

O,10-H)-C(NO₂)₄, 91452-22-1; D⁺-(9-CHO,10-H), 91547-89-6; D(9-H,10-H)-C(NO₂)₄, 36301-08-3; D⁺-(9-H,10-H), 34512-28-2; D(9-Ph,10-H)-C(NO₂)₄, 91452-18-5; D⁺-(9-Ph,10-H), 40807-34-9; D(9-Br,10-H)-C(NO₂)₄, 91452-19-6; D⁺-(9-Br,10-H), 84985-63-7; D(9-C₆H₅-CH=CH,10-H)-C(NO₂)₄, 96689-10-0; D⁺-(9-CH₂=CH,10-H), 96689-17-7; D(9-CHO,10-Cl)-C(NO₂)₄, 96689-11-1; D⁺-(9-CHO,10-Cl), 93350-37-9; D(9-CHO,10-Me)-C(NO₂)₄, 96689-12-2; D⁺-(9-CHO,10-Me), 96689-18-8; D(9-Br,10-Br)-C(NO₂)₄, 96689-13-3; D⁺-(9-Br,10-Br), 51939-74-3; D(9-Ph,10-Ph)-C(NO₂)₄, 96689-14-4; D⁺-(9-Ph,10-Ph), 34480-04-1; D(9-Me,10-Me)-C(NO₂)₄, 96689-15-5; D⁺-(9-Me,10-Me), 34526-95-9; D(9-NO₂,10-H)-C(NO₂)₄, 91452-21-0; D⁺-(9-NO₂,10-H), 84367-93-1; D(9-CN,10-H)-C(NO₂)₄, 91452-20-9; D⁺-(9-CN,10-H), 84985-64-8; D(9-OMe,10-H)-C(NO₂)₄, 96689-16-6; D⁺-(9-OMe,10-H), 84367-94-2; C(NO₂)₃⁻, 20143-63-9; NO₂⁻, 10102-44-0.

Inter- and Intramolecular Oxidative Addition of Phosphine, Methane, Alkane, and Alkene C-H Bonds to Rhenium

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Received February 4, 1985

Intermolecular oxidative addition of C-H bonds in alkanes to soluble transition-metal complexes, leading to stable hydrido(alkyl)metal complexes (eq 1), has so far been observed only with

$$M + R-H \rightarrow R-M-H \quad (1)$$

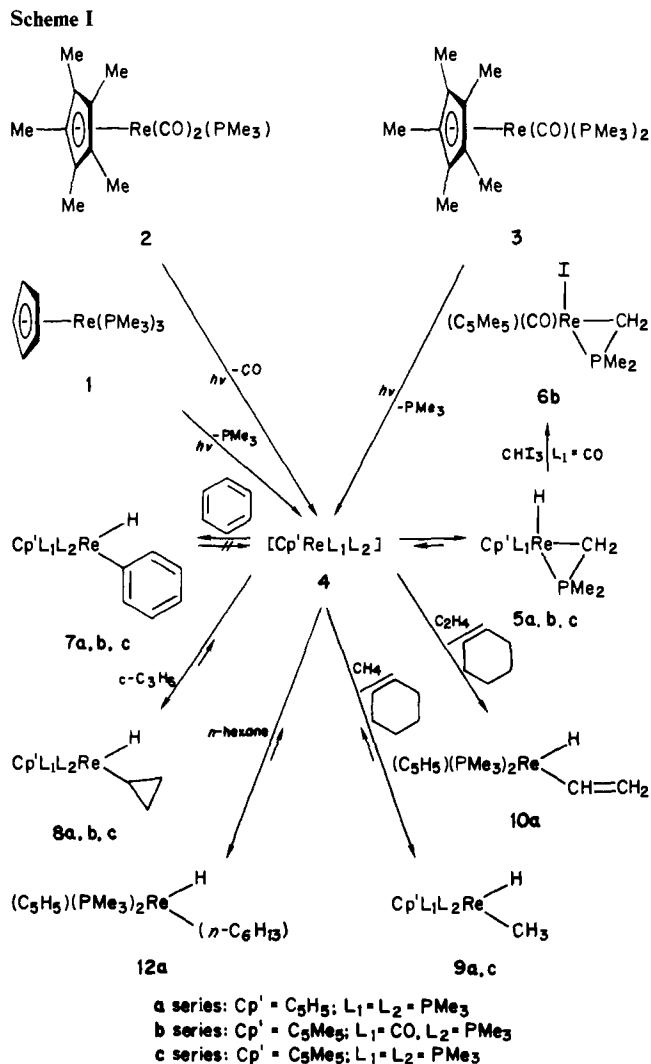
iridium and rhodium complexes.¹ We now wish to report the first direct observation of this reaction at rhenium. These new C-H activation reactions exhibit the following behavior which contrasts with that observed in the earlier-studied systems: (1) Competitive intermolecular alkane C-H activation and intramolecular attack on C-H bonds in PMe₃ ligands is observed. (2) The cyclometalated products provide a route to thermal activation of hydrocarbons under mild conditions. (3) Despite lowered inter/intra selectivity, selectivity with respect to different alkanes is substantially increased. Primary, cyclopropyl, methane, aromatic, and vinyl hydrogens are attacked, but secondary and tertiary C-H bonds are not. Thus cyclohexane can be used as an inert solvent, providing a convenient method for activating gaseous substrates such as methane and ethylene. (4) The efficiency of oxidative addition depends markedly upon the ligands attached to the metal.

