 91.5°. Clearly the 2-butyne to $(Me_5C_5)_2Yb$ interaction is weak as judged by spectroscopic and crystallographic data. The complex is best viewed as a Lewis acid–base adduct with little or no π-back-bonding.

Acknowledgment. We thank the Fannie and John Hertz Foundation for a fellowship (C.J.B.) and Dr. F. J. Hollander for his help with the X-ray crystallography. This work was supported by the Director, Office of Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract DE-AC03-76SF0098.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

---

(10) Pignataro, E.; Post, B. *Acta Crystallogr.* **1955**, *8*, 672-674.

(11) (a) Davies, B. W.; Payne, N. C. *Can. J. Chem.* **1973**, *151*, 3477-3485. (b) Davies, B. W.; Payne, N. C. *J. Organomet. Chem.* **1975**, *99*, 315-328.

Activation of C–H Bonds with Intermediates Produced by Mild Thermal and Photochemical Decomposition of the Metallacycle $(\eta^5\text{-}C_5Me_5)\overline{Ir[C(p\text{-}ClC_6H_4)=NOC(=O)]}(CO)$ in Hydrocarbon Solvents

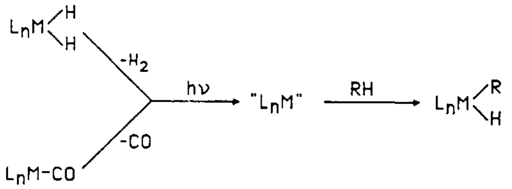
Peter A. Chetcuti and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California—Los Angeles
Los Angeles, California 90024

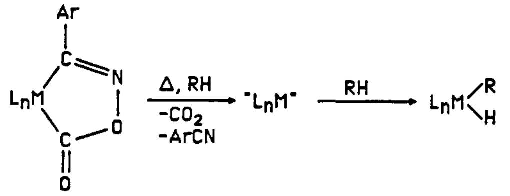
Received July 24, 1986

In recent years a number of transition-metal complexes have been found to undergo photochemically induced intermolecular C–H bond activation of their hydrocarbon solvents.[1–6] The aryl and alkyl metal hydride products of these reactions are believed to result from the oxidative addition of the 16-electron coordinatively unsaturated metal fragments, "ML_n", generated by the photolytically induced loss of H_2 or CO, into the C–H bonds of hydrocarbons (Scheme I). Insertion into C–H bonds also occurs with thermal activation, suggesting that these reactions do not specifically require the reactive metal fragment to be in a photoexcited state.[1a,4,7–18] A preponderance of the previously reported examples of thermal C–H bond activation, in which the products of direct oxidative addition are observed, involve the reductive elimination of the reactive species, ML_n, from an alkyl or aryl metal hydride followed by its oxidative addition into the C–H bond of another hydrocarbon.[1b,4,7–9,15–18] In effect, these reactions require as a reactant a metal center which has already undergone C–H activation into a C–H bond and constitute hydrocarbon exchange reactions.

Scheme I



Scheme II



We now wish to report the thermal activation of C–H bonds of hydrocarbons using the precursor metallacycle $(\eta^5\text{-}C_5Me_5)\overline{Ir[C(p\text{-}ClC_6H_4)=NOC(=O)]}(CO)$ (**1**).[19,20] Thermolysis of **1** would be expected to generate the 16-electron four-coordinate species "$(\eta^5\text{-}C_5Me_5)Ir(CO)$" (Scheme II) which is presumed to be responsible for the activation of a number of hydrocarbons when generated photolytically from $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[2] When the metallacycle **1** was maintained in the dark at 50 °C in benzene solution for 5 weeks, a hydride resonance at −15.07 ppm was observed and attributed to the product $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_5)$[2a] (**2**), formed by the oxidative addition of $(\eta^5\text{-}$

---

(1) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (c) Wenzel, T. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

(2) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

(3) Prelana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508.

(4) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(5) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950.

(6) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870.

(7) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121.

(8) Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

(9) Watson, P. A. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

(10) Watson, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

(11) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243.

(12) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.

(13) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

(14) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816.

(15) Fendrick, C. M.; Marks, T. M. *J. Am. Chem. Soc.* **1986**, *10*,, 425.

(16) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

(17) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843.

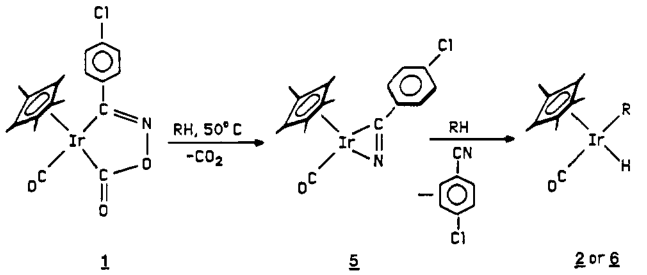
(18) (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073. (b) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080. (c) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

(19) We have synthesized a number of metallacycles by cycloaddition of aryl nitrile *N*-oxides with low-valent metal carbonyl complexes. A preliminary paper has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370) and a complete report will be submitted shortly.

