

alkynes. Hydrogenation in the presence of CO regenerates **5** quantitatively.

**Acknowledgment.** This work was supported by 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. The crystal structure analyses of **6** and **11** were performed by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility, and that of **8** by Dr. W. Tötsch and J. Bularzik, K. Kourtakis, and J. Nitschke, at the same location. We thank Professor H. B. Abrahamson, University of Oklahoma for a preprint. M.T. is the recipient of a Royal Fellowship of Norway. K.P.C.V. was a Camille and Henry Dreyfus Teacher-Scholar (1978-1983).

**Supplementary Material Available:** A listing of positional and thermal parameters and tables of bond lengths and angles of **6**, **8**, and **11** (17 pages). Ordering information is given on any current masthead page.

### Reactivity of Phosphido-Bridged Heteronuclear Compounds: Insertion of CO and Diphenylacetylene into the Phosphido Bridge of $\text{RuCo}(\text{CO})_7(\mu\text{-PPh}_2)$ .

#### X-ray Structure of $\text{RuCo}(\text{CO})_5(\mu\text{-CO})[\mu\text{-}\eta^2\text{-PPh}_2\text{C}(\text{O})\text{C}(\text{Ph})\text{C}(\text{Ph})]$

Rachid Regragui and Pierre H. Dixneuf\*  
Laboratoire de Chimie de Coordination Organique  
Université de Rennes, Campus de Beaulieu  
35042 Rennes Cedex, France

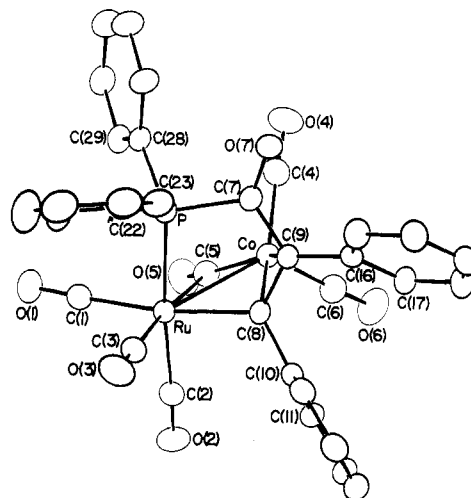
Nicholas J. Taylor and Arthur J. Carty\*  
Guelph-Waterloo Centre, Waterloo Campus  
Department of Chemistry, University of Waterloo  
Waterloo, Ontario, N2L 3G1 Canada

Received September 20, 1983

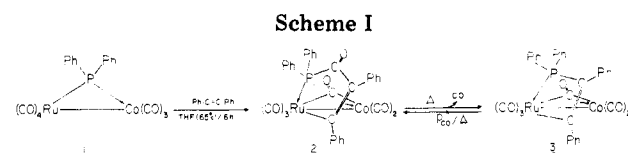
**Summary:** The reaction of the heterobinuclear phosphido-bridged compound  $\text{RuCo}(\text{CO})_6(\mu\text{-PPh}_2)$  (**1**) with diphenylacetylene leads, via acetylene and CO insertion into the phosphido bridge, to the novel complex  $\text{RuCo}(\text{CO})_5[\text{Ph}_2\text{PCOC}(\text{Ph})\text{C}(\text{Ph})]$  (**2**). X-ray analysis (space group  $P\bar{1}$ ,  $a = 9.820$  (1) Å,  $b = 12.419$  (2) Å,  $c = 14.966$  (2) Å,  $\alpha = 99.58$  (1)°,  $\beta = 99.55$  (1)°,  $\gamma = 90.10$  (1)°,  $Z = 2$ ;  $R = 0.028$ ,  $R_w = 0.031$  based on 4191 reflections) has revealed the presence of a  $\mu\text{-Ph}_2\text{PCOC}(\text{Ph})\text{C}(\text{Ph})$  ligand coordinated to ruthenium via phosphorus and one carbon atom of the original alkyne and to cobalt via an  $\eta^2$ -interaction. **2** undergoes facile decarbonylation to  $\text{RuCo}(\text{CO})_5[\text{Ph}_2\text{PC}(\text{Ph})\text{C}(\text{Ph})]$  (**3**). The conversion of **1** to **2** and **3** may have wide implications for the reactivity of  $\mu\text{-PPh}_2$ -bridged polynuclear compounds toward unsaturated substrates.

