

Figure 2. Stereopair drawing of a molecule of *p*-bromobenzoic anhydride. The large black circles are bromine atoms and the small ones are oxygen atoms. The view is down the polar *b* axis. Note that the molecular 2-fold axis is parallel to the crystal's *b* axis (perpendicular to the page) and passes through the central oxygen atom.

to single crystals of *p*-bromobenzoic anhydride with one pointed end shown previously² by X-ray anomalous scattering to correspond to the direction toward which the oxygen atoms of the C=O bonds were pointing; the blue (positively charged) particles adhered to the pointed (oxygen) end and the yellow and the red (negatively charged) to the other (carbon) end as shown in Figure 1. Thus it is suggested that the end of the crystal toward which the carbonyl oxygen atoms are pointing is negatively charged and the opposite end along the polar axis positively charged. The molecular dipole moment of benzoic anhydride in benzene solution has been found¹¹ to be 4.15 D. Determination¹²⁻¹⁵ of structures of a number of substituted benzoic anhydrides has shown that the dihedral angle between the two planes containing the carbonyl groups and the central oxygen atom is $47 \pm 8^\circ$. It seems likely, then that the preferred conformation of the molecules in the crystal is determined primarily by intramolecular forces rather than by packing and, thus, that the molecules in solution have approximately the same conformation as those in the crystal. Molecules of *p*-bromobenzoic anhydride in the crystal^{14,2} lie on a 2-fold crystallographic axis passing through the central oxygen atom and normal to the long molecular axis (Figure 2). The substantial molecular dipole moments of molecules in the crystal are thus aligned along the polar axis of the crystal. To a first approximation the dipole moment of the crystal can be considered to be the vector sum of the dipoles of the individual molecules so that the net moment should have the negative end of the crystal in the direction of the carbonyl oxygen atoms as found.

The related anhydrides of *m*- and *p*-iodobenzoic acid have been found¹³ to crystallize in the polar space group *Aba2* with the conformations of the anhydride molecules similar to that in *p*-bromobenzoic anhydride. The absolute direction of the polar axis of *p*-iodobenzoic anhydride has been determined¹³ by anomalous scattering. When the pyroelectric test described above was applied it indicated that the negative end of the polar axis of the crystal was that end with carbonyl oxygen atoms directed toward it as had been found with the *p*-bromobenzoic anhydride. Reaction with ammonia gas showed a preferential reaction at faces at the same (negative) end of the crystal as had also been observed in the reaction of ammonia with *p*-bromobenzoic anhydride. Similar results were obtained with polar crystals of *m*-iodobenzoic anhydride.

Application of the pyroelectric test to crystals of *p*-chlorobenzoic anhydride¹⁵ and *m*-bromobenzoic anhydride¹² known to belong to centrosymmetric space groups showed no separation of yellow

and blue particles, a result consistent with the absence of a polar axis.

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Registry No. S, 7704-34-9; *p*-bromobenzoic anhydride, 1633-33-6; *p*-iodobenzoic anhydride, 75474-06-5; carmine, 1390-65-4; methyl violet, 8004-87-3; ammonia, 7664-41-7.

Hydrogen Exchange between the Methyl and Hydride Ligands of $Cp_2W(H)CH_3$ Prior to Methane Elimination

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Alkyl hydride complexes have attracted our interest¹ and that of other research groups² because of their potential availability from hydrocarbon activation³ and their presumed intermediacy in catalytic reactions with hydrocarbon products (e.g., olefin hydrogenation⁴). Alkyl hydrides which eliminate alkanes by simple coupling of the adjacent ligands are, however, rare and confined to the later transition metals.⁵ Our attention was therefore attracted by the synthesis of $Cp_2W(H)CH_3$ and by reports that it (1) generated Cp_2W upon photolysis under matrix isolation conditions⁷ and (2) generated, upon thermolysis in solution, a species (possibly also Cp_2W) capable of C-H bond activation.⁶ We now report that (1) under sufficiently dilute conditions intramolecular methane elimination from $Cp_2W(H)CH_3$ does indeed occur, and (2) in more concentrated solutions, attack upon the methyl C-H bonds of another $Cp_2W(H)CH_3$, resulting in hydride hydrogen/methyl hydrogen exchange, competes effectively with methane elimination.

