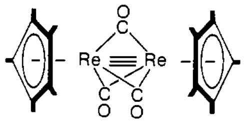
Å in $H_2Os_3(CO)_{10}$[18]). Both $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ undergo interesting reactions involving the $M(\mu\text{-}H)_2M$ core,[19] and we anticipate that **3** will be reactive as well. In preliminary investigations, we have found that **3** reacts slowly with CO (30 psig) to form **1**,[20] while reaction with CH_2N_2 results in addition of CH_2 to the molecule.

The third product of irradiation of **1** with H_2 purge is the dinuclear 30-electron complex **4**, which on the 18-electron formalism would contain an osmium-osmium triple bond.[22] It is isoelectronic with the recently described $Re(\mu\text{-}CO)_3Re$ complex **5**[23] and may be compared with the dinuclear rhodium complex $L_2Rh(\mu\text{-}H)_2(\mu\text{-}CO)RhL_2$ ($L = P(O\text{-}i\text{-}C_3H_7)_3$) characterized, although not isolated, from reaction of CO with the catalyst precursor $[L_2Rh(\mu\text{-}H)]_2$.[24] Reactions of **4** will likewise be of interest; preliminary investigations show that it reacts readily with CO to form **1** and **3**.



5

Details of the processes that give rise to **3** and **4** are not clear, but eq 3-5 may be involved. Equation 5 has been demonstrated

$$2[(\eta\text{-}C_5Me_5)Os(CO)H] \rightarrow (\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) \quad (3)$$

$$[(\eta\text{-}C_5Me_5)Os(CO)H] + \mathbf{2} \rightarrow (\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) + H_2 \quad (4)$$

$$(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) \xrightarrow{h\nu} (\eta\text{-}C_5Me_5)_2Os_2(\mu\text{-}CO)(\mu\text{-}H)_2\ (\mathbf{4}) + CO \quad (5)$$

by irradiation of solutions of pure **3** (N_2 or H_2 purge) whereby **4** forms as the only product accompanied by some decomposition. Furthermore, irradiation of **2** (N_2 atmosphere) affords **3** in good yield. The question remains as to the path leading to **3**, whether straight dimerization (eq 3) or another process such as dinuclear hydrogen elimination[25] as suggested in eq 4. On this point, a key observation is that irradiation of **1** under identical conditions except for substitution of an N_2 for H_2 purge gave only low conversion to **3** and **4** (and no **2**). Thus, dimerization of the 16-electron intermediate (eq 3) may constitute only a minor pathway, with the role of hydrogen to provide a second pathway via **2**.[26] Further study of the mechanism is in progress.[14]

We also have found that photolysis[6] of $(\eta\text{-}C_5H_5)Re(CO)_3$ with hydrogen purge provides a more convenient route to $(\eta\text{-}C_5H_5)Re(CO)_2H_2$, a compound recently prepared through a hydridosilylrhenium intermediate.[27] A similar hydrogen-purge photolysis[6] of $(\eta\text{-}C_5Me_5)Re(CO)_3$ gave the new pentamethyl analogue $(\eta\text{-}C_5Me_5)Re(CO)_2H_2$ (**6**).[28] Additionally, hydrogen-mediated photolysis of $(\eta\text{-}C_5Me_5)Re(CO)_3$ using only a water-cooled quartz jacket (no Pyrex filtration) afforded **5** in better yield (under optimized conditions) than did the reported method.[23]

The results summarized above demonstrate the synthetic utility of dihydrogen addition to 16-electron intermediates generated by loss of a carbonyl ligand through ultraviolet irradiation. The hydrogen-mediated photolysis reaction has also led to interesting carbonyl- or hydrido-bridged dimers having formal double and triple bonds. We are currently investigating the reactivity of these dimers and attempting to extend the general reaction to metals other than rhenium and osmium.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Registry No. 1, 81554-96-3; **2**, 81753-10-8; **3**, 81740-97-8; **4**, 81740-98-9; **5**, 81740-99-0; **6**, 81741-00-6; $(\eta\text{-}C_5Me_5)Re(CO)_3$, 12130-88-0.

Supplementary Material Available: Detailed results of the X-ray crystal structure of $(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2$, tables of experimental details, positional and thermal parameters, general temperature factor expressions (*U*, *B*), bond distances, and bond angles, and the structure of $(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2$ (8 pages). Ordering information is given on any current masthead page.

