Inter- and Intramolecular Insertion of Rhenium into Carbon-Hydrogen Bonds

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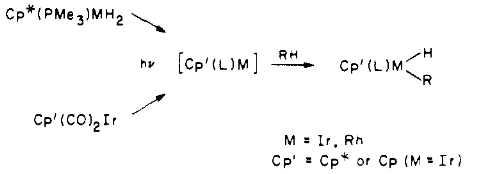
Abstract: $CpRe(PMe_3)_3$ (**1**) was synthesized in 38% yield by Na/Hg reduction of $ReCl_3(PMe_3)_3$ (**3**) with cyclopentadiene. UV irradiation of **1** in benzene and cyclopropane liberated PMe_3 and gave the respective C-H insertion products $Cp(PMe_3)_2Re(Ph)H$ (**4**, 64%) and $Cp(PMe_3)_2Re(c\text{-}C_3H_5)H$ (**5**, 38%). Irradiation of **1** in *n*-hexane or cyclopentane provided $Cp(PMe_3)_2Re(n\text{-}C_6H_{13})H$ (**8**, 15%) and $Cp(PMe_3)_2Re(c\text{-}C_5H_9)H$ (**9**, 17%) but only at less than -30 °C. Irradiation of **1** at 5-10 °C in cyclohexane afforded cyclometalated product $Cp(PMe_3)Re(\eta^2\text{-}CH_2PMe_2)H$ (**10**, 31%) and $Cp(PMe_3)_2Re(\eta^1\text{-}CH_2PMe_2)H$ (**11**, 14%). **10** can dimerize to **16** and **17**. The structure of **16** was determined by X-ray crystallography. Irradiation of **1**, or thermolysis (20 °C) of **10** in cyclohexane with methane gave $Cp(PMe_3)_2Re(Me)H$ (**12**, 43%). Irradiation of **1** with ethylene in cyclohexane gave $Cp(PMe_3)_2Re(CH{=}CH_2)H$ (**14**), which isomerized quantitatively to $Cp(PMe_3)_2Re(\eta^2\text{-}(CH_2{=}CH_2))$ (**15**, 45%) at 20 °C in benzene. Irradiation of **15** regenerated **14**, regardless of solvent. Thermolysis (20 °C) of **8** with ethylene gave almost exclusively **14**, thus ruling out **15** as the intermediate in the formation of **14**. Isolation of compounds **1**, **5**, **8**, **10**, **12**, **15**, and **16** in pure form required air-free chromatography at ca. -110 °C. An efficient synthesis of $Cp(PMe_3)_2ReH_2$ (**6**, 71% from **3**) is reported. Deprotonation of **6** followed by methylation afforded **12** (72%). All of the alkane C-H insertion products undergo facile reductive elimination of RH at room temperature.

Approaches to the functionalization of alkanes by organometallic complexes remain limited by a lack of unifying principles, despite an impressive surge of research in this area.[1] Although a few systems have recently been found which are capable of inserting into the C-H bonds of alkanes, the discovery of new systems is still in some ways serendipitous. We have begun to systematically examine several systems that involve C-H insertion by low-valent metal complexes, with the goal of understanding the effects of the ligands and the metal on their activity.[2] Of particular interest is the unusual selectivity that these systems exhibit. The C-H bonds that are preferentially attacked are often those having the highest bond dissociation energies, reactivity that is the opposite of that exhibited by free radicals.[3]

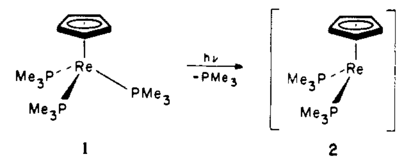
One practical application of a highly selective system might be in the catalytic functionalization of methane in the presence of other hydrocarbons.[4] Recently, a few examples of organometallic complexes that are able to insert into the C-H bonds of methane under thermal[5] and photochemical[6] conditions have appeared. The single photochemical example required the use of a perfluorinated solvent which, although inert, had poor solvating abilities. The other examples depended upon the thermodynamic advantage of inserting into a C-H bond of methane.

Current studies suggest that steric factors can strongly influence C-M bond strengths[1b] which in turn govern the thermodynamic selectivity in those systems where C-H bond insertion is reversible.[7]

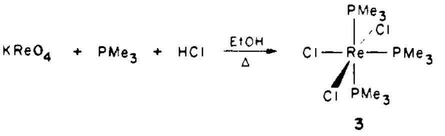
Scheme I



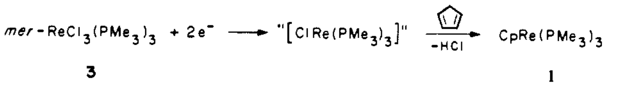
Scheme II



Scheme III



Scheme IV



The kinetic selectivities of C-H activation systems also appear to be influenced by steric factors.[8] To increase these selectivities, one must therefore create an environment that is particularly sterically demanding. However, the steric crowding must be applied judiciously, for two reasons. First, increased steric repulsions will probably weaken all of the possible metal-carbon bonds that can form and might completely inactivate the system.

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(1) General reviews of various aspects of alkane C-H activation: (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel: Dordrecht, 1984. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41-48. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269.

(2) Preliminary communication: Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358-4359.

(3) *Free Radicals*; Kochi, J. K., Ed.; John Wiley: New York, 1973; Vol I, pp 299-304; Vol II, pp 172, 690.

(4) Well-established methane to synthesis gas technology exists (steam reforming): cf. (a) Wittcoff, H. A.; Reuben, B. G. *Industrial Organic Chemicals in Perspective*; John Wiley: New York, 1980; Part 1, pp 108-119. (b) Dybkjaer, I. *CEER Chem. Econ. Eng. Rev.* **1981**, 13, 17-25. (c) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*; Verlag Chemie: Weinheim, 1978.

(5) Homogeneous examples include the following: (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493. (b) Wax, M. J.; Stryker, J. J.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121-1122. (c) Fendrick, C. M.; Marks, T. J. *Ibid.* **1984**, *106*, 2214-2216. (d) Goldschleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174-2175. Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725-733.

(6) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190-7191.

(7) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537-1550.

(8) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352-354; **1983**, *105*, 3929-3939. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723-3725. (c) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562-563. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650-1663. (d) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508-510.

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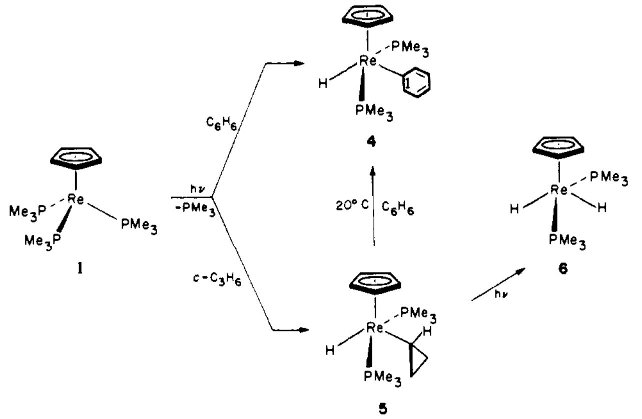
Scheme V



Second, it has been specifically demonstrated,[9] and also generally observed,[10] that increased steric crowding can promote cyclometalation, a normally unproductive side reaction.

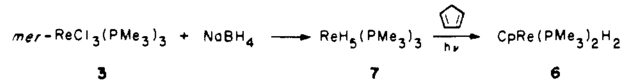
A better understanding of alkane functionalization should be achievable by studying systems that allow the observation of the initial C–H insertion product; subsequent steps that might be used for functionalization, such as ligand insertion or β-elimination, are already fairly well understood. Systems which can generate an observable hydridoalkyl complex are known for both rhodium and iridium (Scheme I).[8] By systematically varying the ligands and/or metal, one might be able to understand how they influence the C–H insertion step and then use this information to design new systems. Following our work with iridium, we reasoned that an ideal candidate for further explorations might be rhenium.[11] The cyclopentadienylrhenium system needs an additional two-electron ligand to make it isoelectronic with the rhodium and iridium complexes. The result should be an increase in steric demand, and we anticipated increased selectivity in its reactions.

Our specific goal, then, was to generate the coordinatively unsaturated rhenium fragment CpRe(PMe$_3$)$_2$. For several reasons, we decided that trisphosphine **1** (Scheme II) might be an excellent precursor. We intended to generate the unsaturated intermediate **2** by photolysis of **1**, since ligand loss is a common result of light absorption.[12]

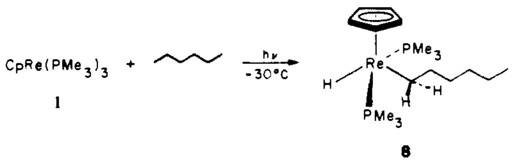
Results and Discussion

Synthesis of CpRe(PMe$_3$)$_3$. *mer*-Trichlorotris(trimethylphosphine)rhenium (**3**) was synthesized in 85% yield by the reduction of potassium perrhenate with trimethylphosphine in the presence of aqueous HCl, in analogy with similar literature procedures (Scheme III).[13] We envisioned that a two-electron reduction of **3** might afford a highly reactive, coordinatively unsaturated rhenium (I) trisphosphine complex, perhaps ClRe(PMe$_3$)$_3$,[14] which could add to the C–H bond of cyclopentadiene (Scheme IV). Loss of HCl would then provide the desired η^5-cyclopentadiene trisphosphine complex **1**.

Scheme VI



Scheme VII



Of several reducing agents that we tried, only sodium amalgam provided a species capable of being converted to the cyclopentadienyl compound. Treatment of **3** with Na/Hg, followed by addition of cyclopentadiene and potassium carbonate, provided η^5-cyclopentadienyltris(trimethylphosphine)rhenium (CpRe(PMe$_3$)$_3$) (**1**).[15] In practice, cleaner preparations of **1** were obtained by combining all of the reagents simultaneously.

Isolation of this highly air-sensitive material proved to be difficult. It is unstable to the common chromatographic supports (alumina, silica gel, Florisil) and is not easily recrystallized due to its high solubility in most solvents. Purification was finally achieved by rapid, air-free filtration through alumina(III) at −100 to −110 °C. Trisphosphine **1** was obtained in 38% yield after lyophilization from cyclohexane and was pure by spectroscopic and combustion analyses. Particularly characteristic of this material was the Cp resonance in the ^{1}H NMR spectrum, which was a binomial quartet (J = 0.8 Hz) due to coupling to three identical phosphorus nuclei. Similar attempts to make the η^5-pentamethylcyclopentadienyl analogue were unsuccessful.

UV Irradiation of CpRe(PMe$_3$)$_3$

Irradiation in Benzene or Cyclopropane. Irradiation of either benzene or cyclopropane solutions of **1** at 5–10 °C in Pyrex vessels liberated trimethylphosphine and cleanly provided the products of C–H insertion, **4** and **5** (Scheme V). Hydridophenyl complex **4**, although air sensitive, was easily isolated in 64% yield by recrystallization from pentane. In contrast, the analogous cyclopropyl complex **5** could not be crystallized from the reaction mixture, nor did it survive room temperature chromatography. Purification attempts were further hampered by its thermal instability. Reductive elimination occurred in benzene solution ($\tau_{1/2}$ ≈ 24 h) to provide phenyl complex **4** and free cyclopropane (identified by ^{1}H NMR spectroscopy). Careful air-free chromatography on alumina(III) at −100 to −110 °C addressed all of these concerns and provided colorless, analytically pure crystals of **5** in 38% yield.

NMR spectroscopy indicated that the PMe$_3$ ligands in **4** and **5** were chemically equivalent. This, coupled with the fact that the hydride resonances were split into a 1:2:1 triplet, suggests that phosphorus ligands are located trans to one another in these adducts.[16] Additional information concerning the nature of the alkyl group is provided by the fine splitting of the hydride resonance in **5**, which is coupled to the α-hydrogen of the cyclopropyl group with J = 4.9 Hz. No H–H coupling to the hydride resonance was observed for **4**.

Prolonged irradiation of cyclopropane solutions of CpRe(PMe$_3$)$_3$ caused extensive decomposition of the C–H insertion product, an event that did not occur in the case of benzene photolyses. The

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(9) Chency, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 754–763; 860–865.

(10) Examples of (η^2-CH$_2$PMe$_2$)MH complexes include (L = PMe$_3$) (a) L$_4$(η^2-CH$_2$PMe$_2$)MoH, L$_2$(η^2-CH$_2$PMe$_2$)MoH$_2$: Cloke, F. G. N.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393–394. (b) L$_4$(η^2-CH$_2$PMe$_2$)WH: Gibson, V. C.; Grebenik, P. D.; Green, M. L. H. *Ibid.* **1983**, 1101–1102. (c) L$_4$(η^2-CH$_2$PMe$_2$)(HNPh)ReH: Chiu, K. W.; Wong, W.-K.; Wilkinson, G. *Ibid.* **1981**, 451–452. (d) L$_3$(η^2-CH$_2$PMe$_2$)FeH: Karsch, J. J.; Klein, H. F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637–638. Karsch, H. H.; Klein, H. F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212. Rathke, J. W.; Muetterties, E. L.; *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273. (e) L$_3$(η^2-CH$_2$PMe$_2$)RuH: Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *201*, C60–C64. (f) L$_3$(η^2-CH$_2$PMe$_2$)OsH: Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547–549.

(11) Other homogeneous rhenium systems that activate alkanes: (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243–1244. Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606–607. Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235–1236. Baudry D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788–789. Baudry, D.; Epritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283–1286. (b) Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39–C43.