The phosphido ( $\text{PR}_2$ ) group has recently attracted particular attention as a strongly bound yet flexible ligand capable of maintaining the integrity of a polynuclear framework during chemical transformations.<sup>1</sup> A sub-

(1) For recent references see: (a) Carty, A. J. *Adv. Chem. Ser.* 1982, No. 196, 163. (b) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* 1983, 22, 319. (c) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* 1982, 1, 1379. (d) Fischer, K.; Vahrenkamp, H. *Z. Anorg. Allg. Chem.* 1981, 475, 109. (e) Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* 1982, 224, C45. (f) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* 1983, 2, 53. (g) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* 1982, 21, 1349. (h) Yu, Y.-F.; Galluci, J.; Wojcicki, A. *J. Am. Chem. Soc.* 1983, 105, 4826.



**Figure 1.** A perspective view of the molecular structure of  $\text{RuCo}(\text{CO})_5[\text{Ph}_2\text{PCOC}(\text{Ph})\text{C}(\text{Ph})]$  drawn to illustrate the interaction of the new ligand with the metal atoms.



stantial number of polynuclear phosphido-bridged compounds have now been synthesized,<sup>2</sup> and several examples of potentially significant, reversible metal-metal bond cleavage have been reported.<sup>3</sup> With  $\mu\text{-PPh}_2$  compounds a possible complicating factor that has not however received much attention is reactivity associated with the bridge, a problem which might be accentuated in heterobimetallic systems. To date few instances of bridge cleavage have been reported.<sup>1,4</sup>

While investigating the behavior of the heteronuclear phosphido-bridged dimer  $\text{RuCo}(\text{CO})_7(\mu\text{-PPh}_2)$  (**1**)<sup>5</sup> toward alkynes for comparison with homodinuclear compounds such as  $\text{Co}_2(\text{CO})_8$ , we discovered that the dominant reaction pathway involves CO and acetylene insertion into the  $\mu\text{-PPh}_2(\text{RuCo})$  bridge leading to the novel derivative  $\text{RuCo}(\text{CO})_5(\mu\text{-CO})[\mu\text{-PPh}_2\text{COC}(\text{Ph})\text{C}(\text{Ph})]$  (**2**) which subsequently decarbonylates to  $\text{RuCo}(\text{CO})_5(\mu\text{-CO})[\mu\text{-PPh}_2\text{C}(\text{Ph})\text{C}(\text{Ph})]$  (**3**). These reactions that may have wider implications for the reactivity of  $\mu\text{-PPh}_2$  systems and for the use of heterobimetallics in organic synthesis are reported herein.

(2) See for example: (a) Carty, A. J.; MacLaughlin, S. A.; Van Wagner, J.; Taylor, N. J. *Organometallics* 1982, 1, 1013. (b) Young, D. A. *Inorg. Chem.* 1981, 20, 2049. (c) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Chem. Commun.* 1981, 407. (d) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *Ibid.* 1981, 587. (e) Jones, D. F.; Dixneuf, P. H.; Benoit, A.; Le Marouille, J. Y. *Ibid.* 1982, 1217. (f) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* 1982, 1, 1008.

(3) (a) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics*, 1983, 2, 470. (b) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Ibid.* 1983, 2, 1194. (c) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* 1981, 204, C27.

(4) (a) The only examples of insertion of an unsaturated ligand into a diphenylphosphido bridge, of which we are aware, are given in: Smith, W. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* 1976, 896. (b) Examples of hydrogenation of a  $\mu\text{-PPh}_2$  bridge to a terminal phosphine have recently been observed: see ref 1b, 1f, and 1h. (c) Hydrogen abstraction from the more reactive  $\mu\text{-PPhH}$  groups has been used to generate face capping  $\mu_3\text{-PPh}$  groups, but the nucleating properties of the phosphorus ligand are not destroyed in this conversion. See, e.g.: Iwasaki, F.; Mays, M. J.; Raithby, G. R.; Taylor, P. L.; Wheatley, P. J. *J. Organomet. Chem.* 1981, 213, 185.

(5) Regragui, R.; Dixneuf, P. H. *J. Organomet. Chem.* 1982, 239, C12.