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(18) (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697. (b) Broach, R. W.; Williams, J. W. *Ibid.* **1979**, *18*, 314. (c) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.

(19) (a) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (b) Calvert, R. B.; Shapley, J. R. *Ibid.* **1977**, *99*, 5225. (c) Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *Ibid.* **1980**, *102*, 6156. (d) Adams, R. D.; Dawoodi, A. *Ibid.* **1981**, *103*, 6510. (e) Adams, R. D.; Katahira, D. A.; Yang, L. W. *J. Organomet. Chem.* **1981**, *219*, 85. (f) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *219*, 103. (g) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318.

(20) It appears that **3** forms mononuclear products more readily than $H_2Os_3(CO)_{10}$,[19a] perhaps because it lacks the bridging $\mu\text{-}Os(CO)_4$ group of the latter. A derivative of $H_2Re_2(CO)_8$ bridged by $Ph_2PCH_2PPh_2$ is also less susceptible to fragmentation than the parent compound.[21]

(21) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171.

(22) Completion of the X-ray structure of **4** has been delayed by a disorder problem, but a preliminary value for the Os-Os distance is 2.441 Å (R. Ball, personal communication). This compound involves Os(II), and the bond length is longer than values reported recently (2.344 (2) and 2.357 (1) Å) for an Os(III)-Os(III) triple bond: Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

(23) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

(24) Burch, R. R.; Muetterties, E. L.; Schultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5517.

(25) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(26) A two-pathway dimerization mechanism, with one pathway facilitated by H_2, has also been proposed for dimerization of $H_5Re(PMe_2Ph)_2$.[4d]

(27) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

(28) **6**: colorless crystals, mp 75-76 °C; IR (hexane, ν_{CO}) 2008 (ms), 1938 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.24 (s, 15 H), -9.63 (s, 2 H). Anal. Calcd for $C_{12}H_{17}O_2Re$: C, 37.98; H, 4.52. Found: C, 38.00; H, 4.42.

Oxidative Addition of the Carbon-Hydrogen Bonds of Neopentane and Cyclohexane to a Photochemically Generated Iridium(I) Complex

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We report the stoichiometric oxidative additon of carbon-hydrogen bonds of alkanes to a photochemically generated iridium complex.[1] The results demonstrate clearly that in the proper circumstances, such a reaction of totally unactivated sp^3 C-H bonds is both energetically and kinetically favorable.

Irradiation[2a] of a solution of $(\eta\text{-}C_5Me_5)Ir(CO)_2$[2b] (**1**) in neopentane (2,2-dimethylpropane) at room temperature proceeded according to eq 1, with formation of the new hydridoneopentyl-

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(1) Shortly after the submission of this communication, we learned that similar results had been reported for a closely related iridium system: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *Chem. Eng. News.* **1982**, *60*, 59. These workers photolyzed $(\eta\text{-}C_5Me_5)Ir(PMe_3)H_2$ and found that C-H bonds of neopentane and cyclohexane added readily to the presumed intermediate $[(\eta\text{-}C_5Me_5)Ir(PMe_3)]$, forming Me_3P derivatives of **2** and **4**. The more electron-rich Me_3P species should have an even greater tendency than the carbonyl to undergo oxidative-addition reactions, although the behavior seems roughly similar in the reactions so far examined. Differences in selectivities might be expected, and distinctions may arise in secondary reactions of the phosphine and carbonyliridium(III) complexes.

(2) (a) In this and other irradiations, degassed solutions in closed quartz tubes were placed approximately 5 cm from a Hanovia 450-W medium-pressure mercury lamp fitted with a cylindrical Pyrex filter and a water-cooled quartz jacket. In this experiment the solution contained 10 mg of **1**/g of neopentane. At the end of the 5 h of irradiation, neopentane was removed in vacuum and hexane was added. The IR spectrum of the products in hexane showed no carbonyl stretching bands other than those of **1** and **2**. (b) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. The IR spectrum of **1** in hexane exhibits ν_{CO} at 2020 (s), 1953 (s) cm^{-1}, and the ^1H NMR a singlet at δ 1.73 in C_6D_6.