(12) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

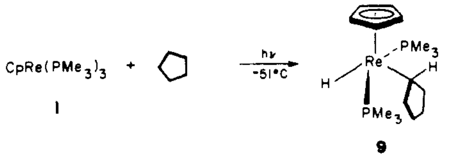
(13) Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64–66.

(14) ClRe(PMe$_2$Ph)$_4$(N$_2$) and similar complexes are known: Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc.* **1969**, 687–688.

(15) 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*, 441–451.

(16) A fluxional geometry is unlikely in view of the nonfluxional character of compound **16** (vide infra).

Scheme VIII



major decomposition product was dihydride **6**.[17] To confirm this assignment we independently synthesized **6** (Scheme VI). Sodium borohydride reduction of $ReCl_3(PMe_3)_3$ in ethanol cleanly provided the pentahydride **7**.[18] Subsequent UV irradiation in benzene with 10 equiv of cyclopentadiene afforded a 71% yield (based on $ReCl_3(PMe_3)_3$) of the trans dihydride **6**, after chromatography.[19]

Irradiation in *n*-Hexane. Irradiation of $CpRe(PMe_3)_3$ in *n*-hexane at 5–10 °C produced C–H insertion product **8** (Scheme VII), but the reaction was complicated by the presence of several other products (**10** and **11**—see cyclohexane photolysis section). The discovery of the high thermal sensitivity of the hexane adduct prompted subsequent photolyses to be performed at −30 °C; this resulted in substantially cleaner reaction mixtures.

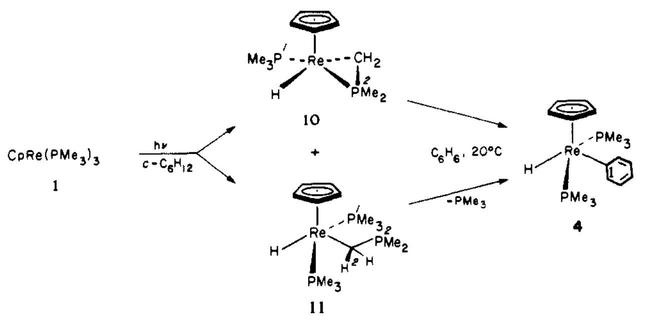
Hydrido(*n*-hexyl) complex **8** has a room temperature half-life in solution of ca. 14 minutes, rapidly decomposing in benzene to give phenyl adduct **4** and free hexane. Nevertheless, **8** could still be isolated as colorless crystals in 15% yield, by modifying the low-temperature chromatography procedure used to isolate the cyclopropyl complex. The overall recovery of **8** was poor because of the steady decomposition to dihydride **6** that occurred while on the column.

Both ^1H and proton-coupled ^{13}C NMR spectroscopy support the assignment of the *n*-hexyl derivative as the sole product of C–H insertion. In particular, the hydride resonance is a triplet of triplets due to coupling to phosphorus ($^2J_{PH}$ = 50.1 Hz) and to the α-CH_2 protons of the hexyl group ($^3J_{HH}$ = 3.5 Hz). UV irradiation of $CpRe(PMe_3)_3$ in hexane-d_{14} produced a complex with the same Cp and PMe_3 resonances but without hexyl or M–H protons.

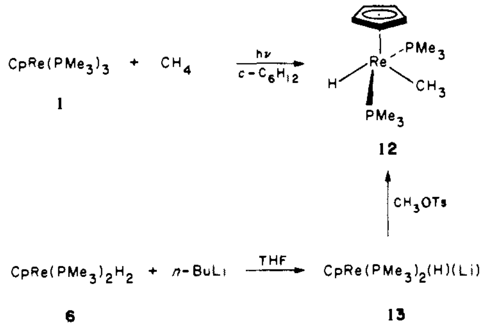
Irradiation in Cyclopentane and Cyclohexane. The absence of products due to insertion into the secondary C–H bonds of hexane prompted a similar irradiation in cyclopentane at −51 °C. At low conversions, an adduct identified as the C–H insertion product of cyclopentane **9** was readily produced, but the reaction was inefficient (Scheme VIII). Results were consistently hampered by low yields (maximum 17% at 63% conversion by ^1H NMR external standard) and by competing formation of dihydride **6**. Isolation was not attempted because of the extreme tendency of the complex to reductively eliminate cyclopentane ($\tau_{1/2} < 30$ s at room temperature). Identification was based on ^1H NMR spectroscopy, which showed by the multiplicity of the hydride signal (dt, J = 5.4, 51.3 Hz) that a secondary center had been attacked. Warming **9** in toluene-d_8 caused the liberation of cyclopentane (88% of theory by ^1H NMR spectroscopy) and the formation of the C–H insertion products of toluene.[20]

The above results suggest that C–H insertion into medium-sized cycloalkane C–H bonds ought to be entirely reversible at temperatures higher than −30 °C, and they therefore might function as inert solvents. This is borne out by irradiation of $CpRe(PMe_3)_3$ in cyclohexane at 5–10 °C. No solvent derived C–H insertion products are observed; irradiation in cyclohexane or cyclohexane-d_{12} produced the same two hydride products (Scheme IX). Prolonged irradiation resulted in formation of dihydride **6** (whether or not the solvent was deuterated).

Scheme IX



Scheme X



The major product of the irradiation in cyclohexane was identified as cyclometalated complex **10**, formed by insertion of the metal center in the unsaturated intermediate **2** into a C–H bond in one of the bound PMe_3 groups. This material was isolated in 31% yield as a colorless, crystalline solid by chromatography at −110 °C, although some loss of material was incurred. Like the other C–H insertion products, **10** is both air and thermally sensitive. It reacts with benzene to give hydridophenyl complex **4** and can also dimerize (vide infra).

The assigned structure is fully supported by spectroscopic and combustion analyses. The presence of the η^2-CH_2PMe_2 moiety is convincingly demonstrated by the large upfield shift of the ring phosphorus in the ^{31}P NMR spectrum, an observation that is well-precedented for such structures.[21] We assign a trans relationship to the phosphorus atoms on the basis of their nearly identical NMR couplings to the hydride ligand.

The minor product (14% NMR yield after 50% conversion) was never observed to elute from a chromatography column under any conditions. It is also unstable at room temperature ($\tau_{1/2} \approx$ 2 h); warming in benzene caused reductive elimination of trimethylphosphine (98% of theory) and formation of phenyl complex **4**. The photolysis mixtures are simple at early conversion times, with cyclometalated complex **10** being the only coproduct (ca. 1:1 ratio). Spectroscopic evidence implicates the hydrido((η^1-dimethylphosphino)methyl) structure **11** for this product.[22] The ^{31}P NMR spectrum indicates that two of the three phosphorus atoms are equivalent (δ −37.15, d, J = 20.7 Hz) and that they

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[17] (a) Green, M. L. H.; O'Hare, D.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1985**, 356–357. (b) Jones, W. D.; Maguire, J. A., personal communication.

[18] Based on a similar preparation of $ReH_5(PMe_2Ph)_3$: Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64–66.

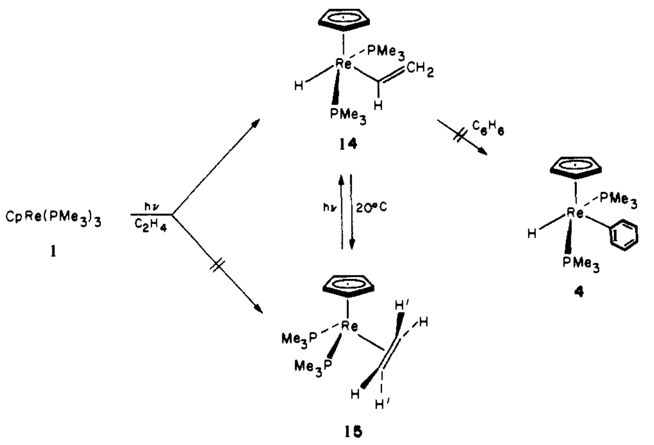
[19] Other researchers report that little CpL_2ReH_2 is formed upon photolysis of L_3ReH_5 with cyclopentadiene: (a) (L = PMe_2Ph) ref 11b. (b) (L = PPh_3) Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951–953.

[20] When **1** is irradiated (or any of the alkyl(hydrides) $CpReL_2(R)(H)$ is allowed to decompose thermally) in toluene, two products are formed. These were not isolated or fully characterized. ^1H NMR spectra of these products were obtained by generating them in perprotiotoluene, followed by solvent removal and redissolution in toluene-d_8. Partial ^1H NMR (toluene-d_8): (isomer A) δ 4.51 (s), 1.30 (virtual d, J = 8.2 Hz), −13.07 (t, J = 52.3 Hz); isomer B differs only in the shift of its Cp resonance δ 4.49 (s).

[21] Andersen, R. A.; Mainz, V. V. *Organometallics* **1984**, *3*, 675–678 and references cited therein.

[22] Examples of η^1-CH_2PMe_2 groups are rare. With Zr: (a) Karsch, H. H.; Appelt, A. *Phosphorus Sulfur* **1983**, *18*, 287–290. (b) Karsch, H. H.; Mullen, G.; Kruger, C. *J. Organomet. Chem.* **1984**, *273*, 195–212. (c) Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220–222. With Re: (d) Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 37–44. With Al, Li, and Sn: (e) Karsch, H. H.; Appelt, A.; Kohler, F. H.; Muller, G. *Organometallics* **1985**, *4*, 231–238. (f) Karsch, H.; Schmidbauer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 762–767. (g) Karsch, H. H.; Appelt, A. *Ibid.* **1983**, *38B*, 1399–1405. The ^{31}P NMR shift of the noncoordinated PMe_2 group of **11** is substantially downfield from that of free trimethylphosphine. This is also observed in the above compounds.

Scheme XI



couple equally to the third (δ -26.60, t, J = 20.5 Hz). The multiplicity of the methylene resonance in the ^{1}H NMR spectrum confirms the presence of these phosphorus atoms. It consists of a triplet of doublet of doublets (J = 10.2, 5.9, 2.4 Hz), which collapses to a doublet ($^3J_{H\text{-}ReH}$ = 2.4 Hz) upon broadband ^{31}P decoupling.[23]

Irradiation with Methane or Ethylene in Cyclohexane. Irradiation of CpRe(PMe$_3$)$_3$ in cyclohexane at 5–10 °C under 25 atm of methane produced the C–H insertion product of methane **12** as the major product (Scheme X). Chromatography of this mixture at −110 °C afforded analytically pure **12** (43%) as a pale yellow oil, along with cyclometalated complex **10** (12%). Spectral data were entirely analogous to those of the other C–H insertion products and fully support the assigned structure. In particular, the coupling to the methyl protons is revealed as a quartet (J = 2.6 Hz) in the hydride resonance of the ^{1}H NMR spectrum.

The hydridomethyl complex is thermally unstable at room temperature. In benzene it reductively eliminates methane and cleanly forms hydridophenyl complex **4**. Independent synthesis of hydridomethyl complex **12** was achieved in 78% yield (NMR) by deprotonation of dihydride **6** with *n*-butyllithium in tetrahydrofuran, followed by treatment with methyl *p*-toluenesulfonate (Scheme X).

We anticipated that a similar photolysis with ethylene might provide either the C–H insertion product **14** or the η^2 complex of ethylene **15**. In practice the former predominates. Irradiation of CpRe(PMe$_3$)$_3$ under ca. 25 atm of ethylene (5–10 °C, cyclohexane) produced hydridovinyl complex **14** in 45% yield (Scheme XI). Unfortunately, **14** could not be purified, even by chromatography at −110 °C on a variety of supports. Structural characterization therefore depends upon NMR and IR spectroscopy and on the fact that warming **14** to room temperature converts it quantitatively to the η^2-ethylene complex **15**. This reaction takes place in benzene or other solvents without any production of free ethylene. Purification of **15** required chromatography at −110 °C, even though it is thermally stable at room temperature under nitrogen. The resulting volatile, pale yellow, crystalline material was obtained in 45% yield.

Full characterization, including combustion analysis, supported the assigned structure. The η^2-ethylene ligand is rapidly rotating on the NMR time scale (300 MHz) at room temperature. The two magnetically inequivalent sets of ethylene protons couple with different coupling constants to the phosphorus nuclei, resulting in a non-first-order ^{1}H NMR splitting pattern. Decoalescence of this peak occurs near −80 °C at 300 MHz in toluene-d_8, but significant line broadening prevented the observation of the static spectrum.

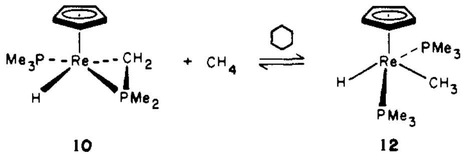
Interestingly, irradiation (5–10 °C, 10 h) of purified **15** in toluene-d_8 regenerated hydridovinyl complex **14**. Under these conditions a 6:1 mixture of **14**:**15** could be reached, without major side reactions. Full spectroscopic characterization of **14** was achieved from this solution.