Thin-layer chromatography and IR monitoring of the reaction of  $\text{RuCo}(\text{CO})_7(\mu\text{-PPh}_2)$  (**1**)<sup>5</sup> (0.54 g, 1.0 mmol) in THF (50 mL) with diphenylacetylene (0.20 g, 1.0 mmol) at 65 °C for 6 h showed the gradual consumption of starting material (1: IR ( $\text{C}_6\text{H}_{12}$ )  $\nu(\text{CO})$  2107 (m), 2046 (sh), 2039 (s), 2022 (vs), 2015 (w), 1967 (w)  $\text{cm}^{-1}$ ) and the synthesis of two new products. Column chromatography on Florisil afforded a trace of **1** (eluant hexane) followed by a yellow red band (eluant hexane) containing the major product **3** and a third, yellow band (eluant  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 1:3) of **2**. Crystallization of **3** from hexane yielded yellow-orange hexagonal crystals (60%) [mp 180–182 °C; IR ( $\text{C}_6\text{H}_{12}$ )  $\nu(\text{CO})$  2080 (m), 2027 (s), 2021 (m), 2007 (w), 1984 (m), 1897 (w)  $\text{cm}^{-1}$ ; <sup>31</sup>P NMR ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  -28.6] and of **2** from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  yellow prisms (10%) [mp 168–170 °C; IR ( $\text{C}_6\text{H}_{12}$ )  $\nu(\text{CO})$  2093 (m), 2039 (s), 2022 (m), 1994 (m), 1878 (w), 1608 (w)  $\text{cm}^{-1}$ ; <sup>31</sup>P NMR ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  +38.6]. At 30 °C IR spectroscopy showed the formation of **2** as the major product of the reaction. Infrared monitoring showed a relatively clean conversion of pure, isolated **2** to **3** in THF at 65 °C (Scheme I). After 2 h the major product was **3** (~60%), with unreacted **2** and trace amounts of other, as yet unidentified complexes.

Precise details of the molecular structure of **2** were provided by an X-ray structure determination.<sup>6</sup> A perspective view of the molecule is shown in Figure 1. Whereas in the precursor **1** the phosphido group bridges the Ru–Co bond,<sup>7</sup> in **2** the phosphorus atom is coordinated only to the ruthenium atom (Ru–P = 2.3335 (8) Å) and is part of a new  $\text{Ph}_2\text{PC}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Ph})$ -chelating ligand formed via the formal insertion of CO and diphenylacetylene into the P–Co bond of **1**. A notable feature of the ketophosphine ligand, relevant to the facile conversion of **2** to **3**, is the P–C(7) distance (1.865 (3) Å) which is substantially elongated when compared to the P–C(phenyl) (average 1.820 Å) bond lengths. The cobalt atom acquires an 18-electron configuration via coordination to two carbonyl groups, to the ruthenium atom via a short Ru–Co bond (2.6577 (4) Å), to a semibridging CO group, C(5)–O(5), and to the hydrocarbon moiety via  $\eta^2$ -bonding to C(8) and C(9), the original acetylenic carbon atoms. The ru-

thenium atom interacts with three terminal carbonyl groups, the phosphine, the cobalt atom, and the carbon C(8) of the new ligand and more weakly with C(5) of the bridging CO group.

Consideration of the molecular structure of **2** together with a comparison of spectroscopic data<sup>9</sup> for **2** and **3** suggests that thermal conversion of **2** to **3** occurs via extrusion of the ketonic carbonyl group with linkage of C(9) and the phosphido group. In particular the shift of the <sup>31</sup>P resonance ( $\Delta P = 67.2$  ppm) to high field is consistent with the change from a five-membered  $\text{Ru}(\text{C})_3\text{P}$  chelate ring in **2** to a four-membered  $\text{Ru}(\text{C})_2\text{P}$  system in **3**.<sup>10</sup>

The structure of **3**<sup>11</sup> is closely related to that of **2** but lacks the ketonic CO group C(7)–O(7) and has a P–C(Ph)(acetylene) bond length of 1.810 (9) Å. The Ru–Co bond length of 2.648 (1) Å is similar to that in **2**, and a semibridging CO group (Co–C(6) = 1.758 (11) Å; Ru–C(6) = 2.517 (11) Å) is retained.