(20) Selected data for **1** (full details will be reported elsewhere[19]). **1**: Anal. Calcd for $C_{19}H_{19}ClIrNO_3$: C, 42.57; H, 3.58; Ir, 35.85; N, 2.61. Found: C, 42.12; H, 3.64; Ir, 35.88; N, 2.40. ^1H NMR (C_6D_6) δ 7.39 (d, 2 H, *J* = 8.5 Hz), 7.10 (d, 2 H, *J* = 8.4 Hz), 1.23 (s, 15 H).

0002-7863/87/1509-0942$01.50/0

Scheme III



$C_5Me_5)Ir(CO)$ into the C–H bonds of benzene;[21] addition of CCl_4 converted **2** to the known $(\eta^5\text{-}C_5Me_5)Ir(CO)(Cl)(C_6H_5)$[22,2a] (**3**) in 90.4% overall yield while the known dimer $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)]_2$ (**4**),[23] identified by its ^1H NMR resonance at 1.58 ppm in C_6D_6, was produced in 8.6% yield as determined by NMR. When the reaction of **1** was carried out in 100% deuterated benzene and monitored by ^1H NMR, two sets of doublets at δ 7.71 (J = 8.3 Hz) and 7.01 (J = 8.3 Hz) appeared;[24] as the reaction proceeded these resonances decreased in intensity as the resonances due to the free $p\text{-}ClC_6H_4CN$ increased. The same intermediate resonances were observed when the reaction was carried out in cyclohexane and the ^1H NMR of the reaction products obtained before the reaction had gone to completion, thus suggesting the existence of a common intermediate which is formed before oxidative addition of the solvent occurs. In order to isolate the intermediate, a THF solution of **1** was stirred at 50 °C for 14 h in the dark. Upon removal of the THF under vacuum and extraction of the residue with pentane, a yellow solution was obtained which on cooling afforded a yellow crystalline product in 66% yield. The complex obtained is a side-bonded nitrile complex $(\eta^5\text{-}C_5Me_5)Ir(\eta^2\text{-}NCC_6H_4Cl)CO$[24] (**5**), identified by its characteristic low CN stretching frequency observed at 1781 cm^{-1} in the IR spectrum.[25,26] Complex **5** was also characterized by ^1H NMR spectroscopy and complete elemental analyses, and its molecular structure has been determined by a single-crystal X-ray diffraction study.[27] The resonances in the ^1H NMR spectrum of **5**[24] coincide with those of the intermediate observed when the thermolysis of **1** was monitored by ^1H NMR as described above. In order to confirm that **5** independently activates C–H bonds of hydrocarbons, a 0.07 M solution of **5** in benzene was maintained in the dark at 50 °C for 4 weeks, generating the phenyl hydride product **2** and the dimer **4**, in 76.2% and 18.4% yield, respectively. A mechanism consistent with these observations involves the loss of CO_2 from **1** to generate the nitrile complex **5** which at 50 °C is labile and loses the coordinated nitrile to release the metal fragment "$(C_5Me_5)Ir(CO)$" which undergoes C–H bond activation (Scheme III). The metallacycle **1** was also found to be very photosensitive; when a sample of **1** was maintained in benzene at 50 °C and photolyzed[28] for 36 h, **2** was obtained in 75.4% yield and **4** in 7.5% yield. The side-bonded nitrile **5** was observed when the ^1H NMR spectrum of the reaction mixture was obtained before the reaction had gone to completion, although the steady-state concentration of **5** was low since this compound was particularly photosensitive. When **5** was photolyzed[28] in benzene for 12 h at 50 °C, **2** was obtained in 80.6% yield by ^1H NMR; compound **4** was obtained in 4.7% yield. Photolysis of metallacycle **1** in cyclohexane for 13 days under the same conditions yielded the cyclohexylhydride product $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_{11})$ (**6**); addition of CCl_4 converted **6** to the known $(\eta^5\text{-}C_5Me_5)Ir(CO)(Cl)(C_6H_{11})$ (**7**)[2a] in 48.6% overall yield. The dimer **4** was obtained in 33.7% yield. When the side-bonded nitrile complex **5** was photolyzed for 24 h in cyclohexane at 50 °C, **6** was obtained which was converted to the chloride derivative to yield **7** in 67.1% overall yield; compound **4** was obtained in 13.1% yield.

The rhodium metallacycle $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh[C(p\text{-}FC_6H_4)=NOC(=O)]$ demonstrates a reactivity similar to that of **1** since the formation of a side-bonded nitrile complex and thermal C–H activation of hydrocarbon solvents are observed. Full details concerning this reaction will be reported shortly.

Acknowledgment. We are grateful to the Office of Naval Research for support of this research and the Johnson-Matthey Corporation for a generous gift of iridium and rhodium chloride. We thank Professor W. A. G. Graham for helpful discussions.