Our observations are summarized in Scheme I. Analogous, although not identical, results have been obtained in three systems for which CpRe(PMe₃)₂ (**4a**), (C₅Me₅)Re(CO)(PMe₃) (**4b**), and (C₅Me₅)Re(PMe₃)₂ (**4c**) are postulated as intermediates. These reactive species are accessible via the new photochemical precursors **1**, **2**, and **3** and/or thermally from the cyclometalated complexes (vide infra) **5**. Carbonyl(phosphine) complexes **2** and **3** are prepared (41% and 22% isolated yield, respectively) in straightforward photosubstitution reactions involving (C₅Me₅)Re(CO)₃ and PMe₃. Complex **1** was formed in 35% yield by reduction of ReCl₃(PMe₃)₃³ in the presence of cyclopentadiene; a similar synthesis of the analogous C₅Me₅ complex by this route could not be accomplished.

(1) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *Ibid.* **1983**, *105*, 3929. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (c) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902. (d) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562; *J. Am. Chem. Soc.* **1984**, *106*, 1650. (e) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508; *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(2) For an interesting dinuclear relative of this complex, see: Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

(3) The preparation of this material involved modification of procedures worked out earlier for related (phosphine)rhenium complexes; cf.: Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64.



Our cleanest results overall have been obtained on photolysis of the cyclopentadienyltris(phosphine) complex **1**. For example, photolysis⁴ of **1** in benzene or cyclopropane leads to the corresponding products of C-H oxidative addition **7a** and **8a**.⁵ These materials can be isolated in good yields (64% and 21%, respectively) by recrystallization (**7a**) or by air-free chromatography at -100 °C on alumina III (**8a**) and were characterized fully by spectroscopic and conventional analytical methods. Irradiation of **1** in *n*-hexane at -30 °C produces a C-H activation product identifiable by ¹H NMR (hydride resonance appears as t of t, ³J_{H-H} = 3.6, ²J_{H-P} = 50.1 Hz) as the primary C-H insertion product **12a** (38% NMR yield after 72% conversion).⁶ Most of these C-H activation products are stable for significant lengths of time (e.g., several hours) at 25 °C. Hydrido *n*-hexyl complex **12a** is significantly less stable, reductively eliminating *n*-hexane at 20 °C with a half-life of ca. 12 min. We have not yet succeeded in isolating this material in pure form. In contrast to earlier observations in the iridium and rhodium series, irradiation of **1** in cyclohexane does *not* lead to intermolecular C-H insertion.

(4) Photolyses were performed in Pyrex vessels using a 450-W medium-pressure Hanovia lamp at ca. 5 °C unless otherwise noted. A 100-W medium-pressure Hanovia lamp was used in the synthesis of compounds **3**, **5b**, and **5c**.