The synthesis of **2** from **1** might occur via either initial attack by the acetylene on the phosphido bridge followed by CO insertion or alternatively acetylene coordination, CO insertion, and intramolecular coupling of  $\mu\text{-PPh}_2$  and  $\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{O})$ -ligands. Since **3** does not insert CO to give **2** at 65 °C under a CO atmosphere, the former route seems unlikely. Moreover reaction of the parent carbonyl **1** with 1 mol of  $\text{Ph}_3\text{P}$  results exclusively in substitution at the ruthenium atom.<sup>7b</sup> The monosubstituted compound  $(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$  is unreactive to diphenylacetylene under the conditions of formation of **2**. These observations strongly suggest that the initial steps in the reaction may be CO displacement at ruthenium followed by formation of a parallel  $\mu$ -alkyne complex<sup>12</sup> which subsequently undergoes insertion of CO into the Co–alkyne  $\sigma$ -bond, a reaction for which adequate precedent exists.<sup>13</sup>

Several aspects of the unusual chemistry displayed by the heterobinuclear complex **1** are noteworthy. It is significant that under the mild conditions necessary for the carbonylation–decarbonylation sequence **1** → **2** → **3**,  $\text{Co}_2(\text{CO})_8$  and diphenylacetylene afford predominantly the  $\mu$ -alkyne complex  $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CPh})$ .<sup>14</sup> Facile carbonylation of organic substrates may well be an important feature of heterobinuclear carbonyl chemistry especially in view of the propensity of such systems to form semibridging carbonyl groups. In the context of phosphido bridge reactivity, the facile formation of **2** and **3** via insertion of CO and alkyne into the  $\mu\text{-PPh}_2$  bridge of a mixed-metal binuclear compounds is unprecedented but

(6) Crystals of  $\text{RuCo}(\text{CO})_6[\text{Ph}_2\text{PCOC}(\text{Ph})\text{C}(\text{Ph})]$  (**2**), mol wt 719.50, crystallize in the triclinic space group  $P\bar{1}$  with  $a = 9.280$  (1) Å,  $b = 12.419$  (2) Å,  $c = 14.966$  (2) Å,  $\alpha = 99.58$  (1)°,  $\beta = 99.55$  (1)°,  $\gamma = 90.10$  (1)°,  $V = 1495.8$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{meas}}$  = 1.60  $\text{g}\cdot\text{cm}^{-3}$ ,  $\rho_{\text{calcd}}$  = 1.597  $\text{g}\cdot\text{cm}^{-3}$ , and  $\mu(\text{Mo K}\alpha) = 11.73$   $\text{cm}^{-1}$ . Intensity data were collected on a crystal of dimensions  $0.24 \times 0.25 \times 0.28$  mm with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) on a Syntex P2, diffractometer. Intensities were measured by using the  $\theta$ - $2\theta$  scan method with a scan width of 0.8° below  $K\alpha_1$  to 0.8° above  $K\alpha_2$  and a variable scan speed of 2.93–29.3°  $\text{min}^{-1}$  out to a maximum  $2\theta$  of 50°. Standard reflections (137, 410) monitored every 100 measurements showed no change in intensity over the course of data collection. From a total of 5281 independent reflections 4191 with  $I \geq 3\sigma(I)$  were observed and used in the structure solution and refinement. Lorentz and polarization but not absorption corrections were made. The structure was solved by heavy-atom and Fourier methods. Refinement of the structure by full-matrix least-squares methods, with all non-hydrogen atoms having isotropic temperature factors gave an  $R$  value ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.062. With anisotropic parameters  $R$  refined to 0.039. At this stage a difference Fourier map revealed all hydrogen atom positions and isotropic thermal parameters were refined in subsequent cycles. The final  $R$  and  $R_w$  ( $R_w = [\sum w|F_o| - |F_c|]^2 / \sum wF_o^{-1/2}$ ) values were 0.028 and 0.031. A final difference map was featureless. Atomic positions are listed in Table S1, thermal parameters in Table S2, and bond lengths and angles in Table S3. Structure factors are also available as supplementary material.

(7) (a) Spectroscopic data, particularly the low-field <sup>31</sup>P shift ( $\text{CH}_2\text{Cl}_2$ , 223 K)  $\delta$  187.3, confirm that in **1** a  $\mu\text{-PPh}_2$  group bridges the Ru–Co bond. (b) The crystal structure of the monosubstitution product  $(\text{OC})_3(\text{Ph}_2\text{P})\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$  recently determined (Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J., unpublished results) has Ru–Co = 2.7681 (4) Å and Ru–P–Co = 75.5 (0)°.