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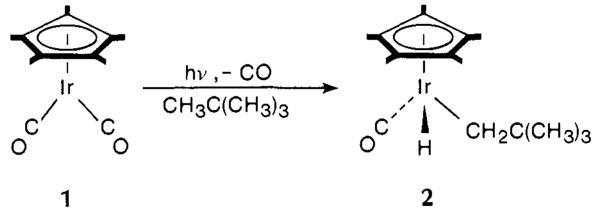

1 **2**

iridium compound **2**. Owing to the similar volatility and solubility of **1** and **2** and the slow decomposition of **2** in concentrated solutions or as a neat oil, completely pure **2** could not be isolated from this reaction mixture. To estimate the yield, we stirred the reaction mixture under nitrogen for several hours with CCl_4, converting **2** to the stable chloride derivative (η-C_5Me_5)Ir(CO)(Cl)(CH_2CMe_3) (**3**).[3] The yield of **3** on the basis of irradiated **1** was 55%. Since only about half of the initial **1** had been consumed (from IR intensities), the conversion of reacted **1** to **2** and hence to **3** was nearly complete. Analytically pure samples of **2** were prepared by $NaBH_4$ reduction of **3** in 2-propanol.[4]

A similar irradiation of **1** in cyclohexane cleanly produced the cyclohexylhydrido derivative (η-C_5Me_5)Ir(CO)(H)(C_6H_{11}) (**4**) in good yield,[5] while in cyclohexane-d_{12} the product was (η-C_5Me_5)Ir(CO)(D)(C_6D_{11}).[6] Like **2**, **4** was stable only in dilute solution and was easily converted to the more tractable chloride (η-C_5Me_5)Ir(CO)(Cl)(C_6H_{11}) (**5**) by CCl_4.[7] Coupling constants between the cyclohexyl protons α and β to iridium in **5** suggest that the bulky iridium substituent is equatorial while the two strong carbonyl stretching bands separated by 4 cm^{-1} are attributed to the presence of two conformations about the iridium–cyclohexyl bond.

We presume that irradiation of **1** produces the 16-electron iridium(I) intermediate (η-C_5Me_5)Ir(CO), to which the carbon-hydrogen bonds of neopentane and cyclohexane oxidatively add. The C–H bonds in these molecules should be typical of unactivated sp^3 C–H bonds generally, and it seems reasonable to suppose that most other sp^3 C–H bonds will also react.[8] A reaction of this kind had not been observed for unactivated sp^3 C–H bonds before,[1,9,10] although it has been proposed as a step in the catalysis of hydrogen–deuterium exchange for alkanes in aqueous acidic media by Pt(II) salts.[12]

On the other hand, a number of transition-metal complexes are known to which there is facile intermolecular oxidative addition of *aromatic* C–H.[10] The continuing investigation of photochemically or thermally generated "tungstenocene", (η-C_5H_5)$_2$W, largely by Green and collaborators, should be mentioned here,[13] as should the observations by Rausch et al.[14] on the photolysis of (η-C_5H_5)Ir(CO)$_2$ in benzene. There was good evidence in the latter reaction for the formation of (η-C_5H_5)Ir(CO)(H)(C_6H_5), although this reactive and unstable intermediate was not isolated.

When (η-C_5Me_5)Ir(CO)$_2$ (**1**) is irradiated in benzene, a product is formed that is also rather unstable when the solution is concentrated. There is little doubt that this is (η-C_5Me_5)Ir(CO)(H)(C_6H_5) (**6**),[15] and it is smoothly converted by CCl_4 to the known[16] stable (η-C_5Me_5)Ir(CO)(Cl)(C_6H_5) (**7**). We next irradiated **1** in equimolar benzene/neopentane to ascertain the relative rates of reaction of aromatic and aliphatic C–H with the iridium intermediate.[17] The ratio of phenyl to neopentyl product was 2.0:1, implying a 4-fold statistical preference for an aromatic C–H bond over an aliphatic (primary) C–H bond.[18] In a similar competition experiment with equimolar benzene/cyclohexane, the ratio of phenyl to cyclohexyl product was 2.5:1.