Table I. Stabilities of the C–H Insertion Products in Benzene-d_6

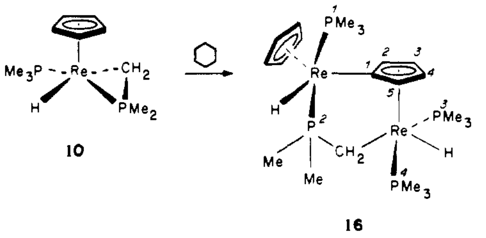
compound		ca. $\tau_{1/2}$[a] (20 °C)
Cp(PMe$_3$)$_2$(H)Re(Ph)	**4**	5.1 h[b]
Cp(PMe$_3$)$_2$(H)Re(c-C$_3$H$_5$)	**5**	24 h
Cp(PMe$_3$)$_2$(H)Re(CH=CH$_2$)	**14**	24 h[c]
Cp(PMe$_3$)$_2$(H)Re(CH$_3$)	**12**	8 h
Cp(PMe$_3$)(H)Re(η^2-CH$_2$PMe$_2$)	**10**	6 h
Cp(PMe$_3$)$_2$(H)Re(η^1-CH$_2$PMe$_2$)	**11**	2 h
Cp(PMe$_3$)$_2$(H)Re(n-C$_6$H$_{13}$)	**8**	14 min
Cp(PMe$_3$)$_2$(H)Re(c-C$_5$H$_9$)	**9**	<30 s[d]

[a] Reductive elimination of RH in benzene-d_6 to form **4**-d_6. [b] At +56 °C. [c] Isomerizes to form η^2-ethylene complex **15**. [d] Not observable at room temperature by ^{1}H NMR spectroscopy.

Scheme X II



Scheme XIII



Reactions of the C–H Insertion Products

Product Stability and Thermal C–H Activation. Warming any of the C–H insertion products to room temperature or above causes the reductive elimination of R–H (R = phenyl, alkyl, or vinyl). In all but the case of **14** (R = vinyl), the complex either reacts with solvent (if aromatic) to form a C–H insertion product or else cyclometalates (e.g., in cyclohexane). Benzene adduct **4** is the most stable, requiring heating to +56 °C in order to effect exchange with benzene-d_6 solvent. This reaction exhibited clean first-order kinetics with $k = 3.8 \times 10^{-5}$ s^{-1}. The reaction of the vinyl complex **14** is unique in that the ethylene does not leave the coordination sphere of rhenium—reductive elimination is concurrent with η^2-olefin coordination. Although the absolute stabilities of the insertion products are lower for rhenium than for iridium,[7] the relative stabilities parallel each other (Table I).

With the proper choice of C–H activation precursor and hydrocarbon, one can easily carry out several C–H activation reactions thermally rather than photochemically. Thus a solution of cyclometalated complex **10** in cyclohexane under 25 atm of methane will equilibrate during 3 days to achieve a ratio of **12**/**10** of 2.5 (K_{eq} = 1.0)[24] (Scheme XII). Similarly, **10** in neat cyclopropane quantitatively forms the cyclopropane adduct, which is indefinitely stable in this solvent.

Dimerization of Cyclometalated Complex 10. If **10** alone is allowed to stand at room temperature in cyclohexane or *n*-hexane, it undergoes bimolecular C–H insertion to form dimeric complexes. The resulting mixture consists of two products, **16** and **17**, in a ratio of ca. 2:1. Upon low-temperature chromatography, these two materials are either inseparable (alumina) or else are destroyed (silica gel). However, when the crude mixture was allowed to

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(23) The apparent magnetic equivalence of the CH$_2$ protons can arise by rapid rotation about the CH$_2$–M bond. This observation as well as the downfield shift of the PMe$_2$ phosphorus nucleus indicates that there is little contribution from an η^2-CH$_2$PMe$_2$ structure.

(24) The concentration of methane was determined by ^{1}H NMR integration (using conventional medium-walled NMR tubes, rated to 25 atm) of the methane resonance vs. the Cp of cyclometalated complex **10**.

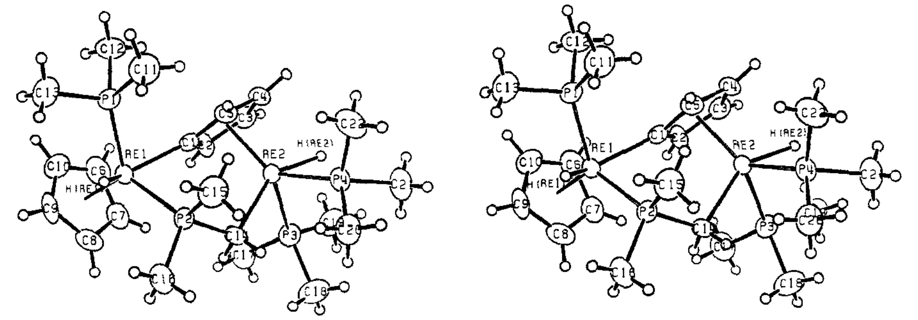


Figure 1. Ortep stereoview of the structure of dimer **16** at −108 °C. The ellipsoids represent the 75% probability surface.

Table II. ^{13}C NMR data for **16**[a]

δ(ppm)	assigned	{^{1}H} appearance (J, Hz)	$^1J_{CH}$ (Hz)
89.51	C2 (C5)	d, J = 8.9	d, J = 170
86.25	C5 (C2)	dt, J = 14.0, 8.9	d, J = 167
80.22	η^5-Cp	s	d, J = 176
64.60	C3 (C4)	s	d, J = 174
64.25	C4 (C3)	s	d, J = 174
36.07	C15 (C16)	d, J = 23.9	q, J = 125
28.84	C16 (C15)	d, J = 27.5	obscured
27.87	PMe$_3$	d, J = 29.5	q, J = 127
27.28	PMe$_3$	d, J = 27.9	q, J = 127
25.83	PMe$_3$	d, J = 28.1	q, J = 127
15.85	C14	q, J = 10.8	t, J = 121

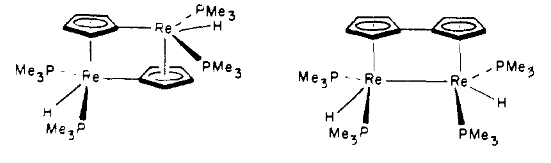
[a] At 125.76 MHz in benzene-d_6, 20 °C. C1 was not observed, due in part to the limited solubility at **16**.

stand at room temperature in hexane, some of the major product crystallized from solution. Chromatography of this material (−100 °C, alumina(III)) allowed its isolation as colorless crystals in 18% yield.

Full spectroscopic analysis, including mass spectroscopy, suggested the structure shown in Scheme XIII,[25] which could arise by a mutual C–H insertion between two molecules of **10**. ^{1}H NMR spectroscopy revealed most of the essential features, such as two nonequivalent hydride ligands, three different coordinated trimethylphosphine groups, the dimethylphosphinomethyl moiety, and the two different cyclopentadienyl groups: one η^5 and freely rotating, the other μ-η^1:η^5 and conformationally fixed. In the ^{13}C NMR spectrum, the μ-η^1:η^5 Cp ring carbons showed unusual coupling to the phosphorus nuclei (Table II): C3 and C4 were both singlets, C2 (or C5) was a doublet (J = 8.9 Hz), and C5 (or C2) was a doublet of apparent triplets (J = 14.9, 8.9 Hz). The ^{31}P NMR spectrum was also interesting in that P2 couples to P3 and P4 with vastly different coupling constants (3.3 vs. 45.4 Hz).

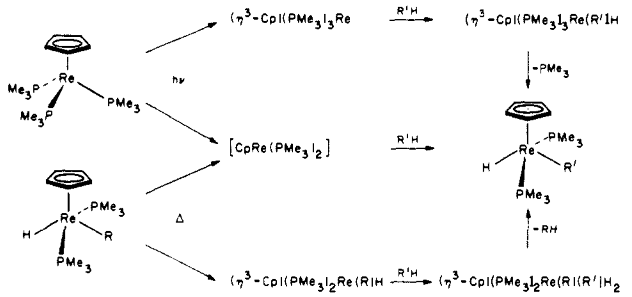
In order to confirm our structural assignment, we performed an X-ray diffraction study. Colorless, blocklike crystals of **16** were obtained from pentane–toluene solution. X-ray data were collected at −108 (4) °C. The structure was solved by Patterson methods and was refined by standard least-squares Fourier techniques; crystal and data collection parameters, along with data from the results of the study, are given in Tables III–VI. The hydride ligands were located but not refined. Each of the rhenium centers has approximately a four-legged piano stool geometry (Figure 1), with some variation in the bond angles (Tables III–V). The bonding of the rhenium atoms to the Cp rings is not regular; each ring is slipped. The Re1–Cp centroid vector forms an angle of 87° relative to the plane of the Cp ligand, leaning toward C7. The corresponding vector for Re2 forms an angle of 83°, tilted away from C1. Re1 and its hydride lie within the plane of the μ-η^1:η^5 Cp ring.

Scheme XIV



17a **17b**

Scheme XV



The structural results provide explanations for some of the unusual features of the NMR spectra of **16**. The anomalous coupling between P2, P3, and P4 can be explained by invoking a Karplus-like argument. The dihedral angle between P2 and P3 is 155° while that between P2 and P4 is 105°. This suggests that the smaller coupling constant (3 Hz) is that due to $^3J_{P2P4}$, whose dihedral angle is closer to 90°. The larger coupling constant would then be due to $^3J_{P2P3}$.

The ^{13}C NMR coupling constants are less straightforward. Of the four μ-η^1:η^5 Cp carbons that were observed in the ^{13}C NMR spectrum (C2–C5), those that couple to phosphorus (C2 and C5) share the common factor of being nearly trans to a geminal phosphorus atom (Table IV). It is reasonable to assign an 8.9-Hz value to each of these. One of these carbons (C2 or C5) then couples to two additional phosphorus nuclei (J = 8.9, 14.9 Hz), probably P1 and P2.

If vicinal couplings such as these obey a Karplus rule, one anticipates that C2 and C5 would couple to P1 and P2 in nearly identical ways, since their dihedral angles differ by exactly 180°.[26] Since they apparently do not, we offer two explanations: either a normal Karplus-like relationship is not valid in this molecule or else through-space coupling is responsible.[27] The latter possibility is suggested by the C5–P1 and C5–P2 distances, which are among the shortest nonbonded C–P distances in the molecule (Table III).

The identity of the second product is as yet unconfirmed, since we have not been able to isolate it from the reaction mixture. ^{1}H and ^{31}P NMR data are consistent with structures **17a** or **17b** (Scheme XIV).[28]

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[25] Other examples of μ-η^2-CH$_2$PMe$_2$ ligands: (a) Graimann, C. E.; Green, M. L. H. *J. Organomet. Chem.* **1984**, *275*, C12–C14. (b) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601–603. (c) Klein, H.-F.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1391–1397. (d) Reference 21. (e) Reference 22b. See, also: (d) Cotton, F. A. et al. *Inorg. Chim. Acta* **1975**, *15*, 155.

[26] A dinuclear Ir–W complex appears to conform to such a Karplus rule: Pregosin, P. S.; Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 668–669.

[27] Through-space coupling from phosphorus to Cp protons has been postulated: Coolbaugh, T. S.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 6310–6318 and references cited therein.

Table III. Selected Intramolecular Distances and esd's (Å) for Dimer **16**[a]

atom 1	atom 2	distance
Re1	P1	2.319 (1)
Re1	P2	2.321 (1)
Re1	C1	2.152 (4)
Re1	H (re1)	1.56
Re1	C6	2.264 (5)
Re1	C7	2.222 (4)
Re1	C8	2.256 (4)
Re1	C9	2.311 (4)
Re1	C10	2.314 (5)
Re1	CP2	1.929
Re2	P3	2.321 (1)
Re2	P4	2.315 (1)
Re2	C14	2.246 (4)
Re2	H (Re2)	1.71
Re2	C1	2.445 (4)
Re2	C2	2.295 (4)
Re2	C3	2.196 (4)
Re2	C4	2.192 (4)
Re2	C5	2.258 (4)
Re2	CP1	1.929
P2	C14	1.794 (4)
P2	C15	1.827 (5)
P2	C16	1.837 (5)
C1	C2	1.407 (6)
C1	C5	1.453 (6)
C2	C3	1.431 (6)
C3	C4	1.429 (6)
C4	C5	1.423 (6)
C6	C7	1.434 (7)
C6	C10	1.406 (7)
C7	C8	1.405 (6)
C8	C9	1.436 (7)
C9	C10	1.391 (7)

atom 1	atom 2	distance[b]
P1	P2	3.763 (2)
P3	P4	3.525 (2)
C1	P1	3.006 (4)
C1	P2	2.816 (4)
C2	P2	3.851 (5)
C2	P3	3.537 (5)
C5	P1	3.353 (4)
C6	P2	3.314 (4)
C5	P4	3.556 (4)
C3	P3	3.596 (4)
C4	P4	3.469 (5)
C6	P1	3.737 (5)
C7	P2	3.554 (5)
C8	P2	3.396 (5)
C9	P1	3.779 (5)
C10	P1	3.346 (5)

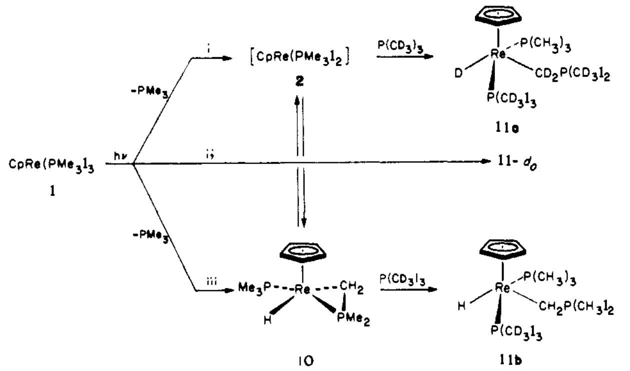
[a] CP1 and CP2 are the centroids of the cyclopentadienyl rings that are η^5-bonded to RE2 and RE1, respectively. [b] Intramolecular nonbonded distances to phosphorus (less than 4.0 Å).