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- (2) Alkyl hydride complexes reported before 1979 are listed in ref 1c. Other hydride complexes with monodentate alkyl ligands, in addition to those arising from hydrocarbon activation³ and olefin hydrogenation,⁴ have been reported by: (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (c) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263. (d) McAlister, D.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (e) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (f) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221 and references therein. (g) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (h) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (i) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (j) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (k) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325 and references therein. (l) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (m) Kellenberger, B. Ph.D. Dissertation, ETH, Zurich, Switzerland, 1982. (n) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.
- (3) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (c) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624. (d) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (e) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650 and references therein.
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- (5) Alkyl hydride complexes of the later transition metals that are known to eliminate alkanes intramolecularly can be found in ref 2a, 2b, 2f, and 4. Other alkyl hydride complexes of the later transition metals that eliminate alkanes (probably also intramolecularly) are reported in ref 2c, 2i, 3d, 3e, and 3f. Alkyl hydride complexes of Zr eliminate alkanes only by more complex processes involving other C-H bonds^{2d} or external nucleophiles: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.
- (6) (a) Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557. (b) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29.
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(11) Oesper, P. F.; Smyth, C. P. *J. Am. Chem. Soc.* **1942**, *64*, 768-771. This moment is opposed in *p*-bromobenzoic anhydride by components of two C-Br dipoles that make an angle of 70° with the polar axis. Corrected for this, the moment is still approximately 3 D along the polar axis.

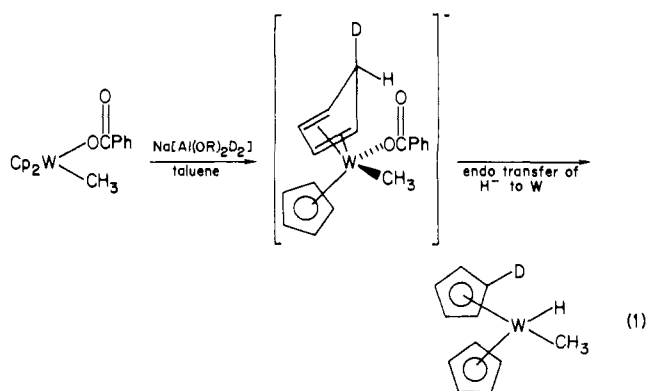
(12) Kress, R. B.; Patil, A. A.; Wilson, R. B.; Pennington, W. T., unpublished work.

(13) Patil, A. A.; Pennington, W. T., unpublished work.

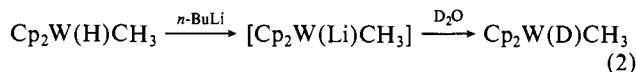
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(15) Calleri, M.; Ferraris, C.; Viterbo, D. *Atti. Acad. Sci. Torino, Cl. Sci. Fis. Mat. Nat.* **1966**, *100*, 145-150.

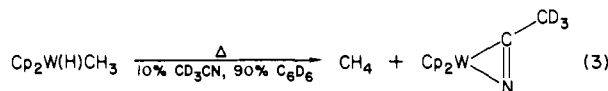
Scheme I



Examination of the molecularity of the elimination process required the synthesis of appropriately labeled derivatives, which proved both more difficult and more interesting than expected. The attempted preparation of $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ by reaction of $\text{Na}[\text{D}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_5)_2]$ with $\text{Cp}_2\text{W}(\text{CH}_3)(\text{OCOPh})$ (an analogue of the reported^{6a} preparation of the undeuterated material) gave $(\eta^5\text{-C}_5\text{H}_4\text{D})(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{H})\text{CH}_3$, apparently due to exo transfer of D^- onto a cyclopentadienyl ring,⁸ followed by endo transfer of H^- to W (Scheme I). The attempted preparation of $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ by treatment of Cp_2WD_2 with $n\text{-BuLi}$ ¹⁰ followed by MeOTs also led to scrambling of the deuterium label. $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ was successfully synthesized by deprotonation of $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ with $n\text{-BuLi}$, followed by reaction with D_2O (eq 2).