It has been suggested that the reaction of aromatic C–H bonds with transition-metal complexes is assisted by an intermediate π complex,[10,13a] and the usual inertness of alkane C–H has been attributed to the absence of nonbonding electrons to bind the hydrocarbon to the metal prior to C–H bond cleavage.[10a] This may well be a factor in accounting for the more rapid addition[18] of the thermochemically stronger C–H bonds of benzene in the present work. We were surprised that the effect was not larger.[19]

The presumed intermediate in these remarkable C–H activation processes, (η-C_5Me_5)Ir(CO), has characteristics usually considered to promote oxidative additions:[10] a coordinately unsaturated and reasonably electron-rich metal center. What is it about this particular intermediate that accounts for its unique reactivity? Our knowledge of the scope and mechanism of the reaction is still too limited to permit a satisfactory answer. We think that a favorable steric situation is part of the explanation, however. Iridium could be considered 2-coordinate, with one large ligand and one small; thus it might be possible for the C–H bonds of these substrates to approach the metal in an orientation more suitable for further reaction than is the case in other complexes.

When reaction with unactivated substrates is sought, a factor that comes to the fore is that *the coordinatively unsaturated intermediate must not preferentially metalate one of its own*

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(3) **3**: pale yellow solid, mp 98–99 °C; IR (hexane) 2002 cm^{-1} (ν_{CO}); ^1H NMR (25 °C, C_6D_6, 200 MHz) δ 1.26 (s, 9 H, CMe_3), 1.33 (s, 15 H, C_5Me_5), 2.02 (d, J = 9.5 Hz, 1 H, C*H*HCMe$_3$), 3.16 (d, J = 9.5 Hz, 1 H, CH*H*CMe$_3$); mass spectrum (16 eV, 120 °C) M^+, $(M - C_5H_{11})^+$, $(M - C_5H_{11} - CO)^+$. Anal. Calcd for $C_{16}H_{26}ClIrO$: C, 41.59; H, 5.67. Found: C, 41.96; H, 5.71.

(4) **2**: pale yellow oil, darkening after ca. 20 min under N_2; IR (hexane) 2174 (w, br, ν_{IrH}), 1986 cm^{-1} (s, ν_{CO}); ^1H NMR (C_6D_6, 200 MHz) δ −15.68 (br s, 1 H, IrH), 1.20 (s, 9 H, CMe_3), 1.32 (d, J = 10.3 Hz, 1 H, IrC*H*HCMe$_3$), 1.63 (d, $J_{H(hydride)}$ = 0.8 Hz, 15 H, η-C_5Me_5), 2.26 (d, J = 10.3 Hz, 1 H, IrCH*H*CMe$_3$); mass spectrum (16 eV, 25 °C) M^+, $(M - C_5H_{12})^+$. Anal. Calcd for $C_{16}H_{27}IrO$: C, 44.94; H, 6.36. Found: C, 44.88; H, 6.21. The analytical sample was prepared just prior to the analysis by evaporation of a dilute hexane solution (2–3 mg mL^{-1}) that had suffered no noticeable decomposition during storage at 5 °C for 2 weeks.

(5) **4**: IR (hexane) 1982 (s, ν_{CO}), 2149 (w, ν_{IrH}) cm^{-1}; ^1H NMR (C_6D_6, 25 °C, 200 MHz) δ −15.92 (br s, 1 H, IrH), 1.66 (s, slightly broadened, 15 H, C_5Me_5), 1.6–1.9 (m, 10 H), 2.30 (m, 1 H, α-H); mass spectrum of sample containing some **1** (14 eV, 60 °C) M^+, $(M - H_2)^+$, $(C_5Me_5Ir(CO)_2)^+$, $(C_5Me_5IrCO)^+$.

(6) The deuterium compound in hexane showed ν_{CO} at 1982 cm^{-1} (unshifted) and ν_{IrD} at 1543 cm^{-1}.

(7) **5**: IR (hexane) 2011 (s), 2007 (s) (ν_{CO}) cm^{-1}; ^1H NMR (C_6D_6, 25 °C, 200 MHz) δ 1.38 (s, 15 H, C_5Me_5), 1.30–1.40 (m, 2 H), 1.72–1.92 (m, 6 H), 2.32 (m, 2 H), 3.12 (tt, 1 H, J = 11.5, 3.5 Hz, α-H); mass spectrum (16 eV, 110 °C): M^+, $(M - HCl)^+$, $(M - C_6H_{11})^+$, $(M - C_6H_{11}Cl)^+$. Anal. Calcd for $C_{17}H_{26}ClIrO$: C, 43.07; H, 5.53. Found: C, 42.36; H, 5.42.

(8) For example, irradiation of **1** in hexane gives rise to new IR bands at 1984 cm^{-1} (ν_{CO}) and 2150 (ν_{IrH}) cm^{-1}, which we attribute to the still uncharacterized hexylhydrido derivative.