(8) The semibridging CO (C(5)–O(5)) interacts strongly with Co (Co–C(5) = 1.789 (4) Å) and more weakly with Ru (Ru–C(5) = 2.380 (4) Å). The Co–C(5)–O(5) angle is 154.6 (1)°.

(9) The  $\nu(\text{CO})$  absorption at 1608  $\text{cm}^{-1}$  in **2** can be attributed to the keto group and the band at 1878  $\text{cm}^{-1}$  to the semibridging CO. Conversion of **2** to **3** results in the complete disappearance of the 1608- $\text{cm}^{-1}$  band but only a slight frequency shift for the semibridging CO. Moreover the terminal  $\nu(\text{CO})$  band pattern is similar in both compounds with a shift of all  $\nu(\text{CO})$  bands to lower frequency in **3**. Anal. Calcd for  $\text{C}_{32}\text{H}_{20}\text{O}_6\text{P}\text{RuCo}$  (**3**): C, 55.58; H, 2.84; P, 4.48. Found: C, 55.38; H, 2.94; P, 4.18.

(10) Garrou, P. E. *Chem. Rev.* 1981, 81, 229.

(11) Crystals of **3**,  $\text{RuCoPO}_6\text{C}_3\text{H}_2\text{O}_5\text{C}_2\text{H}_2$ , are monoclinic of space group  $P2_1/c$  with  $a = 17.042$  (2) Å,  $b = 10.721$  (1) Å,  $c = 17.514$  (2) Å,  $\beta = 101.56$  (1)°,  $V = 3135.0$  (5) Å<sup>3</sup>,  $Z = 4$ , and  $\mu(\text{Mo K}\alpha) = 11.6$   $\text{cm}^{-1}$ . The structure was solved and refined to a current  $R$  value of 0.048 by using 3450 observed diffractometer data. Full structural details of this molecule will be published elsewhere.

(12) Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, 104, 3858.

(13) See for example: Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; Chapter 8.

(14) (a) Disubstitution with phosphines affords isomers based on displacement of two carbonyls at the ruthenium site of **1** (Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J., to be submitted for publication). (b) The structure of  $(\text{OC})_3(\text{Ph}_2\text{P})\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2\text{PPh}_3$  has also been determined,<sup>16</sup> but the complex is obtained by another route.

(15) Hubel, W. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; pp 273–342.

bears a striking resemblance to coupling reactions reported for the homobinuclear acetylide compound  $\text{Fe}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-C}\equiv\text{CPh})(\text{PPh}_2)_4$ .<sup>4</sup> These observations suggest that for certain substrates, in particular acetylenes, attack at a  $\mu\text{-PPh}_2$  bridge may be a preferred reaction mode. Whether such reactivity precludes the use of phosphido-bridged clusters in the catalytic hydrogenation of substrates remains to be demonstrated.

**Acknowledgment.** This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada (AJC) and from the Centre National de la Recherche Scientifique of France (PHD). One of us (R.R.) is grateful to the University of Waterloo for facilities provided during a 4 month visit.

**Registry No.** 1, 82544-75-0; 2, 89486-23-7; 3, 89462-28-2; Co, 7440-48-4; Ru, 7440-18-8;  $\text{PhC}\equiv\text{CPh}$ , 501-65-5.

**Supplementary Material Available:** Table of atomic positions, anisotropic thermal parameters, bond lengths and angles, and structure factors (28 pages). Ordering information is given on any current masthead page.