Table IV. Selected Intramolecular Bond Angles and esd's (deg) for Dimer **16**[a]

atom 1	atom 2	atom 3	angle
CP2	Re1	P1	123.59
CP2	Re1	P2	126.62
CP2	Re1	C1	115.94
CP2	Re1	H (Re1)	114.28
P1	Re1	P2	108.37 (4)
C1	Re1	H (Re1)	129.76
C1	Re1	P1	84.39 (12)
C1	Re1	P2	77.9 (12)
H (Re1)	Re1	P1	68.98
H (Re1)	Re1	P2	71.78
CP1	Re2	P3	129.51
CP1	Re2	P4	129.55
CP1	Re2	C14	109.62
CP1	Re2	H (Re2)	104.47
P3	Re2	P4	98.98 (4)
C14	Re2	H (Re2)	145.67
C14	Re2	P3	80.95 (11)
C14	Re2	P4	88.44 (12)
H (Re2)	Re2	P3	74.32
H (Re2)	Re2	P4	72.62
C1	Re2	P3	124.02 (11)
C2	Re2	P3	100.03 (11)
C3	Re2	P3	105.45 (12)
C4	Re2	P3	139.96 (12)
C5	Re2	P3	158.75 (11)
C1	Re2	P4	131.93 (11)
C2	Re2	P4	160.54 (13)
C3	Re2	P4	131.90 (12)
C4	Re2	P4	100.62 (11)
C5	Re2	P4	102.07 (11)
Re1	C1	Re2	130.49 (19)
Re1	C1	C2	125.7 (3)
RE1	C1	C5	130.5 (3)
RI1	P2	C14	114.58 (15)
P2	C14	Re2	114.58 (21)
C2	C1	C5	103.8 (4)
C1	C2	C3	111.5 (4)
C2	C3	C4	107.0 (4)
C3	C4	C5	106.5 (4)
C1	C5	C4	110.8 (4)
C7	C6	C10	107.5 (4)
C6	C7	C8	108.0 (4)
C7	C8	C9	107.4 (4)
C8	C9	C10	100.2 (4)
C6	C10	C9	108.9 (4)

[a] CP1 and CP2 are the centroids of the cyclopentadienyl rings that are η^5-bonded to RE2 and RE1, respectively.

Scheme XVI



Mechanisms of Rhenium C–H Insertions

The simplest mechanistic hypothesis for both the thermal and the photochemical C–H insertion reactions of these rhenium compounds involves an unsaturated intermediate **2** (Scheme XV). An alternative way to open the necessary coordination site would be by an η^5 to η^3 isomerization of the cyclopentadienyl ring. This seems less likely as a mechanism common to both the photochemical and thermal routes, since they must proceed through intermediates that have the metal in different oxidation states (Re^I) vs. Re^{III}). In addition, the hydridoalkyl complexes are cleanly converted to **4**-d_6 when thermolyzed in benzene-d_6. This argues against an intermediate such as $(\eta^3\text{-Cp})(PMe_3)_2Re(R)(R')H_2$ (Scheme XV), which might interchange the hydrogen isotopes bonded to the metal.

We have not determined the role of cis–trans isomerism at the metal center in the rhenium reactions. If a cis geometry is required for reductive elimination[29] and its microscopic reverse, C–H in-

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[28] Examples of hydridometal complexes having structures similar to **17a** and **17b**: (a) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99–100. (b) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29–40. (c) Barral, M. d. C.; Green, M. L. H.; Jimenes, R. *Ibid.* **1982**, 2495–2498.

[29] Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

Table V. Positional Parameters and Their Estimated Standard Deviations for Dimer **16**

atom	*x*	*y*	*x*	*B* (Å^2)
Re1	0.05847 (1)	−0.00167 (2)	0.36813 (1)	1.292 (5)
Re2	0.00165 (1)	0.00007 (2)	0.16218 (1)	1.169 (5)
P1	0.05738 (9)	−0.2571 (2)	0.37433 (7)	1.55 (3)
P2	−0.0835 (1)	−0.0753 (2)	0.30066 (7)	1.48 (3)
P3	−0.0229 (1)	0.3267 (2)	0.13843 (7)	1.77 (3)
P4	−0.1395 (1)	0.0406 (2)	0.08516 (7)	1.60 (3)
C1	−0.0758 (4)	−0.0384 (6)	0.2689 (3)	1.5 (1)
C2	0.1393 (4)	0.0354 (7)	0.2402 (3	1.7 (1)
C3	0.1383 (4)	−0.0232 (6)	0.1756 (3)	1.6 (1)
C4	0.0681 (4)	−0.1344 (6)	0.1608 (3)	1.7 (1)
C5	0.0275 (4)	−0.1378 (6)	0.2162 (3)	1.5 (1)
C6	0.2072 (4)	−0.0794 (7)	0.3972 (3)	2.3 (1)
C7	0.1445 (4)	0.2013 (6)	0.3788 (3)	2.0 (1)
C8	0.0916 (4)	0.2112 (6)	0.4260 (3)	2.3 (1)
C9	0.1214 (4)	0.0947 (7)	0.4739 (3)	2.4 (1)
C10	0.1912 (4)	0.0160 (7)	0.4556 (3)	2.2 (1)
C11	−0.0327 (4)	−0.3824 (7)	0.3284 (3)	2.5 (1)
C12	−0.1598 (4)	−0.3464 (7)	0.3591 (3)	2.3 (1)
C13	0.0614 (4)	−0.3239 (7)	0.4579 (3)	2.7 (1)
C14	−0.0759 (4)	0.1863 (6)	0.2302 (3)	1.6 (1)
C15	−0.1738 (4)	−0.0612 (7)	0.2673 (3)	2.5 (1)
C16	−0.1504 (4)	0.1891 (8)	0.3454 (3)	2.4 (1)
C17	−0.1084 (5)	0.4278 (7)	0.2029 (3)	2.7 (1)
C18	−0.0731 (5)	0.4561 (8)	0.1224 (3)	2.9 (2)
C19	0.0663 (4)	0.3649 (7)	0.0646 (3)	2.5 (1)
C20	−0.2510 (4)	0.1084 (8)	0.0961 (3)	2.6 (1)
C21	−0.1534 (4)	0.1016 (7)	−0.0013 (3)	2.6 (1)
C22	−0.1699 (4)	−0.1531 (7)	−0.0688 (3)	2.8 (1)
H (Re2)	0.0215	0.0820	0.0840	4.8[a]
H (Re1)	−0.0195	−0.0566	0.4004	4.0[a]

[a] Atoms included but not refined.

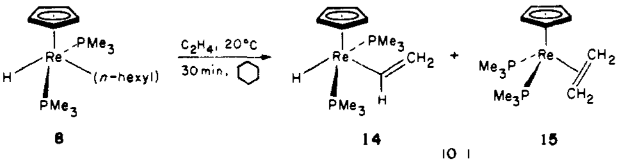
sertion, then a lower limit for the rate of cis–trans isomerization can be estimated from the rate of reductive elimination of cyclopentane from **9** ($k \geq 2 \times 10^{-2}$ s^{-1} at 20 °C).

Formation of (Dimethylphosphino)methyl Complex 11. The trimethylphosphine leaving group in the photolysis of trisphosphine **1** is itself susceptible to C–H insertion, since (dimethylphosphino)methyl complex **11** can be formed. There are at least three plausible mechanisms for the photolytic transformation of CpRe(PMe$_3$)$_3$ to **11** (Scheme XVI): (i) intermolecular C–H activation of free trimethylphosphine by the unsaturated intermediate **2**; (ii) intramolecular C–H insertion without loss of free trimethylphosphine; and (iii) intermolecular nucleophilic attack by free trimethylphosphine on the cyclometalated complex **10**.

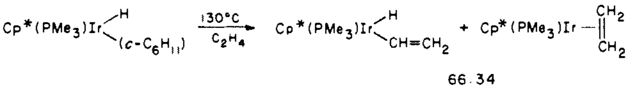
Of these we can definitely exclude mechanism i. Irradiation of a solution of CpRe(PMe$_3$)$_3$ with 1 equiv of P(CD$_3$)$_3$ in C$_6$D$_{12}$ showed <5% incorporation of deuterium into the –PMe$_2$ position by ^{1}H NMR spectroscopy. We were unable to accurately determine the extent of deuterium incorporation into the coordinated PMe$_3$ groups due to overlap with the remaining **1**, information that might have tested mechanism iii. An alternate test of mechanism iii was performed by irradiating a solution that was 0.01 M in both cyclometalated complex **10** and P(CD$_3$)$_3$—conditions that simulate the early part of a CpRe(PMe$_3$)$_3$ photolysis. Less than 5% conversion to **11** was observed by ^{1}H NMR spectroscopy after irradiation for 1 h at 5–10 °C, in contrast to similar CpRe(PMe$_3$)$_3$ irradiations where ca. 1:1 mixtures of **10**:**11** are observed. These results are most consistent with mechanism ii[30] and indicate that free trimethylphosphine is not involved in the photolytic isomerization of CpRe(PMe$_3$)$_3$ to **11**.

Interestingly, photoexcited **10** can enter into a reaction manifold similar to that of mechanisms i and iii, but only at higher concentrations of trimethylphosphine. Irradiation of a solution that is 0.01 M in cyclometalated complex **10** and 0.4 M in P(CD$_3$)$_3$ for 1 h (5–10 °C) results in a 1:1 mixture of CpRe(PMe$_3$)$_3$ and **11**. ^{1}H NMR spectroscopy disclosed only 4.0 (1) protons in the PMe$_2$ resonance of **11**, which is consistent with a 1:2 mixture of **11a** and **11b**. A similar reaction mixture kept in the dark (5–10 °C) showed no reaction after 1 h. One useful result of this experiment is that irradiation of CpRe(PMe$_3$)$_3$ with a large excess (>20 equiv) of PMe$_3$ provides solutions that contain only **11** and unreacted starting material; these are more amenable to spectroscopic analysis.

Scheme XVII



Scheme XVIII



Formation of Hydridovinyl Complex 14. Irradiation of trisphosphine **1** in an ethylene/cyclohexane solution provided hydridovinyl complex **14** as the major product. Warming **14** to room temperature resulted in its quantitative isomerization to the ethylene complex **15**, even in benzene. If unsaturated complex **2** was an intermediate in the latter process, one would expect to see the formation of hydridophenyl complex **4** and the liberation of free ethylene. Since neither was seen by ^{1}H NMR spectroscopy, **2** cannot be an intermediate in this process. Reductive elimination of ethylene from hydridovinyl complex **14** must be concurrent with olefin complexation to form **15**.

Irradiation of η^2-ethylene complex **15** in toluene-d_8 for 10 h reformed the hydridovinyl complex **14**, as a 6:1 mixture (**14**:**15**). Although no free trimethylphosphine was detected, ca. 7% of **15** lost a molecule of ethylene and subsequently formed the C–H insertion products of toluene.[20]

The observation of the photochemical isomerization of ethylene complex **15** to hydridovinyl complex **14** means that **15** might be the first formed species in the photolysis of CpRe(PMe$_3$)$_3$ with ethylene to give **14**. This would be in accord with the precoordination hypothesis expounded on by Parshall which postulates the intermediacy of an η^2-arene complex in the C–H activation of arenes.[31] To test this possibility, the presumed unsaturated intermediate **2** was thermally generated in the presence of ethylene (25 atm in cyclohexane-d_{12}) by decomposition of hydrido-*n*-hexyl adduct **8** at room temperature. The predominant product after 30 min (80% reaction) was that of C–H insertion (Scheme XVII). The ratio of **14**:**15** at this time was 10:1, but all of the ethylene complex **15** could be due to the thermal isomerization of **14** which occurs at this temperature. Therefore, hydridovinyl complex **14** is the major (and perhaps sole) kinetic product of the reaction. Since **15** is stable to these thermal reaction conditions, precoordination of the olefin (to form **15**) cannot precede C–H insertion.

The system **15**/**14** bears a striking resemblance to the analogous iridium system.[32] The major difference is that thermal generation of the iridium unsaturated intermediate in the presence of ethylene provides significant amounts of both the π-bound ethylene complex and the C–H insertion product as kinetic products (Scheme XVIII). Both the iridium and the rhenium systems contrast with arene activation by the [Cp*Rh(PMe$_3$)] fragment, which has been shown to proceed via the η^2-arene complex.[33]

Conclusion

The rhenium fragment [CpRe(PMe$_3$)$_2$] presents an apparent dichotomy—it exhibits a remarkably high selectivity with respect

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(30) As pointed out by a referee, our data are also consistent with an intermolecular version of mechanism ii in which the rhenium center in **2** first inserts into the C–H bond of a phosphine in a second molecule of **1** to give CpL$_2$(H)Re-CH$_2$P(Me)$_2$-ReL$_2$Cp. This might then undergo photochemical Re–P cleavage, leading to **11**-d_0 and another molecule of **2**.