(9) As discussed by Parshall,[10] C–H bonds may be activated toward oxidative addition by electronic or by proximity effects. A pertinent example of the latter is the intramolecular oxidative addition of methyl C–H bonds of a neopentyl group *coordinated* to Ir(I).[11]

(10) (a) Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

(11) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.

(12) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147.

(13) (a) Giannotti, C.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1114. (b) Wong, K. L. T.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. (c) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc. A* **1971**, 1508. (d) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans* **1979**, 1950. (e) Cooper, J. N.; Green, M. L. H.; Mahtab, R. *Ibid.* **1979**, 1557.

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

(15) **6**: IR (hexane) 2002 (s, ν_{CO}), 2146 (w, br, ν_{IrH}) cm^{-1}.

(16) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393. We observe for **7**: IR (hexane) 2029 (ν_{CO}) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 1.28 (s, 15 H), 7.0–7.15 (m, 3 H), 7.66 (d, J = 7.5 Hz, 2 H).

(17) Irradiation conditions were as described,[1] concentration of **1** was 3.0 mg mL^{-1}, and irradiation was continued 5–7 h, by which time conversion of **1** to products was ca. 50% complete. CCl_4 was then added to the reaction mixture, which was stirred under N_2 for several hours to allow complete conversion to the chlorides **7** and **3**. Solvents were removed, and C_6D_6 was added; relative yields were determined by ^1H NMR integration.

(18) Our present *assumption* is that this ratio is kinetically controlled, and this will be tested shortly. It has been reported that there is no exchange with the solvent when (η-C_5H_5)$_2$W(H)(C_6H_5) is irradiated in C_6D_6.[13a]

(19) Studies by Green et al.[13d,13e,20] have shown preferential addition of methyl C–H to "(η-C_5H_5)$_2$W" in the cases of *p*-xylene and mesitylene. This may well be a steric effect, since the only arene C–H available is ortho to a methyl group.[21] Moreover, the methyl C–H bonds in those molecules might be considered activated. Although neither neopentane[22] nor cyclohexane[23] adds to the tungstenocene intermediate, tetramethylsilane does.[13d]

(20) Elmitt, K.; Green, M. L. H.; Forder, R. A.; Jefferson, I.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1974**, 747.

(21) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

(22) Green, M. L. H. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 229.

(23) Green, M. L. H.; Otero, A. *J. Organomet. Chem.* **1980**, *202*, 421.

ligands as is the case with $(\eta\text{-}C_5H_5)_2W$[24] and $Ru(Me_2PCH_2CH_2PMe_2)_2$[25] or in the more familiar intramolecular processes such as orthometalation.[10a] Methyl substituents on the cyclopentadienyl ligand in $[(\eta\text{-}C_5Me_5)Ir(CO)]$ may make self-metalation less likely while at the same time increasing the electron density on iridium somewhat.[26]

The factors involved will become clearer as other complexes are found to which the C–H bonds of paraffins will readily add. We are seeking further examples among other metals of the third transition series, where we expect the energetics of the process to be most favorable and the products most stable. The work is being carried out in conjunction with our investigation of the hydrogen-mediated photolysis of similar complexes.[27]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for generous financial support.

Registry No. 1, 32660-96-1; **2**, 81753-14-2; **3**, 81753-15-3; **4**, 81753-16-4; **5**, 81753-17-5; **6**, 81753-18-6; **7**, 32609-75-9; neopentane, 463-82-1; cyclohexane, 110-82-7; benzene, 71-43-2.

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[24] Berry, M.; Cooper, J. N.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29.

[25] (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (b) Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155.

[26] The behavior of $(\eta\text{-}C_5H_5)Ir(CO)_2$ upon irradiation in alkanes is of obvious interest.

[27] Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.*, preceding communication in this issue.