---

[21] The reactions were carried out in NMR tubes by using dried and degassed solvents. In a typical experiment, 0.8 mL of reactant solvent was vacuum transferred into 8 mg of the metallacycle **1** and the reactants were maintained at a constant temperature. When the reaction was complete the reactant solvent was removed under vacuum, and deuteriated benzene was then vacuum transferred in and the tube sealed. The alkyl and aryl metal hydrides formed were identified by matching the ^1H NMR chemical shifts with the reported values published by other workers or by conversion to the chloro derivatives by addition of CCl_4.[2a] Relative yields were measured by ^1H NMR integration.

[22] Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393.

[23] Graham, W. A. G., personal communication.

[24] **5**: IR (Nujol) 1949 (br, ν_{CO}), 1781 (m, ν_{CN}) cm^{-1}; ^1H NMR (C_6D_6) δ 7.72 (d, 2 H, J = 8.3 Hz), 7.01 (d, 2 H, J = 8.3 Hz), 1.69 (s, 15 H).

[25] Storhoff, B. N.; Huntley, C. L., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

[26] Side-bonded nitrile complexes have been isolated and characterized as the major products in the thermolysis of the metallacycles $(C_5H_5)Ir[C(Ar)=NOC(=O)](PPh_3)$ (Ar = $p\text{-}ClC_6H_4\text{-}$, $p\text{-}FC_6H_4\text{-}$): Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1986**, *5*, 1913.

[27] Complete details on the X-ray crystal structure of **5** will be given in a full report discussing the reactivity of metallacycles of rhodium and iridium.

[28] Photochemical experiments were carried out using a 100-W tungsten bulb which was supported 6 in. above an oil bath in which the NMR tubes were maintained at constant temperature. The radiated light was contained within the system by aluminum foil and a stream of cold nitrogen gas was used to cool the system to the desired temperature.

On the Difference between Iron–Molybdenum Cofactor of Wild-Type and *nif*V Mutant Molybdenum–Iron Proteins of *Klebsiella pneumoniae*: ENDOR, EXAFS, and EPR Evidence

Paul A. McLean,[1a,b] Anne E. True,[1c] Mark J. Nelson,[1d]
Steve Chapman,[1a] Martin R. Godfrey,[1c] Boon K. Teo,*[1e]
W. H. Orme-Johnson,*[1a] and Brian M. Hoffman*[1c]

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, Massachusetts 02139
Northwestern University, Department of Chemistry
Evanston, Illinois 60201
AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received August 1, 1986

Nitrogenase comprises two metalloproteins, the iron protein (Fe protein) and the molybdenum–iron protein (MoFe protein).[2-5] The active site of the enzyme is thought to be associated with the MoFe protein and to include the iron–molybdenum cofactor

---

[1] (a) Massachusetts Institute of Technology. (b) Massachusetts Institute of Technology. Current address: Biotechnica International, Inc., Cambridge, MA 02140. (c) Northwestern University. (d) Massachusetts Institute of Technology. Current address: Experimental Station, E. I. Du Pont de Nemours and Co., Wilmington, DE 19898. (e) AT&T Bell Laboratories. Current address: Chemistry Department, University of Illinois at Chicago, Chicago, IL 60680.

[2] (a) Thornley, R. N. F.; Mortenson, L. E. *Annu. Rev. Biochem.* **1979**, *48*, 387–418. (b) Nelson, M. J.; Lindahl, P. A.; Orme-Johnson, W. H. In *Advances in Inorganic Biochemistry*; Eichard, G. L., Marzilli, L. G., Eds.; New York: Elsevier Scientific: New York, 1982; Vol. 4, pp 1–40. (c) Orme-Johnson, W. H. *Annu. Rev. Biophys. Chem.* **1985**, *14*, 419–459.

[3] Abbreviations: MoFe, molybdenum–iron; FeMo-co, iron–molybdenum cofactor; *Kp*1, MoFe protein of *K. pneumoniae*; WT, wild type; V^-, *nif*V; EXAFS, extended X-ray absorption fine structure; ENDOR, electron nuclear double resonance.

[4] Nelson, M. J.; Levy, M. A.; Orme-Johnson, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 147–150.

[5] (a) MacNeil, T.; MacNeil, D.; Roberts, G. P.; Supiano, M. A.; Brill, W. J. *J. Bacteriol.* **1978**, *136*, 253–266. (b) Merrick, M.; Filser, M.; Dixon, R. A.; Elmerich, C.; Sibold, L.; Houmard, J. *J. Gen. Microbiol.* **1980**, *117*, 509–520. (c) Puhler, A.; Klipp, W. In *Biology of Inorganic Nitrogen and Sulfur*; Bothe, H., Trebst, A., Eds.; Spring-Verlag: Berlin/Heidelberg, 1980; pp 276–286.

0002-7863/87/1509-0943$01.50/0