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(32) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(33) (a) Reference 8c. (b) Jones, W. D., personal communication.

to intermolecular C–H bond insertion, yet it also undergoes competitive cyclometalation. Other known C–H activating systems containing the PMe_3 ligand give isolable products formed from cyclometalation or intermolecular C–H insertion but not both. As has been pointed out (both by a referee and by others[34]), it is not clear whether this is a kinetic or thermodynamic phenomenon. However, in at least a few cases, hydrido(alkyl) complexes are not formed even though they are stable to reductive elimination. For example, irradiation of $CpRe(CO)_3$ in the presence of trialkyl- and triarylsilanes gives $CpRe(CO)(H)(SiR_3)$[35] and in THF leads to $CpRe(CO)_2(THF)$ (apparently without insertion into the THF C–H bonds),[36] indicating that the photolysis of the tricarbonyl gives the reactive fragment $CpRe(CO)_2$. Furthermore, both $CpRe(CO)_2(H)(CH_3)$ and $CpRe(CO)_2(H)(CH_2Ph)$ are stable for reasonable periods of time at room temperature in solution.[37] In spite of these facts, irradiation of $CpRe(CO)_3$ in alkane and arene solvents gives only dimers apparently formed from attack of $CpRe(CO)_2$ upon the starting rhenium tricarbonyl.[38] Thus, at least in this case, there appears to be a significant kinetic barrier to intermolecular C–H insertion.

The intermolecular selectivities seem to mirror the thermodynamic stabilities of the products: aryl > cyclopropyl ≈ vinyl > methyl > 1° alkyl ≫ 2° alkyl. Therefore, irradiation of **1** with methane in cyclohexane results only in methane activation. Similarly, only the primary C–H bond is activated in hexane, even when **1** is irradiated in hexane at −70 °C. The distinction between thermodynamic vs. kinetic control in these selectivities is not clear, especially in those cases where possible unstable products (e.g., secondary C–H bond insertion products) are not observed. In either case, the high selectivity of this rhenium system may be due to the sterically demanding metal center.

However, the steric crowding may also be responsible for the propensity of **2** to cyclometalate.[34] One is therefore faced with a trade-off—the increased intermolecular selectivity is offset by an increased tendency to cyclometalate. However, as demonstrated by us and by others,[39] in some cases one can clearly tip the balance in favor of intermolecular C–H insertion by operating at low temperatures. This can provide the products of kinetic control which, in the case of cyclopentane, favors even the extremely unstable hydridocyclopentyl complex **9** over cyclometalation by ca. 4:1 at −30 °C; warming to room temperature in cyclopentane produced exclusively the thermodynamic product, cyclometalated complex **10**.

Experimental Section

General Methods. All manipulations were performed under nitrogen or argon, by using standard Schlenk, drybox, or vacuum line techniques, unless stated otherwise. Drybox manipulations were performed in a nitrogen-filled Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train, equipped with a −40-°C freezer. All NMR data were recorded at ambient temperature unless noted otherwise on either a Bruker AM500 or a 300-MHz instrument constructed at the University of California at Berkeley (UCB) NMR facility. Chemical shifts are reported in ppm downfield of tetramethylsilane. ^1H NMR shifts are relative to residual protiated solvent: benzene-d_5, δ 7.15; toluene-d_7, δ 2.09; cyclohexane-d_{11}, δ 1.38. ^{13}C NMR chemical shifts are relative to the solvent resonance: benzene-d_6, δ 128.00; toluene-d_8, δ 20.40; cyclohexane-d_{12}, δ 26.40. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. "Virtual doublets" refer to non-first-order multiplets that resemble filled doublets; the apparent coupling constant is the separation between the two largest peaks. The term "six-line multiplet" refers to the X portion of an ABX system; the coupling constant given is the separation between the two most intense peaks (equal to $J_{AX} + J_{BX}$). Coupling constants were assigned by selective hetero- or homonuclear decoupling. Quantitative NMR data employed a delay of $>5T_1$ or else a single pulse after sufficient equilibration time. Absolute NMR yields were determined by integrating vs. ferrocene in toluene-d_8 held in an external capillary.

Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer or a Perkin-Elmer 1550 Fourier transform spectrometer. Ultraviolet spectra were recorded on a Hewlett-Packard 8450A UV-vis spectrophotometer using 1-cm path quartz cells. Mass spectra were recorded by the UCB mass spectrometry facility, and elemental analyses were conducted by the UCB microanalytical laboratory. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Cylindrical, Pyrex vessels equipped with Kontes K-826510 Teflon stopcocks are referred to as glass bombs and are of normal wall thickness unless noted otherwise. Heavy walled bombs for high-pressure work were equipped with Ace 8193-07 Teflon stopcocks. Evaporation means evaporation of the volatile materials at reduced pressure without exposure to air. Vacuum transfers were performed at $<10^{-5}$ torr. Gas phase mass measurements were performed by measuring the pressure in calibrated known-volume bulbs by using a MKS Baratron attached to a high-vacuum line.

Tetrahydrofuran, benzene, benzene-d_6, toluene, diethyl ether, and di-*n*-butyl ether were distilled from sodium benzophenone ketyl. Hexane, pentane, and cyclohexane were "UV grade" and were distilled from a refluxing lithium aluminum hydride slurry. Tetrahydrofuran-d_8, toluene-d_8, and cyclopentane were vacuum transferred after stirring over 1:5 sodium:potassium alloy. Cyclopropane was stirred 2 h at room temperature over a mixture of 2 g of $HgSO_4$, 6 mL of concentrated H_2SO_4, and 25 mL of H_2O. The mixture was then degassed by freeze–pump–thaw cycles, and the cyclopropane vacuum was transferred at −78 °C onto 1:5 sodium:potassium alloy. After having been stirred 12 h at room temperature, the cyclopropane was vacuum transferred into a glass vessel where it was stored. Cyclohexane-d_{12} was stirred with 30:70 v/v concentrated HNO_3:concentrated H_2SO_4 for 1 h, then washed 4–6 times with 25% NaOH and then water, and dried over $MgSO_4$. It was stirred 12 h over 1:5 sodium:potassium alloy before vacuum transfer and storage under dry nitrogen. Trimethylphosphine was purchased from Strem, dried over 1:5 sodium:potassium alloy, and always handled by vacuum transfer. CP grade methane and ethylene were used as received from Matheson. Cyclopentadiene was freshly cracked and then vacuum transferred from 4-Å molecular sieves. Methyl-d_3 iodide was obtained from MSD Isotopes and was vacuum transferred from 4-Å molecular sieves before use. Potassium perrhenate was obtained from Alfa Corporation.

UV Irradiations. Two UV irradiation arrangements were used, one maintained at 5–10 °C A and the other at −30 °C B. All UV irradiations were performed by using arrangement (A) at 5–10 °C unless stated otherwise. A consisted of a 450-W medium pressure Canrad-Hanovia mercury immersion lamp with an Ace 7830-60 power supply and an Ace 7874b-38 quartz immersion well. The well was immersed in a water-filled vessel that was cooled to 5–10 °C by means of a Lauda K-4/RD refrigerated circulator. B consisted of a 450-W medium pressure Canrad-Hanovia mercury immersion lamp in a double-jacketed quartz immersion well. The outer jacket was evacuated. This was immersed in a 4-L dewar containing spectral grade methanol that was cooled to various temperatures by a Neslab ULT-80DD circulating cooler. UV irradiation experiments were performed by securing the irradiation vessel in the bath next to the immersion well. All NMR tubes used for UV irradiation experiments were constructed from Pyrex glass.

Low-Temperature Chromatography. Alumina was purchased from EM Reagents (70–230 mesh) and was brought to the desired activity by the addition of the appropriate amount of water. It was degassed before storage in the drybox by several pump–flush cycles with argon. Columns were double-jacketed, the outer jacket being evacuated. These were packed in the drybox, with all subsequent operations being performed outside of the drybox. Cooling was provided by nitrogen gas, which was bubbled through liquid nitrogen and then passed through the inner jacket. The temperature was controlled by the flow rate and was monitored by inserting a thermocouple into the coolant inlet of the column. Deoxygenated solvents were precooled to −78 °C and transferred via cannula. Substrate solutions were added via syringe to a layer of sand atop the solvent-wet column and allowed to equilibrate before eluting. Elution was generally performed under 3–5 psi of nitrogen. Fractions were detected by using an Altex model 153 analytical UV detector equipped with a preparative scale UV cell operating at 254 nm and interfaced with a Houston Instruments Omni-Scribe recorder. Fractions were collected under argon by inserting a needle from the detector into a chilled Schlenk vessel equipped with a rubber septum. All mixtures which contained residual $CpRe(PMe_3)_3$ were first eluted for 12 min with 100% pentane in order to destroy that material. The compounds of interest were then

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eluted with the designated ether/pentane mixture.

$ReCl_3(PMe_3)_3$ (3). A slurry of $KReO_4$ (1.50 g, 5.18 mmol) in 10 mL of absolute ethanol was degassed in a 3 × 12 cm glass bomb equipped with a stir-bar by evacuating while stirring at −78 °C. Trimethylphosphine (3.5 mL, 2.6 g, 34 mmol) was condensed into the bomb by vacuum transfer. This mixture was brought to −78 °C and 36% aqueous HCl (1.2 mL, 14 mmol), deoxygenated by bubbling for 5 min with nitrogen, was added via syringe with a Teflon needle against an argon flow. The resulting colorless slurry was warmed to 110 °C for 19 h, rapidly attaining a bright lime-green color. After having been cooled to −78 °C, a second aliquot of 36% aqueous HCl (5.0 mL, 58 mmol) was added as before. The resulting black solution was heated at 110 °C for 4 days and gradually changed color to dark red. This solution was concentrated by a water aspirator to ca. one half of its volume and then partioned between water (100 mL) and benzene (50 mL) in the air. The aqueous phase was reextracted with 50 mL of benzene, and the combined organic phases were washed with water (100 mL) and brine (100 mL) before drying over potassium carbonate. Rotary evaporation provided a brown-yellow, crystalline solid which was purified by flash chromatography in air (silica gel, 12 × 5 cm). Elution with ether/hexane (2:1) produced an orange band (discarded) followed by a yellow band. Evaporation of the yellow fraction provided 2.29 g (4.40 mmol, 85%) of **3** as a bright yellow powder: mp 174–175 °C; ^1H NMR (benzene-d_6) δ 2.26 (s, 18 H), −2.59 (s, 9 H);[40] IR (KBr) 950 (s) cm^{-1}; MS, (EI), *m/e* (rel intensity) 520 (M^+, 7), 76 (100). Anal. Calcd for $C_9H_{27}Cl_3P_3Re$: C, 20.76; H, 5.23; Cl, 20.42. Found: C, 20.98; H, 5.42; Cl, 20.50. $ReCl_3(PMe_3)_3$ decomposed to a blue solid when exposed to air for several months.

$CpRe(PMe_3)_3$ (1). A slurry of $ReCl_3(PMe_3)_3$ (3.00 g, 5.77 mmol), cyclopentadiene (25 mL, ca. 310 mmol), K_2CO_3 (1.94 g, 14.0 mmol), and tetrahydrofuran (80 mL) was prepared in a 500-mL Morton flask equipped with a large egg-shaped stir-bar. Sodium amalgam (0.787% Na, 40.34 g, 13.8 mmol Na) was added at once to the rapidly stirred slurry causing a color change to green and then to brown. After having been stirred for 18 h, the dark green slurry was filtered and evaporated to a dark green solid. Rapid, strictly air-free filtration through a 4 × 14 cm column of alumina(III) (5% ether/pentane) at −105 °C provided 150 mL of a pale yellow solution which was evaporated to a pale yellow solid. This material, which contained small amounts of dicyclopentadiene, was dissolved in 75 mL of cyclohexane, and the solution was frozen. The coolant was removed, and the volatile materials were sublimed off under high vacuum (lyophilization) to afford 1.04 g (2.172 mmol, 38%) of **1** as an extremely air sensitive, fluffy white powder: mp (dec above 200 °C without melting); ^1H NMR (benzene-d_6) δ 4.19 (q, J = 0.8 Hz, 5 H), 1.40 (virtual d, J = 7.0 Hz, 27 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 71.93 (q, J_P = 1.7 Hz), 30.10 (m); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ −37.67 (br s); IR (benzene) 927 (s) cm^{-1}; MS, (EI), *m/e* (rel intensity) 480 (M^+, 100); UV (hexane) λ_{max} 234 nm (ϵ 1.6 × 10^4). Anal. Calcd for $C_{14}H_{32}P_3Re$: C, 35.07; H, 6.73; P, 19.38. Found: C, 34.78; H, 6.78; P, 18.18.

$Cp(PMe_3)_2Re(Ph)H$ (4). A solution of $CpRe(PMe_3)_3$ (117 mg, 0.245 mmol) in 20 mL of benzene was irradiated in a Pyrex bomb for 19 h, with periodic removalof small amounts of solvent by vacuum transfer to lower the PMe_3 concentration. A ^1H NMR analysis of an aliquot revealed ca. 90% conversion. After removal of the volatile materials, the resulting brown residue was recrystallized twice from pentane to provide 75.5 mg (0.197 mmol, 64%) of **4** as light yellow crystals: mp 110.5–111.5 °C dec; ^1H NMR (benzene-d_6) δ 7.54 (m, 2 H), 7.01 (m, 3 H), 4.51 (d, J = 0.5 Hz, 5 H), 1.29 (virtual d, J = 8.1 Hz, 18 H), −12.98 (t, J = 52.5 Hz, 1 H); ^{13}C NMR (benzene-d_6) δ 147.15 (t, J_P = 19.0 Hz, $^1J_{C\text{-}H}$(s), C_{ipso}), 146.94 (t, J_P = 7.5 Hz, $^1J_{C\text{-}H}$(d) = 152.5 Hz, C_{ortho}), 126.12 (s, $^1J_{C\text{-}H}$(d) = 150.0 Hz, C_{meta}), 119.97 (t, J_P = 1.6 Hz, $^1J_{C\text{-}H}$(d) = 157.6 Hz, C_{para}), 80.33 (t, J_P = 1.6 Hz, $^1J_{C\text{-}H}$(d) = 176.3 Hz, Cp), 26.28 (six-line multiplet, J_P = 31.0 Hz, $^1J_{C\text{-}H}$(q) = 127.1 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ −35.08 (br s); IR (benzene) 1932 (w) cm^{-1}; MS, (EI), *m/e* (rel intensity) 482 (M^+, 7), 404 (100). Anal. Calcd for $C_{17}H_{29}P_2Re$: C, 42.40; H, 6.07; P, 12.86. Found: C, 42.58; H, 6.20; P, 12.71.