(5) On the basis of NMR spectra we assign the stereochemistry of the oxidative addition products as *trans*, although we cannot rule out rapidly equilibrating geometries. The stereochemistry of the cyclometalated products **5** has not yet been assigned.

(6) Small amounts (<5%) of Cp'ReL₂H₂ (Cp' = C₅H₅, C₅Me₅; L = PMe₃) are observed in many of the photolyses. Prolonged photolysis results in somewhat higher yields of the dihydride, along with concurrent destruction of the C-H oxidative addition product. The related complex CpRe(PPh₃)₂H₂ is known: Baudry, D. H.; Ephretikhine, M. *J. Chem. Soc., Chem. Commun.* **1980**, 249.

Instead, irradiation of **1** in cyclohexane leads to cyclometalation, producing **5a**, isolated by low-temperature chromatography in 31% yield and fully characterized.⁷

The reluctance of reactive intermediate **4a** to react with secondary C-H bonds provided, for the first time, a readily available hydrocarbon which could be used as an inert solvent for carrying out intermolecular C-H activation of materials that are difficult to liquefy under ambient conditions. Thus, upon photolysis of **1** in cyclohexane under CH₄ (25 atm)⁸ or ethylene (25 atm), significant quantities of hydrido methyl complex **9a** (42% isolated yield) and hydrido vinyl complex **10a** (42% NMR yield) are formed, respectively. Compound **9a** was isolated and fully characterized; NMR evidence supports the assignment of **10a**.

In the pentamethylcyclopentadienyl series, irradiation of dicarbonyl complex **2** results in loss of CO, and irradiation of bis(phosphine) complex **3** results in loss of phosphine;⁹ thus both systems lead to the same carbonyl(phosphine)rhenium intermediate **4b**. Irradiation in benzene leads to **7b** and in cyclopropane **8b** is formed; both can be observed by NMR but were too sensitive to isolate. Further photolysis of phenyl hydride **7b**, particularly in the presence of added PMe₃, provided the corresponding bis(phosphine) complex **7c**. This material was much more amenable to purification: chromatography at 15 °C on alumina III under air-free conditions provided **7c** (64%), which was fully characterized.

No intermolecular C-H activation products are formed directly from **2** or **3** in the presence of larger cycloalkanes, *n*-alkanes, or methane (however, certain ones can be obtained from cyclometalated products **5**; see below). Cyclometalation is the favored process under these conditions, and complex **5b** is formed (ca. 20% yield from **2** by ¹H NMR). Treatment of **5b** with iodoform led to the corresponding iodide **6b**; it was isolated in 18% yield based on **2** and fully characterized. Exhaustive photolysis of **2** at low concentration (10⁻⁴ M) in alkanes such as *n*-hexane and cyclohexane in the presence of added PMe₃ leads to cyclometalated bis(phosphine) complex **5c** (>20% yield by NMR). Although thermally stable (up to 125 °C in *n*-hexane), this material proved difficult to purify fully even by chromatography at -110 °C; it was characterized by ¹H, ¹³C, and ³¹P NMR and high-resolution MS.¹⁰

In both the parent Cp and C₅Me₅ series, many of the hydrido(alkyl)rhenium complexes, including the cyclometalated products **5**, react with benzene (and certain other hydrocarbons) to give intermolecular C-H insertion products, as illustrated in Scheme I. This provides evidence that these materials form small amounts of the corresponding coordinatively unsaturated reductive elimination products **4** at room temperature. The half-lives of the elimination reactions correlate with expected relative strengths of the metal-carbon bonds in these complexes.^{8b,11}

This propensity for reductive elimination was utilized in the C₅Me₅ series, with the cyclometalated complex **5c** being the most useful precursor to the bis(phosphine) C-H insertion products. However, the relative stabilities of starting material and product here are nearly comparable. Thus equilibrating mixtures of cyclometalated complex **5c** and hydridocyclopropylrhenium complex

8c, and **5c** and hydridomethylrhenium complex **9c**, are observed by NMR spectroscopy.¹² Optimum conversion of **5c** to **8c** was 33% at 45 °C with cyclopropane as solvent, and of **5c** to **9c** was 20% at 70 °C under 82 atm of CH₄ in hexane (Parr bomb), as measured by ¹H NMR spectroscopy. Hydrido cyclopropyl complex **8c** was partially purified by fast chromatography at 15 °C on alumina III, whereas **9c** required chromatography at -100 °C. Samples providing satisfactory elemental analysis could not be obtained, but both complexes were characterized fully by spectroscopy, including high-resolution MS.