Tertiary Phosphine Complexes of the f-Block Metals. Crystal Structure of $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$: Evidence for a Ytterbium-γ-Carbon Interaction

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The 4f-block metals have a rich coordination chemistry with nitrogen and oxygen ligands.[1a] In contrast only one example of a tertiary phosphine complex of a lanthanide metal, Cp_3YbPPh_3, has been claimed.[1b–f] Lanthanide ions are generally thought to be examples of class A[1g] or hard[1h] Lewis acids. Thus, the most thermodynamically stable complexes are formed between nitrogen and oxygen donors and lanthanide acceptors rather than between phosphorus and sulfur donors. The isolation of phosphine complexes of the actinide metals (thorium and uranium) of the type $MX_4(dmpe)_2$, where dmpe is 1,2-bis(dimethylphosphino)ethane and X is halide, alkyl, or phenoxide,[2a] and $U(Me_5C_5)_2H(dmpe)$[2b] suggests that phosphine complexes of the lanthanide metals should be isolable. A synthetic route to such compounds would seem to require lanthanide complexes with empty coordination sites or ligands that are readily displaced by tertiary phosphines.

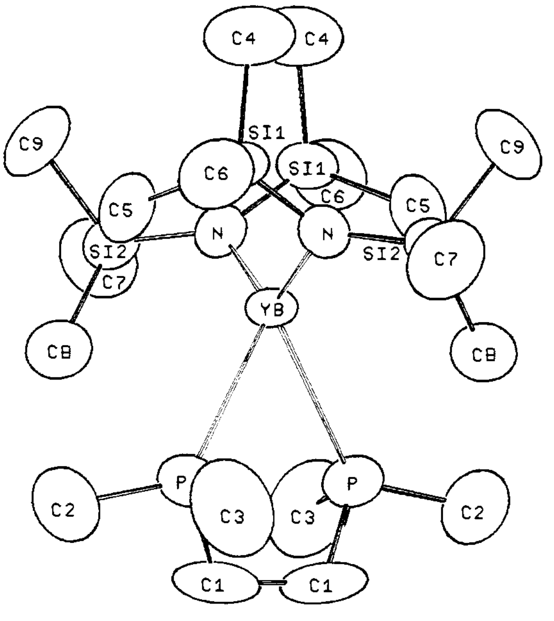

Figure 1. ORTEP diagram of $Yb[N(SiMe_3)_2]_2(dmpe)$. Some bond lengths and bond angles are as follows: Yb–N, 2.331 (13) Å; Yb–P, 3.012 (4) Å; N–Yb–N, 123.6 (6)°; P–Yb–P, 68.4 (2)°; N–Yb–P, 101.2 (3)°.

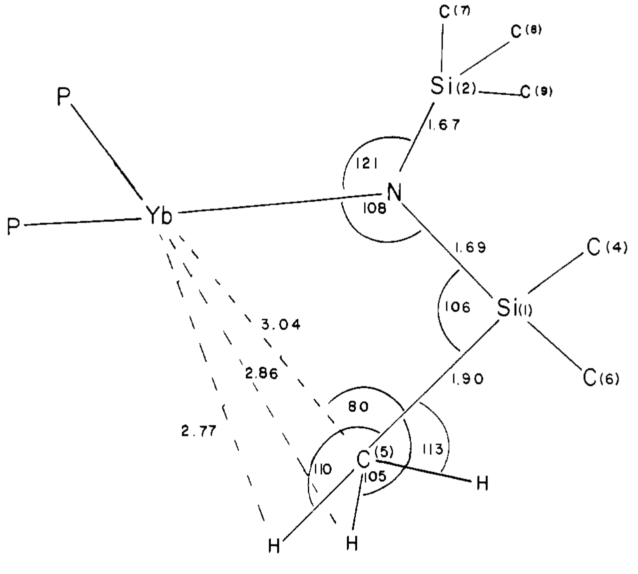

Figure 2. Line drawing showing the Yb–C(5) interaction. The bond angles are in degrees and the bond lengths are in angstroms.

We have described a preparation of the divalent $Eu[N(SiMe_3)_2]_2L_2$, where L = tetrahydrofuran or 1,2-dimethoxyethane, that utilizes sodium naphthalene as a reducing agent.[3] This synthetic method is only applicable in relatively strong donor solvents and was unsuccessful in the preparation of ytterbium(II) derivatives. A much improved synthetic scheme, which allows preparation of europium(II) and ytterbium(II) silylamides in the weak donor solvent diethyl ether, is shown in eq 1.

$$YbI_2 + 2NaN(SiMe_3)_2 \xrightarrow{OEt_2} \underset{\text{I}}{Yb[N(SiMe_3)_2]_2(OEt_2)_2}$$

$$EuI_2 + 2NaN(SiMe_3)_2 \xrightarrow{OEt_2} \underset{\text{II}}{NaEu[N(SiMe_3)_2]_3} \qquad (1)$$

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