$Cp(PMe_3)_2Re(c\text{-}C_3H_5)H$ (5). A solution of $CpRe(PMe_3)_3$ (255 mg, 0.532 mmol) in 20 mL of cyclopropane was irradiated for 25 h. The reaction was monitored by periodically removing the volatile materials by vacuum transfer and then analyzing some of the residue by ^1H NMR spectroscopy. The irradiation was stopped at 58% conversion to avoid excessive formation of dihydride **6**, and the volatile materials were removed by vacuum transfer. The brown residue was chromatographed at −110 °C (1.5 × 18 cm alumina(III), pentane, 1% ether/pentane) to provide 88 mg (0.20 mmol, 38%) of **5** as a white, crystalline solid: mp 43.6–46.0 °C; ^1H NMR (toluene-d_8) δ 4.17 (s, 5 H), 1.40 (virtual d, J = 8.1 Hz, 18 H), 0.82 (dm, J = 9.5 Hz, 2 H), −0.02 (m, 1 H), −0.17 (dm, J = 7.3 Hz, 2 H), −13.29 (td, J = 49.7, 4.9 Hz, 1 H); ^{13}C NMR (toluene-d_8, −15 °C) δ 77.78 (t, J_P = 2.0 Hz, $^1J_{C\text{-}H}$(d) = 175.8 Hz, Cp), 25.69 (six-line multiplet, J_P = 29.4 Hz, $^1J_{C\text{-}H}$(q) = 126.8 Hz, PMe_3), 14.35 (t, J_P = 5.3 Hz, $^1J_{C\text{-}H}$(t) = 155.4 Hz, C2, C2′), −30.03 (t, J_P = 18.8 Hz, $^1J_{C\text{-}H}$(d) = 143.2 Hz, C1); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −33.85 (br s); IR (cyclohexane) 1958 (w); MS, (EI), *m/e* (rel intensity) 446 (M^+, 0.4), 404 (100). Anal. Calcd for $C_{14}H_{29}P_2Re$: C, 37.74; H, 6.56; P, 13.90. Found: C, 38.01; H, 6.82; P, 13.77.

$Cp(PMe_3)_2ReH_2$ (6). $ReCl_3(PMe_3)_3$ (403 mg, 0.775 mmol) and $NaBH_4$ (350 mg, 9.25 mmol) were added to a 50-mL Schlenk flask equipped with a stir-bar. The addition of absolute ethanol (25 mL) caused apparent gas evolution, and the slurry became warm. After degassing by several pump–fill cycles with nitrogen, the yellow slurry was heated to 55 °C for 20 min, causing a color change from yellow to white. The solution was cooled to room temperature, and the volatile materials were evaporated to provide a white solid. Benzene (5 mL) was added by syringe and then evaporated to remove residual ethanol. The resulting white solid was extracted with benzene (5 × 5 mL), and the benzene extracts were evaporated to leave a pale yellow oil. NMR spectroscopy revealed that $ReH_5(PMe_3)_3$ had been cleanly formed: ^1H NMR (benzene-d_6) δ 1.53 (virtual d, J = 7.5 Hz, 27 H), −6.73 (q, J = 19.8 Hz, 5 H); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ −35.37 (s).

A solution of the crude pentahydride **7**, cyclopentadiene (0.7 mL), and benzene (5 mL) in a Pyrex bomb was irradiated for 43 h, providing an intensely green solution which was evaporated to a green solid. Air-free flash chromatography (alumina(II), 2 × 15 cm, doped with zinc silicate "UV-254" indicator, 5% ether/pentane, quartz column) afforded dihydride **6** (222 mg, 0.548 mmol, 71% based on **3**) as an air sensitive, white, silky solid: mp 76.5–78.5 °C; ^1H NMR (benzene-d_6) δ 4.54 (s, 5 H), 1.53 (virtual d, J = 8.3 Hz, 18 H), −12.14 (t, J = 43.6 Hz, 2 H); ^{13}C NMR (benzene-d_6) δ 74.29 (t, J_P = 1.7 Hz, $^1J_{CH}$(d) = 175.8 Hz, Cp), 31.87 (six-line multiplet, J_P = 30.8 Hz, $^1J_{CH}$(q) = 129.0 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ −36.34 (s); IR (benzene-d_6) 1913 (w) cm^{-1}; MS, (EI), *m/e* (rel intensity) 406 (M^+, 45), 404 (100). Anal. Calcd for $C_{11}H_{25}P_2Re$: C, 32.59; H, 6.21. Found: C, 32.65; H, 6.26.

$Cp(PMe_3)_2Re(n\text{-}C_6H_{13})H$ (8). (Note: all manipulations were carried out by vacuum transfer except where noted). A solution of $CpRe(PMe_3)_3$ (253 mg, 0.527 mmol) in 25 mL of *n*-hexane was irradiated for 72 h at −30 °C. The solvent was removed at 0 °C and replaced by 3 mL of pentane. The resulting dark brown mixture was rapidly transferred via syringe to a precooled column of alumina(II) (15 × 2 cm, −110 °C) and eluted with pentane (15 min) followed by 1% ether/pentane. The column flow rate was high enough to cause frosting of the lines into and out of the UV detector. The first eluting band was collected in a −78-°C chilled Schlenk flask, and the solvent was evaporated at 0 °C to provide a colorless, crystalline material. Residual solvent was removed by redissolution in toluene-d_8 (0.3 mL) followed by evaporation at 0 °C. After redissolving the residue in 0.8 mL toluene-d_8, the colorless solution was brought to −78 °C under argon and rapidly transferred via syringe to an NMR tube that was cooled to −78 °C and actively purged with argon. The solution was degassed, and the NMR tube was sealed under vacuum. NMR spectroscopy revealed pure **8**: ^1H NMR (toluene-d_8, −20 °C) δ 4.35 (s, 5 H, Cp), 1.48 (br m, 8 H, CH_2's), 1.35 (virtual d, J = 7.9 Hz, 18 H, PMe_3), 1.14 (m, 2 H, α-CH_2), 1.03 (br t, J = 6.8 Hz, 3 H, CH_3), −12.53 (tt, J = 50.1, 3.5 Hz, M–H); $^1H\{^{31}P\}$ NMR (toluene-d_8, −20 °C) only two resonances affected: δ 1.35 (s), −12.53 (t, J = 3.5 Hz); selective ^1H homonuclear decoupling at δ 1.48:δ 1.03 (br s), decoupling at δ 1.14:δ −12.53 (t, J = 50.1 Hz); ^{13}C NMR (toluene-d_8, −30 °C) δ 76.75 (t, J_P = 2.1 Hz, $^1J_{CH}$(d) = 176.1 Hz, Cp), 40.19 (t, J_P = 6.1 Hz, $^1J_{CH}$(t) = 123.5 Hz, C2), 38.42 (s, $^1J_{CH}$(t) = 124.6 Hz, C3), 32.65 (s, $^1J_{CH}$(t) = 124.4 Hz, C4), 25.14 (six-line multiplet, J_P = 29.4 Hz, $^1J_{CH}$(q) = 127.4 Hz, PMe_3), 23.76 (s, $^1J_{CH}$(t) = 123.4 Hz, C5), 14.76 (s, $^1J_{CH}$(q) = 123.9 Hz, CH_3), −14.853 (t, J_P = 12.8 Hz, $^1J_{CH}$(t) = 119.8 Hz, C1); $^{31}P\{^1H\}$ NMR (toluene-d_8, −20 °C) δ −36.22 (s). The tube was then cooled to −196 °C and opened under high vacuum.[41] A measured amount of gaseous tetramethylsilane (0.0323 mmol) was added by vacuum transfer, and the tube was resealed. ^1H NMR spectroscopy (−20 °C) showed that a 15% yield of **8** had been obtained.

$Cp(PMe_3)_2Re(c\text{-}C_5H_{11})H$ (9). A solution of $CpRe(PMe_3)_3$ (18.1 mg, 0.038 mmol) in 0.6 mL of cyclopentane was prepared in a NMR tube that contained a capillary tube filled with 0.14 M ferrocene in toluene-d_8. Irradiation at −51 °C for 21 h (63% conversion) provided a brown solution that contained hydridocyclopentyl complex **9** (19%). Also present

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(40) The unusual ^1H NMR chemical shifts of similar compounds have been discussed: Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867–2872.

(41) A simplified version of that described in Coleman, D. D. *Anal. Chem.* **1981**, *53*, 1962–1963. We also employed a Cajon SS-6-UT-6-4 stainless steel reducing union ($^3/_8$–$^1/_4$ in., with a 2-106 Viton o-ring at the $^1/_4$-in. end) instead of the Ace threaded adaptor. This permitted repositioning and subsequent flame resealing of the NMR tube, all under high vacuum.

were **10** (5%), **6** (10%), and **11** (5%). Further irradiation diminished the yield of **9**. The solvent from a similar tube was removed by vacuum transfer at −40 °C and replaced by toluene-d_8 to obtain suitable NMR spectra: partial ^{1}H NMR (toluene-d_8, −20 °C) δ 4.29 (s, 5 H), 1.35 (virtual d, J = 7.9 Hz, 18 H), −12.41 (td, J = 51.3, 5.4 Hz, 1 H): ^{1}H{^{31}P} NMR (toluene-d_8, −20 °C) affected only δ 1.35 (s), −12.41 (d, J = 5.5 Hz); ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C) δ −39.81 (s).

Cp(PMe$_3$)Re(η^2-CH$_2$PMe$_2$)H (10). A solution of CpRe(PMe$_3$)$_3$ (113 mg, 0.236 mmol) in 25 mL of cyclohexane was irradiated for 50 h with periodic removal of small amounts of solvent by vacuum transfer to lower the PMe$_3$ concentration. Evaporation of the solvent at 0 °C provided a brown oil which was chromatographed at −107 °C (1.5 × 18 cm alumina(III), 5% ether/pentane, 30% ether/pentane) to provide two fractions: fraction 1 (5% ether/pentane), mostly dihydride **6**; fraction 2 (30% ether/pentane), 29 mg (0.073 mmol, 31%) of **10** as a white solid: mp 55.5–58.0 °C dec; ^{1}H NMR cyclohexane-d_{12}) δ 4.30 (s, 5 H, Cp), 1.54 (d, J_{P2} = 11.4 Hz, 3 H, (P2)CH$_3$), 1.45 (d, J_{P2} = 11.0 Hz, 3 H, (P2)-CH$_3$), 1.38 (d, J_{P1} = 8.0 Hz, integration obscured by solvent, PMe$_3$), 0.48 (ddd, J_{gem} = 7.5, J_{P1} = 5.6, J_{P2} = 4.9 Hz, 1 H, CH$_2$), −0.14 (ddd, J_{P1} = 10.4, J_{gem} = 7.6, J_{P2} = 2.1 Hz, 1 H, CH$_2$), −12.12 (dd, J_{P1} = 33.6, J_{P2} = 37.4 Hz, 1 H, ReH); ^{1}H{^{31}P} NMR (cyclohexane-d_{12}) δ 4.30 (s), 1.54 (s), 1.45 (s), 1.38 (s), 0.48 (d, J = 7.5 Hz), −0.14 (d, J = 7.6 Hz), −12.12 (s); ^{13}C NMR (cyclohexane-d_{12}) δ 75.17 (s, $^1J_{C\text{-}H}$(d) = 175.9 Hz, Cp), 26.90 (d, J_P = 25.6 Hz, $^1J_{CH}$ obscured by solvent, PMe$_3$), 17.20 (d, J_P = 25.1 Hz, $^1J_{C\text{-}H}$(q) = 128.5 Hz, P(2)CH$_3$), 16.62 (dd, J_P = 27.6, 1.2 Hz, $^1J_{C\text{-}H}$(q) = 128.3 Hz, P(2)CH$_3$), −39.78 (dd, J_P = 7.6, 4.4 Hz, $^1J_{C\text{-}H}$(t) = 150.4 Hz, CH$_2$); ^{31}P{^{1}H} NMR (cyclohexane-d_{12}) δ −38.85 (br s), −79.91 (d, J = 15.5 Hz); IR (cyclohexane) 1944 (w) cm^{-1}; MS, (EI), m/e (rel intensity) 404 (M$^+$, 100). Anal. Calcd for C$_{11}$H$_{23}$P$_2$Re: C, 32.75; H, 5.75; P, 15.35. Found: C, 32.85; H, 5.88; P, 14.80.