In summary, cyclopentadienyl- and pentamethylcyclopentadienylrhenium complexes are capable of both intra- and intermolecular C-H activation if appropriate electron-donating ligands are attached to the metal center. The highly chemoselective behavior of these rhenium systems should allow one to activate small amounts of important hydrocarbons, such as methane, in the presence of large quantities of higher hydrocarbons. By further exploring the effect of the ancillary ligands on reactivity, we hope to find systems in which these ligands can participate in the functionalization of the activated alkanes.

Acknowledgment. We are grateful to Profs. W. A. G. Graham and W. D. Jones for helpful discussions and to the National Science Foundation for a predoctoral fellowship award to P.F.S. 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.

Registry No. **1**, 96760-24-6; **2**, 96791-01-4; **3**, 96760-25-7; **4a**, 96760-26-8; **4b**, 96760-27-9; **4c**, 96760-28-0; **5a**, 96760-29-1; **5b**, 96760-30-4; **5c**, 96760-31-5; **6b**, 96760-32-6; **7a**, 96791-02-5; **7b**, 96760-33-7; **7c**, 96760-34-8; **8a**, 96791-03-6; **8b**, 96760-35-9; **8c**, 96760-36-0; **9a**, 96760-37-1; **9c**, 96760-38-2; **10a**, 96760-39-3; **12a**, 96760-40-6; (C₅Me₅)Re(CO)₃, 12130-88-0; ReCl₃(PMe₃)₃, 96760-41-7; CH₄, 74-82-8; benzene, 71-43-2; cyclopropane, 75-19-4; *n*-hexane, 110-54-3; cyclohexane, 110-82-7; ethylene, 74-85-1; iodoform, 75-47-8.

Supplementary Material Available: Spectral and analytical data for the compounds illustrated in Scheme I (8 pages). Ordering information is given on any current masthead page.

(12) Incorporation of gaseous methane was confirmed by showing that the use of ¹³CH₄ resulted in a strongly enhanced Re-CH₃ resonance in the ¹³C{¹H} NMR spectrum.

Synthetic and Mechanistic Studies of the Retro-Claisen Rearrangement: An Example of Cation Acceleration of a [3,3]-Sigmatropic Rearrangement

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Received February 15, 1985

The Claisen rearrangement and its variants have proven to have wide generality and utility for the construction of unsaturated ketones and aldehydes with a high degree of regiochemical and stereochemical control.¹ As a member of the general class of [3,3]-sigmatropic rearrangements, the reaction is under thermodynamic control with respect to reactants and products. This fact is easily overlooked, since the Claisen rearrangement generally

(7) Intramolecular metalation of trimethylphosphine without competing intermolecular C-H activation has been observed before in several systems; for specific examples involving rhenium, see ref 2 and: Chiu, K. W.; Wong, W.-K.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1981**, 451. We cannot, of course, rule out the reversible formation of a very unstable hydridocyclohexylrhenium complex during this reaction.

(8) For results on oxidative addition of iridium into methane C-H bonds, see: (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121.

(9) We have also confirmed, as reported earlier by Graham and co-workers, that only rhenium dimers are formed on irradiation of CpRe(CO)₃ and (C₅Me₅)Re(CO)₃; cf.: (a) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65. (b) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27. Insertion into silane C-H bonds has been observed: Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, *59*, 1455.

(10) Conversion of **5c** to the corresponding iodide does not occur upon treatment with iodoform.

(11) Buchanan, J. M.; Bergman, R. G., manuscript in preparation.

(1) For reviews of the Cope and Claisen rearrangements, see: Rhodes, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Bennett, G. B. *Synthesis* **1977**, 589. Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 7181 and references cited therein.