Investigation of methane elimination required that we find an efficient trapping agent^{2a,b} for the reactive tungsten species thereby produced. Solvent benzene did not prove to be a particularly efficient trap: 0.2 M $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ in C_6D_6 at 74 °C gave a complex mixture of products.¹¹ Added 10% acetonitrile was much more effective: $\text{Cp}_2\text{W}(\eta^2\text{-CD}_3\text{CN})$ ^{12,13} was the principal product of the thermolysis at 70 °C of 0.003 M $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ in C_6D_6 containing 10% CD_3CN . The presence of 10% CD_3CN did not affect the rate of disappearance of $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ under these conditions. Analysis of the temperature dependence of the rate of reaction 3 over the range 70–96 °C yielded $E_a = 25.8$ (3) kcal



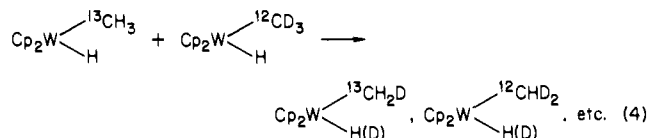
mol^{-1} , $\log A = 12$ (1), $\Delta H^\ddagger = 25.1$ (3) kcal mol^{-1} , and $\Delta S^\ddagger = -4$ (1) eu.

In dilute solution methane elimination from $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ is indeed an intramolecular process. Thermolysis (82.5 °C, 6 h) of a 10% $\text{CH}_3\text{CN}/90\%$ toluene solution of $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ (0.67

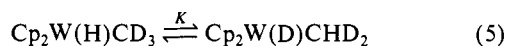
mM) and $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ (0.67 mM) gave methane which was predominantly CH_3D ($43 \pm 3\%$) and CD_3H ($47 \pm 2\%$). Similarly, thermolysis (82.9 °C, 2.5 h) of a 10% $\text{CH}_3\text{CN}/90\%$ C_6H_6 solution of $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3$ (0.54 mM, 93% ^{13}C) and $\text{Cp}_2\text{W}(\text{D})\text{CD}_3$ (0.54 mM, 88% D on tungsten) gave 0.95 equiv of a noncondensable gas in which mass spectrometry detected $^{13}\text{CH}_4$ ($40 \pm 6\%$), CD_4 ($42 \pm 6\%$), and CHD_3 ($14 \pm 6\%$).

In more concentrated solution, however, thermal methane elimination appeared to be intermolecular. For example, a 10% $\text{CH}_3\text{CN}/90\%$ C_6H_6 solution of $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ (14.0 mM) and $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ (9.4 mM) gave appreciable CH_4 , CD_2H_2 , and CD_4 (collectively 48% of total methanes) after 3 h at 82 °C. ^1H NMR examination of these labeled compounds showed that this apparent intermolecular elimination was actually the result of label scrambling before methane elimination. The ^1H NMR of an 0.61 M solution of $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ at 40.1 °C showed over several hours a decrease in its hydride resonance and the appearance of a new signal (δ 0.02, the same chemical shift as that of the methyl ligand in $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$) due to methyl ligand hydrogens; the hydride/methyl intensity ratio approached an equilibrium value of 1.6 (1). Similarly, the ^2D NMR signal from $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ decreased, and a new signal due to methyl ligand ^2D appeared, with an equilibrium intensity ratio of 4.9 (3). No significant exchange of deuterium into the cyclopentadienyl ligands occurred during either equilibration.