Cp(PMe$_3$)$_2$Re(η^1-CH$_2$PMe$_2$)H (11). (A) From Irradiation of CpRe(PMe$_3$)$_3$ in Cyclohexane. A solution of CpRe(PMe$_3$)$_3$ in 0.6 mL of cyclohexane-d_{12} was irradiated in a sealed NMR tube for 3.5 h. ^{1}H NMR analysis (vs. external Cp$_2$Fe in toluene-d_8) revealed only **11** (14%), cyclometalated complex **10** (20%), and residual CpRe(PMe$_3$)$_3$. Characterization of **11**: ^{1}H NMR (cyclohexane-d_{12}) δ 4.40 (s, 5 H, Cp), 1.48 (virtual d, J_{P1} = 8.0 Hz, integration obscured, PMe$_3$), 0.87 (d, J_{P2} = 3.7 Hz, 6 H, PMe$_2$), 0.73 (tdd, J_{P1} = 10.2, J_{P2} = 5.9, J_{MH} = 2.4 Hz, 2 H, ReCH$_2$P), −12.77 (tm, J_{P1} = 50.8 Hz, 1 H, ReH); ^{1}H{^{31}P} NMR (cyclohexane-d_{12}) δ 4.40 (s), 1.48 (s), 0.87 (s), 0.73 (d, J = 2.4 Hz), −12.77 (br s); ^{31}P{^{1}H} NMR (cyclohexane-d_{12}) δ −26.60 (t, J = 20.5 Hz), −37.50 (d, J = 20.7 Hz).

(B) **From Irradiation of CpRe(PMe$_3$)$_3$ in Trimethylphosphine.** A solution of CpRe(PMe$_3$)$_3$ in 0.9 mL of PMe$_3$ was irradiated in a sealed NMR tube for 13 h. Further irradiation did not change the 0.72 ratio of **11**/CpRe(PMe$_3$)$_3$. The tube was opened under high vacuum,[41] and the volatile materials were removed by vacuum transfer at 0 °C. The light brown residue was redissolved in 0.1 mL of toluene-d_8, added by vacuum transfer. The volatile materials were again removed by vacuum transfer at 0 °C, and a final 0.5 mL of toluene-d_8 was distilled onto the residue before flame resealing the tube. NMR analysis revealed only CpRe(PMe$_3$)$_3$ and **11**: ^{1}H NMR (toluene-d_8, −20 °C) δ 4.41 (s, 5 H, Cp), 1.38 (virtual d, J = 8.1 Hz, integration obscured, PMe$_3$), 1.12 (d, J = 3.5 Hz, 6 H, PMe$_2$), 0.84 (tdd, J = 10.1, 6.2, 2.3 Hz, 2 H, ReCH$_2$P), −12.76 (tm, J = 50.7 Hz, 1 H, ReH); ^{1}H{^{31}P} NMR (toluene-d_8, −20 °C) δ 4.41 (s), 1.38 (s), 1.12 (s), 0.84 (d, J = 2.7 Hz), −12.76 (t, J = 3.0 Hz); ^{13}C{^{1}H} NMR (toluene-d_8) δ 75.46 (s, Cp), 24.92 (d of (six-line multiplet), J_P = 3.6, 30.3 Hz, PMe$_3$), 22.36 (d, J_P = 19.4 Hz, PMe$_2$), −18.99 (dt, J_P = 37.8, 12.2 Hz, ReCH$_2$P).

Cp(PMe$_3$)$_2$Re(CH$_3$)H (12). A 27-mL heavy-walled Pyrex bomb was charged with 155 mg (0.323 mmol) of CpRe(PMe$_3$)$_3$, 10 mL of cyclohexane, and 24.3 mmol of CH$_4$ (total methane pressure estimated at 25 atm[42]). Irradiation for 24 h followed by removal of the volatile materials (−196 to 0 °C) provided a dark brown oil. Chromatography at −105 °C (1.5 × 18 cm alumina(III), pentane, 1% ether/pentane, 30% ether/pentane) produced two fractions. Fraction 1 (1% ether/pentane): 57 mg (0.13 mmol, 42%) of **12** as a colorless oil at 0 °C (crystalline at −40 °C); ^{1}H NMR (toluene-d_8, −15 °C) δ 4.30 (s, 5 H), 1.33 (virtual d, J = 8.0 Hz, 18 H), 0.20 (td, J = 11.0, 2.0 Hz, 3 H), −12.34 (tq, J = 48.8, 2.6 Hz, ^{1}H); ^{13}C NMR (toluene-d_8, −15 °C) δ 77.10 (t, J_P = 2.2 Hz, $^1J_{C\text{-}H}$(d) = 176.1 Hz), 25.20 (six-line multiplet, J_P = 29.2 Hz, $^1J_{C\text{-}H}$(q) = 127.2 Hz), −39.89 (t, J_P = 14.7 Hz, $^1J_{C\text{-}H}$(q) = 123.2 Hz); ^{31}P{^{1}H}-NMR (toluene-d_8) δ −35.84 (s); IR (cyclohexane) 1945 (w) cm^{-1}; MS, (EI), m/e (rel intensity) 420 (M$^+$, 3), 404 (100). Anal. Calcd for C$_{12}$H$_{27}$P$_2$Re: C, 34.36; H, 6.49; P, 14.77. Found: C, 34.52; H, 6.52; P, 14.49. Fraction 2 (30% ether/pentane): 16 mg (0.041 mmol, 13%) of pure (by NMR) cyclometallated complex **10**.

Cp(PMe$_3$)$_2$Re(CH$_3$)H (12) from Cp(PMe$_3$)$_2$ReH$_2$ (6). Dihydride **6** (16 mg, 0.040 mmol) in 0.3 mL of tetrahydrofuran-d_8 was treated with 22 μL of n-butyllithium (2.6 M in hexane, 0.057 mmol) to give a bright yellow solution of lithiohydride **13** [^{1}H NMR (tetrahydrofuran-d_8) δ 3.65 (s, 5 H), 1.50 (virtual d, J = 6.4 Hz, 18 H), −14.38 (t, J = 19.7 Hz, 1 H)]. Addition of a solution of methyl p-toluenesulfonate (14 mg, 0.075 mmol) in 0.3 mL tetrahydrofuran-d_8 at −40 °C afforded a pale yellow solution of **12** in 78% yield (vs. added ferrocene) [^{1}H NMR (tetrahydrofuran-d_8) δ 4.443 (5, 5 H), 1.44 (virtual d, J = 7.8 Hz, integration obscured), −0.048 (dt, J = 1.8, 11.0 Hz, 3 H), −12.43 (tm, J = 48.7 Hz, 1 H)]. The NMR tube was opened in the drybox, and the volatile materials were removed in vacuo. The residue was dissolved in toluene-d_8 [^{1}H NMR (toluene-d_8) δ 4.29 (s, 5 H), 1.34 (virtual d, J = 8.1 Hz, 18 H), 0.18 (td, J = 11.0, 2.0 Hz, 3 H), −12.36 (tm, J = 49.4 Hz, 1 H)].

Cp(PMe$_3$)$_2$Re(η^2-(CH$_2$═CH$_2$)) (15). A solution of CpRe(PMe$_3$)$_3$ (214 mg, 0.447 mmol) and ethylene (2.7 mL at −103 °C, 4.7 g, 170 mmol)[43] in 10 mL of pentane was irradiated in a 27-mL, heavy-walled Pyrex bomb for 3 days. After standing at room temperature for 6 days, the volatile materials were removed by careful vacuum transfer (−78 °C to room temperature). Sublimation (40–60 °C, 10^{-5} torr) provided 167 mg of a brown oil with little purification. Chromatography at −105 °C (1.5 × 18 cm alumina(III), pentane, 2% ether/pentane) provided 87 mg (0.200 mmol, 45%) of **15** as a pale yellow crystalline solid: mp >140 °C dec; ^{1}H NMR (benzene-d_6) δ 4.30 (t, J = 0.5 Hz, 5 H), 1.47 (virtual d, J = 8.6 Hz, 4 H), 1.21 (virtual d, J = 7.6 Hz, 18 H); ^{13}C NMR (benzene-d_6) δ 77.92 (t, J_P = 1.4 Hz, $^1J_{C\text{-}H}$(d) = 174.5 Hz, Cp), 24.21 (six-line multiplet, J_P = 31.1 Hz, $^1J_{C\text{-}H}$(q) = 129.0 Hz, PMe$_3$), 3.91 (t, J_P = 3.3 Hz, $^1J_{C\text{-}H}$(t) = 150.2 Hz, CH$_2$═CH$_2$); ^{31}P{^{1}H} NMR (benzene-d_6) δ −29.78 (s); IR (benzene-d_6) 2965 (m), 2902 (m), 1276 (m), 1139 (m), 932 (s) cm^{-1}; MS, (EI), m/e (rel intensity) 432 (M$^+$, 76), 404 (100). Anal. Calcd for C$_{13}$H$_{27}$P$_2$Re: C, 35.07; H, 6.73. Found: C, 34.78; H, 6.78. Brief exposure of solid **15** to air resulted in rapid decomposition.

Cp(PMe$_3$)$_2$Re(CH═CH$_2$)H (14) from Irradiation of η^2-Ethylene Complex (15). Purified ethylene complex **15** (60 mg, 0.14 mmol) in 0.6 mL of toluene-d_8 was irradiated in a sealed NMR tube by using a Pyrex filter for 10 h. ^{1}H NMR analysis revealed the following relative product distribution: **14** (73%), **15** (13%), **6** (4%), toluene C–H insertion products (4%),[20] and ethylene (6%, δ 5.24). Spectroscopic data for **14**: ^{1}H NMR (toluene-d_8) δ 8.32 (dddt, J = 18.6, 12.3, 4.3, 14.1 Hz, 1 H, H$_1$), 6.56 (ddt, J = 12.2, 4.5, 3.4 Hz, 1 H, H$_E$), 5.37 (ddt, J = 18.7, 4.6, 1.8, 1 H, H$_Z$), 4.44 (s, 5 H, Cp), 1.35 (virtual d, J = 8.3 Hz, 18 H, PMe$_3$), −12.57 (dt, J = 4.2, 50.6 Hz, 1 H, M–H); ^{1}H{^{31}P} NMR (toluene-d_8) δ 8.32 (ddd, J = 18.6, 12.3, 4.3 Hz), 6.56 (dd, J = 12.4, 4.7 Hz), 5.37 (dd, J = 18.7, 4.7 Hz), 4.44 (s), 1.35 (s), −12.57 (d, J = 4.1 Hz); ^{13}C NMR (toluene-d_8, −30 °C) δ 144.41 (t, J_P = 21.0 Hz, $^1J_{CH}$(d) = 128.5 Hz, C1), 122.14 (t, J_P = 7.7 Hz, $^1J_{CH}$(t) = 149.5 Hz, C2), 79.432 (s, $^1J_{CH}$(d) = 176.4 Hz, Cp), 24.98 (six-line multiplet, J_P = 31.4, $^1J_{CH}$(q) = 127.9 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (toluene-d_8) δ −33.56 (s); IR (benzene-d_6) 1938 (w) cm^{-1}.

Cp(PMe$_3$)$_2$Re(CH═CH$_2$)H (14) from Irradiation of CpRe(PMe$_3$)$_3$ with Ethylene. A solution of CpRe(PMe$_3$)$_3$ (11 mg, 0.023 mmol) and ethylene (1.93 mmol) in 0.5 mL of cyclohexane-d_{12} was irradiated for 14 h in a medium-walled NMR tube. ^{1}H NMR spectroscopy revealed **14** (43%), **15** (5%), and **6** (3%) (absolute yields vs. 0.14 M ferrocene in toluene-d_8 in an external capillary). The tube was opened under high vacuum, and the solvent was evaporated at 0 °C and replaced by 0.4 mL of benzene-d_6 before resealing. Warming to room temperature for 116 h produced the following distribution (by ^{1}H NMR spectroscopy): **14** (2%), **15** (39%), and **6** (2%). Less than 5% ethylene could be detected. Reirradiation in benzene-d_6 for 7.5 h provided **14** (34%), **15** (5%), **6** (7%), and ethylene (4%, δ 5.24).

Thermal Activation of Ethylene. A medium-walled NMR tube was charged with 12.4 mg of CpRe(PMe$_3$)$_3$ in n-hexane. The tube was sealed under vacuum, irradiated at −30 °C for 12 h, and then transferred to the probe of an NMR spectrometer which had been precooled to −20 °C. Analysis showed 83% conversion of the trisphosphine to products. The predominant product was Cp*ReL$_2$(H)(n-hexyl); this was contaminated with smaller amounts of Cp*ReL$_2$H$_2$, phosphine insertion products **10** and **11**, and a complex we believe to be Cp*ReL$_2$(1-hexene). The tube was cracked open under high vacuum and the solvents were removed at 0 °C during 13 min. After recooling the tube to −196 °C, solvent C$_6$D$_{12}$ and 3.1 mmol of ethylene were added by vacuum transfer. The tube was warmed to room temperature, and the conversion to products monitored by ^{1}H NMR spectroscopy. The hydrido-n-hexyl complex disappeared with a half-life of about 35 min and was converted to a 94:6 ratio of vinyl hydride **14** and ethylene π-complex **15**; the amounts of the other com-

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(42) Solubility of methane estimated from Frolich, P. K.; Tauch, E. J.; Hogan, J. J.; Pear, A. A. *Ind. Eng. Chem.* **1931**, *23*, 548–550.

(43) Density of CH$_2$═CH$_2$ at −103.7 °C = 0.5696 g/mL: Mass, O.; Wright, C. H. *J. Am. Chem. Soc.* **1921**, *43*, 1098–1111.

plexes present did not change during this time.