### Selective Stoichiometric and Catalytic C-H Bond Cleavage Reactions in Hydrocarbons by Iridium Complexes

Mark J. Burk, Robert H. Crabtree,\* Charles P. Parnell, and Richard J. Urlarte<sup>1</sup>

Department of Chemistry, Yale University  
New Haven, Connecticut 06520

Received January 25, 1984

**Summary:** Complexes of the type  $[\text{IrH}_2\text{S}_2\text{L}_2]\text{A}$  ( $\text{S} = \text{Me}_2\text{CO}$ ;  $\text{L} = \text{PPh}_3$  or  $(p\text{-FC}_6\text{H}_4)_3\text{P}$ ;  $\text{A} = \text{SbF}_6$ ), in the presence of  $t\text{-BuCH}=\text{CH}_2$  (tbe) at 85–150 °C, can aromatize cyclohexanes to arenes and dehydrogenate cyclopentanes to cyclopentadienyl complexes of the type  $[\text{IrCpHL}_2]\text{A}$  in good to excellent yields. The intermediates  $[\text{IrH}(\eta^5\text{-C}_6\text{H}_7)\text{L}_2]\text{A}$  and  $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)\text{L}_2]\text{A}$  are observed in the cyclohexane case. Cyclooctane is dehydrogenated to  $[\text{Ir}(\text{cod})\text{L}_2]\text{A}$ , but the addition of base leads to the catalytic formation of free cyclooctene instead. Cyclohexenes can be catalytically aromatized. In some cases, benzene ( $\text{L} = \text{PPh}_3$ ) or fluorobenzene ( $\text{L} = (\text{FC}_6\text{H}_5)_3\text{P}$ ) is formed in a side reaction involving P-C hydrogenolysis.

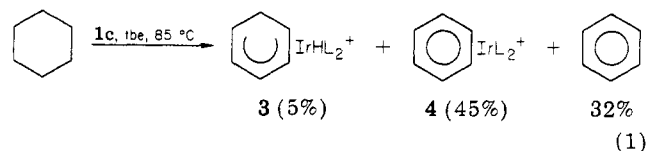
The way in which metals break C-H and C-C bonds in hydrocarbons is a topic of current interest.<sup>2-4</sup> In 1979, we described the homogeneous dehydrogenation of various alkanes to give unsaturated metal-bound organic ligands. We proposed that oxidative addition of an alkane C-H bond to the metal was involved.<sup>2d</sup> Several systems have

now been developed<sup>3,4</sup> including some in which such an oxidative addition has been directly observed.<sup>4</sup> We now describe a system that allows the stoichiometric aromatization of cyclohexane and the catalytic aromatization of cyclohexene via C-H cleavage reactions.

In our original system,<sup>2d</sup>  $[\text{IrH}_2\text{S}_2\text{L}_2]\text{A}$  ( $\text{A} = \text{Me}_2\text{CO}$ ,  $\text{L} = \text{PPh}_3$ ,  $\text{A} = \text{BF}_4$ ) at 80 °C in  $\text{C}_2\text{H}_4\text{Cl}_2$  containing  $t\text{-BuCH}=\text{CH}_2$  (tbe), cyclopentane, cyclooctane, and cycloheptane was converted into  $[\text{IrCpHL}_2]\text{A}$ ,  $[\text{Ir}(\text{cod})\text{L}_2]\text{A}$ , and  $[\text{Ir}(\eta^5\text{-C}_7\text{H}_9)\text{HL}_2]\text{A}$ , respectively, but only in moderate yields (12–70%). Other alkanes did not react.

Alkane activation is rare probably because side reactions usually intercept reactive metal fragments. In our own system we now find that reaction with the halocarbon solvent gives ca. 40% of the two binuclear complexes  $[\text{HL}_2\text{Ir}(\mu\text{-Cl})_2(\mu\text{-X})\text{IrL}_2\text{H}]\text{BF}_4^5$  ( $\text{X} = \text{H}$  or  $\text{Cl}$ ) among the products; these are inactive for alkane reactions. This prompted us to omit the halogenated solvent and carry out the reactions in neat alkane, containing tbe (tbe:M, 4:1 mole ratio), in a resealable 100-mL glass vessel<sup>6</sup> at 85–150 °C. Rather than **1a** itself, we generally used the related complexes  $[\text{IrH}_2\text{S}_2\text{L}_2]\text{A}$  ( $\text{S} = \text{Me}_2\text{CO}$ ,  $\text{L} = \text{PPh}_3$ ,  $\text{A} = \text{SbF}_6$ , **1b**;  $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ ,  $\text{A} = \text{SbF}_6$ , **1c**). Although the salts **1a-c** appear to be entirely insoluble in the alkane, not only are yields greatly improved but also a variety of previously unreactive alkanes now react.

For example, cyclopentane reacts with **1c** at 90 °C for 24 h to give  $[\text{IrCpHL}_2]\text{A}$  (82%). Methyl- and ethylcyclopentane, previously unreactive, now give  $[\text{Ir}(\text{RC}_5\text{H}_4)\text{HL}_2]\text{A}$  (**2**) after 14 h at 120 °C ( $\text{R} = \text{Me}$ , 78%;  $\text{R} = \text{Et}$ , 36%).<sup>7</sup> Cyclohexane, inert under the old conditions, now reacts at 85 °C for 20 h according to eq 1. This is a particularly



interesting case in view of the importance of aromatization reactions in reforming. We see an  $\eta^5$ -cyclohexadienyl complex,<sup>8</sup> **3**, probably isolable because it has an 18-electron configuration, as well as the benzene complex **4**<sup>8</sup> and free benzene.<sup>2b</sup> Pure **3** and **4** both pyrolyze (150 °C) to give benzene. At 150 °C reaction 1 gives free benzene (60%), a trace of **4** (5%), and fluorobenzene (0.8 mol/Ir, which must arise from P-C cleavage) after 18 h. We were able to verify that essentially only  $\text{C}_6\text{D}_6$  (~98% d<sup>6</sup>) was formed from  $\text{C}_6\text{D}_{12}$  at 150 °C (GC-MS).

Methylcyclohexane also reacts, but at a higher temperature. At 130 °C, only the cyclohexadienyl complex of type **2** (25%) is formed after 15 h, and at 150 °C for 36 h free toluene (28%) and fluorobenzene (0.8 mol/Ir) are obtained.

It is the decomposition<sup>9</sup> of the complex that probably prevents the systems from being catalytic. Cyclohexene is a sufficiently good ligand to protect the catalyst from

(1) Crabtree, R. H. *Acc. Chem. Res.* 1979, 12, 331.

(2) This consisted of a triple-thickness vessel with a Teflon vacuum stopcock. Our experimental methods were similar to those reported,<sup>2</sup> and organic products were detected by FID-GC (squalane or  $\text{AgNO}_3$ ) and identified by GC-MS.

(3) The identity of all products was verified by independent synthesis from the corresponding olefin, and the complexes were fully characterized. **2** ( $\text{R} = \text{Me}$ ):  $^1\text{H NMR}$  ( $\text{CD}_3\text{CO}$ )  $\delta$  -14.6 (t (28), IrH), 1.9 (br s, Me), 5.25 and 5.5 (c, Cp), 7.05, -7.65 (c, Ar). **2** ( $\text{R} = \text{Et}$ ):  $^1\text{H NMR}$   $\delta$  14.3 (t (28), IrH), 1.2 (t (7), Me), 2.4 (c,  $\text{CH}_2$ ), 4.9 and 5.7 (c, Cp), 7.1-7.9 (Ar).

(4) **3**:  $^1\text{H NMR}$   $\delta$  -17.8 (t (22), IrH), 1.4, 2.2, 3.6, 4.0, 5.2 (c,  $\text{C}_6\text{H}_7$ ), 7.2 (c, Ar). **4**:  $^1\text{H NMR}$   $\delta$  6.1 (s,  $\text{C}_6\text{H}_6$ ), 7.3 (c, Ar).

(5) Perhaps via the P-C cleavage reaction mentioned above, which may be a general catalyst deactivation pathway in homogeneous catalysis.

(1) Visiting Associate Professor; permanent address: St. Peter's College, Jersey City, NJ.

(2) (a) Ittel, S. D.; Tolman, C. A.; Jesson, J. P. *Adv. Chem. Ser.* 1979, No. 173, 67. (b) Shilov, A. E. *Sov. Sci. Rev., Sect. B* 1982, 4, 71. (c) Groves, J. T.; Kruper, W.; Haushalter, R. C. *J. Am. Chem. Soc.* 1980, 102, 6375. (d) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* 1979, 101, 7738; 1982, 104, 107.

(3) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc. Chem. Commun.* 1983, 1243; 1982, 606, 1235; 1983, 788. Watson, P. L. *J. Am. Chem. Soc.* 1983, 105, 6491.

(4) Bergman, R. G.; Janowicz, A. H. *J. Am. Chem. Soc.* 1982, 104, 352. Hoyano, J. K.; Graham, W. A. G. *Ibid.* 1982, 104, 3743.