Dimerization of 10. $CpRe(PMe_3)_3$ (191 mg, 0.399 mmol) in 25 mL of hexane was irradiated in a Pyrex bomb for 45 h. Ca. 4 mL of volatile materials were removed by vacuum transfer at the reaction midpoint. An aliquot was removed from the bomb in a drybox and was analyzed by ^1H NMR spectroscopy which revealed 80% conversion. After having been concentrated to 2–3 mL, the brown mixture was heated to 60 °C for 3 h and then diluted with 5 mL of pentane. After several days a crystalline material formed on the walls of the vessel, along with a brown precipitate. This mixture was cooled to −40 °C for 5 days, and the mother liquors were decanted. Attempts to separate the brown material from the crystals by recrystallization were unsuccessful. Chromatography at −105 °C (1.5 × 18 cm alumina(III), 2% ether/pentane) provided 29 mg (0.036 mmol, 18%) of **16** as a light yellow solid: ^1H NMR (benzene-d_6) δ 4.62 (s, 5 H, Cp), 4.44 (br s, 2 H, H3, H4), 4.26 (br s, 1 H, H2/H5), 4.21 (br s, 1 H, H5/H2), 2.13 (qm, J = 14.5 Hz, 1 H, H14), 1.95 (d, J = 7.2 Hz, 3 H, Me15/Me16), 1.62 (d, J = 9.1 Hz, 3 H, Me16/Me15), 1.48 (d, J = 8.1 Hz, PMe_3), 1.46 (d, J = 7.4 Hz, sum with δ 1.48 = 18 H, PMe_3), 1.39 (d, J = 7.7 Hz, 10 H, PMe_3, H14), −12.69 (tm, J = 50.7 Hz, 1 H, HRe2), −13.44 (dd, J = 41.6, 51.8 Hz, 1 H, HRe1); ^1H homonuclear decoupling at δ 1.39 caused δ 2.13 (tm, J = 14 Hz); $^1H\{^{31}P\}$ NMR (benzene-d_6) affected only δ 2.13 (dd, J = 11.6, 3.8 Hz), 1.95 (s), 1.62 (s), 1.48 (s), 1.46 (s), 1.39 (s), −12.69 (m), −13.44 (s); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 28.28 (ddd, J = 3.0, 24.1, 45.5 Hz), −37.93 (d, J = 24.4 Hz), −40.25 (dd, J = 22.3, 45.3 Hz), −46.52 (dd, J = 3.3, 22.1 Hz); IR (benzene-d_6) 1968 (w) cm^{-1}; MS, spectrum (EI), m/e (rel intensity) 806 (M^+ [$^{187}Re + ^{185}Re$], 11), 57 (100). Anal. Calcd for $C_{22}H_{46}P_4Re_2$: C, 32.75; H, 5.75. Found: C, 33.21; H, 6.01.

The other compound that was present in the original mixture **17** was not isolated: ^1H NMR (cyclohexane-d_{12}) δ 4.25 (m, 4 H), 4.08 (m, 4 H), 1.59 (virtual d, J = 7.4 Hz, integration obscured), −10.69 (t, J = 51.1 Hz, 2 H); $^1H\{^{31}P\}$ NMR (cyclohexane-d_{12}) δ 4.25 (m), 4.08 (m), 1.59 (s), −10.60 (s); $^{31}P\{^1H\}$ NMR (cyclohexane-d_{12}) δ −40.91 (s).

Crystal Structure of 16. Blocklike colorless crystals of the compound were obtained by slow crystallization from toluene/pentane. One of these crystals was mounted on a glass fiber in the air and coated with polycyanoacrylate cement. Precession photographs indicated monoclinic Laue symmetry and yielded preliminary cell dimensions. Systematic absences were consistent only with space group $P2_1/n$. The crystal was transferred to an Enraf-Nonius CAD-4 diffractometer[44] and centered in the beam. It was cooled to −108 (4) °C by a nitrogen flow apparatus which had been previously calibrated against a thermocouple placed in the sample position. The final cell parameters and specific data collection parameters are given in Table VI.

The 3950 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correlation for crystal decomposition was necessary. Inspection of the azimuthal scan data[45] showed a variation $I_{min}/I_{max} = 0.63$ for the average curve. An absorption correction based on the measured shape and size of the crystal and a 14 × 10 × 6 Gaussian grid of internal points was applied to the data ($T_{max} = 0.18$, $T_{min} = 0.09$). Removal of systematically absent and redundant data left 3509 unique data.

The structure was solved by Patterson methods and refined via 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. Non-hydride hydrogens were included in the structure factor calculations in their expected positions based on idealized bonding geometry. The hydride hydrogens were located on a subsequent difference Fourier map and included in their discovered positions. All hydrogens were assigned isotropic thermal parameters 1–2 Å^2 larger than the equivalent B_{iso} of the atom to which they were bonded. Hydrogen atoms were not refined in the least-squares procedure. A secondary extinction parameter[46] was refined in the final cycles of least-squares. In the final stages of refinement, 10 reflections with low values of F_{obsd} and very poor agreement between F_o and F_c were removed from the data set. The final residuals for 254 variables refined against the 3218 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.23\%$, $R_w = 3.38\%$, $R_{all} = 2.63\%$, and GOF = 1.76.

Table VI. Crystal and Data Collection Parameters for Dimer **16** ($Re_2P_4C_{22}H_{16}$)

(A) Crystal Parameters at −108 ± 5° C[a,b]

a = 14.8973 (24) Å   space group: $P2_1/n$
b = 9.0668 (14) Å   fw = 806.9 amu
c = 20.6056 (34) Å Z = 4
β = 104.879 (13)° d_c = 1.99 g cm^{-3}
V = 2689.9 (14) Å^3 μ(calcd) = 93.6 cm^{-1}
cryst size: 0.21 × 0.33 × 0.38 mm

(B) Data Measurement Parameters[c]

radiatn: Mo Kα(λ = 0.71073 Å)
monochromator highly-oriented graphite (2θ = 12.2°)
detector: crystal scintillatn ctr with PHA
rflctns measd: −h, + k, ± l
2θ range: 3° <<fgt 45°
scan type: θ–2θ
scan width: $\Delta\theta = 0.6 + 0.347 \tan(\theta)$
scan speed: 0.72 → 6.7 (θ, deg/min)
background: measd over 0.25($\Delta\theta$) added to each end of scan
aperture → crystal = 173 mm
verticl aperture = 3.0 mm
horzntl aperture = 2.2 +1.0 tan (θ) mm (variable)
no. of reflctns collctd: 3950
no. of unique reflctns: 3509
intensity standards: $(3,\bar{4},\bar{1}\bar{1})$, $(\bar{6}1\bar{9})$, $(\bar{6}\bar{5}3)$; measured every hour of X-ray exposure time. Over the data collection period no decrease in intensity was observed.
orientation: 3 reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°. Reorientation was necessary once during data collection.

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα component of 24 reflections with 2θ near 28°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given. [c] Reference 37.

The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of sin $(\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed a pseudo-body-centered variation of intensity but otherwise no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 2.87 e^-/Å^3. All peaks with density greater than 0.7 e^-/Å^3 were located near the Re atoms. The positional and thermal parameters of the non-hydrogen atoms are given in Table V. The positions of the hydrogen atoms and a listing of the values of F_o and F_c are available as supplementary material.

Trimethylphosphine-d_9.[47] Methyl-d_3 iodide (2.4 mL, 5.4 g, 37 mmol) was added during 1 h to a stirred mixture of magnesium turnings (1.04 g, 42.6 mmol) in 10 mL of di-n-butyl ether in a 50-mL Schlenk flask under argon. The reaction was initiated at room temperature and then cooled to 0 °C. Upon complete addition of the methyl-d_3 iodide, the grey suspension was brought to room temperature and stirred for 12 h. It was then cooled to 0 °C, and a solution of triphenylphosphite (3.28 g, 10.6 mmol) in di-n-butyl ether (25 mL) was added during 2 h with stirring, followed by warming to room temperature for 45 min. Ca. $^1/_2$ of the volatile materials (containing most of the PMe_3) were removed by vacuum transfer at 0 °C. These were cooled to −78 °C; at this temperature essentially pure $P(CD_3)_3$ can be vacuum transferred with rapid stirring during 7 h into a flask containing 1:5 Na/K alloy. After stirring 1 h, the flask was cooled to −40 °C, and the volatile materials were vacuum transferred into a small glass bomb during 2 h, providing $P(CD_3)_3$ (0.356 g, 4.12 mmol, 40%). ^1H, ^2H, and $^{31}P\{^1H\}$ NMR analyses of the neat liquid disclosed no impurities.

UV Irradiation of $CpRe(PMe_3)_3$ with $P(CD_3)_3$. A solution of $CpRe(PMe_3)_3$ (21 mg, 0.044 mmol) and $P(CD_3)_3$ (0.042 mmol) in 0.6 mL of cyclohexane-d_{12} was prepared in a sealed NMR tube. $^{31}P\{^1H\}$ NMR analysis revealed the ratio **1**/$P(CD_3)_3$ = 0.95. Irradiation for 1 h followed by ^1H NMR analysis disclosed 5.7 H (vs. 5.0 H for the Cp resonance) at the PMe_2 site (δ 0.87) of **11**. Product distribution (relative yields) was the following: **1** (80%), **10** (7%), **11** (13%).

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(44) For a description of the diffraction equipment, computation equipment, and data reduction formula used in the X-ray diffraction study, see: Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5845.

(45) Reflections used for azimuthal scans were located near χ = 90°, and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

(46) Zachariesen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139–1144.

(47) Based on: Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met. Org. Chem.* **1974**, *4*, 149–156. The substitution of di-n-butyl ether for ethyl ether was passed on to us by Professor R. Andersen.

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UV Irradiation of $Cp(PMe_3)Re(\eta^2\text{-}CH_2PMe_2)H$ (10) with $P(CD_3)_3$. A solution of **10** (2 mg, 0.005 mmol, 0.01 M) and $P(CD_3)_3$ (0.005 mmol, 0.01 M) in 0.41 mL of cyclohexane-d_{12} was prepared in a sealed NMR tube. $^{31}P\{^1H\}$ NMR analysis revealed the ratio **10**/$P(CD_3)_3$ = 1.4. Irradiation for 1 h followed by ^1H NMR analysis showed that no reaction had occurred (<5% conversion).

The NMR tube was reopened[41] under high vacuum, and an additional 0.44 mmol of $P(CD_3)_3$ added. The tube was resealed by flame and irradiated 1 h. ^1H NMR spectroscopy showed that a small amount of pentane interfered with integration. The tube was quickly opened under nitrogen in the drybox, and the solution was evaporated and then redissolved in benzene-d_6. ^1H NMR analysis revealed 4.0 H (vs. 5.0 H for the Cp resonance) at the PMe_2 site (δ 1.13) of **11**. The following relative product ratio was observed: **1** (48%), **10** (10%), **11** (42%).

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Supplementary Material Available: Crystal packing diagram, molecular geometry and labeling scheme for **16**, hydrogen positional parameters and their esd's, and listings of F_o and F_c (24 pages). Ordering information is given on any current masthead page.

Main Group Chemistry on a Metal Framework: Reactions of $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$ (R = H, CH_3) with Lewis Bases

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Abstract: The reactions of $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$ (R = H, CH_3) with Lewis bases (L = CO, $PhMe_2P$, NEt_3, and H_2O) are explored. For R = H and L = $PhMe_2P$, substitution via H_2 rather than CO elimination to yield $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$ competes with cluster fragmentation to yield $PhMe_2P{\cdot}BH_3$, $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$, $Fe(CO)_3(PhMe_2P)_2$, and a ferraborane anion spectroscopically characterized in situ. The fragmentation pathway predominates in the presence of excess Lewis base, whereas H_2 elimination is favored by low ligand levels. For L = $PhMe_2P$ the H_2 displacement pathway is promoted with R = CH_3. A kinetic study for L = $PhMe_2P$ reveals a first-order rate dependence on both substrate and ligand for fragmentation, suggesting associative activation. The dual-fragmentation path observed illustrates competitive base displacement of isolobal fragments from a single cluster. An analysis at intermediate ligand levels results in the definition of base-promoted cluster substitution via H_2 elimination. Under the conditions explored here, CO yields only H_2 displacement, H_2O only fragmentation, and NEt_3 adduct formation with slow fragmentation but no H_2 displacement.

The chemistry of trigonal BH_3 as well as tetrahedral adducts with Lewis bases, BH_3L, has been well documented.[1,2] Both the high reactivity of free BH_3 and the varied reactivity of borane adducts with ordinary Lewis bases are expressions of fundamental bonding concepts.[3] However, the effects of the coordination of BH_3 to a transition metal on the reactivity of the main group fragment is not well explored. One would say unexplored except that one of the most interesting and versatile base adducts of BH_3, that with H^- (BH_4^-), forms numerous mononuclear transition-metal complexes of varying hydride hapticity.[4,5] The fact that BH_3 can be displaced from these borohydride complexes[6] suggests that they might well be described as BH_3 metal hydride complexes. We have recently characterized the first example of what can formally be described as a tridentate cluster bound tetrahydroborate ligand spanning three metal atoms, i.e., $(\mu\text{-}H)Fe_3(CO)_9BH_4$ (I′).[7,8] This compound can act as a protonic acid, and with bases I′ initially loses a proton from a B–Fe edge to give I which in turn constitutes an example of a metal cluster bound monoborane.[8,9] Hence, I provides an opportunity to explore the reactivity of an important main group hydride when bound in an unusual fashion to a multinuclear metal framework. In this report we consider reactivity of I with respect to selected Lewis bases.

When attack on exo-cluster CO ligands is ignored, I contains two potential sites of base attack, viz., metal or main group center. There is a considerable body of information on ligand substitution in metal carbonyls although mechanistic studies on cluster systems

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