The molecularity of the scrambling reaction was investigated by heating a C_6D_6 solution of $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3$ (66 mM) and $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ (132 mM) at 47.3 °C. Growth of the ^{12}C methyl ^1H NMR resonance confirmed that the scrambling process was occurring in this system. Additionally, however, the ^{13}C NMR signal from $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3$ decreased with time, and a ^{13}C NMR signal¹⁴ due to $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_2\text{D}$ appeared—demonstrating that the scrambling occurred intermolecularly.



This result meant that the equilibration of $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ had formed small amounts of species ($\text{Cp}_2\text{W}(\text{H})\text{CHD}_2$, $\text{Cp}_2\text{W}(\text{D})\text{-CH}_2\text{D}$, etc.) other than $\text{Cp}_2\text{W}(\text{D})\text{CHD}_2$, and that the hydride/methyl intensity ratio after that equilibration was not a direct measure of the equilibrium constant K of reaction 5. It was



nevertheless possible to determine the equilibrium isotope effect, and therefore to calculate K , from the equilibrium data with initial $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ and initial $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$ (see supplementary material). The resulting value of K , 1.4 (2), is less than the statistical value of 3 and reflects the greater-than-statistical preference of deuterium for the methyl site expected in view of the equilibrium isotope effects reported for other organometallic systems.¹⁵

Knowledge of the $\text{W}(\text{H})\text{CH}_3$ equilibrium isotope effect has permitted the calculation (see supplementary material) of the final mole fractions of all 16 isotopically labeled species arising from the $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3/\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ experiment (reaction 4). The rate of decline ($k_{\text{obsd}}^{\text{C}} = 2.8 \times 10^{-5} \text{ s}^{-1}$) to its equilibrium value of the fraction of ^{13}C present in undeuterated methyl groups ($^{13}\text{CH}_3$) then measures the rate at which equilibrium is approached via intermolecular processes. The fact that the fraction of ^1H

(14) ^{13}C NMR (methyl ligand, $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_2\text{D}_3$) δ -41.60 ($^1J_{\text{CH}} = 125$ Hz, $^1J_{\text{CD}} = 19$ Hz, $^2J_{\text{CH}}(\text{hydride}) = 6.9$ Hz).

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(10) (a) Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1339. (b) Forder, R. A.; Prout, K. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2318.

(11) As reported by Green and co-workers,^{6a} C_6H_6 is an efficient trap (forming $\text{Cp}_2\text{W}(\text{H})\text{Ph}$) when the thermolysis of $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ is carried out in dilute solution (3×10^{-3} M). Presumably as the result of a kinetic isotope effect, C_6D_6 is a less efficient trap. 10% CH_3CN (or CD_3CN) is an efficient trap even at high concentrations of $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ in C_6D_6 .

(12) $\text{Cp}_2\text{W}(\eta^2\text{-CH}_3\text{CN})$: ^1H NMR (C_6D_6) δ 4.12 (Cp), 2.58 (CH_3); IR (Nujol) ν_{CN} 1725 cm^{-1} . Anal. ($\text{C}_{12}\text{H}_{13}\text{NW}$) C, H. $\text{Cp}_2\text{Mo}(\eta^2\text{-CH}_3\text{CN})$ and two related compounds containing an η^2 -nitrile have been reported by Thomas.¹³

(13) Thomas, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5943.

present in ^{12}C methyl groups ($^{12}\text{CH}_n\text{D}_{3-n}$) increases to its equilibrium value by a first-order process with a rate constant ($k_{\text{obsd}}^{\text{H}} = 2.9 \times 10^{-5} \text{ s}^{-1}$) approximately equal to $k_{\text{obsd}}^{\text{C}}$ indicates that no intramolecular scrambling occurs—i.e., $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$ is converted to $\text{Cp}_2\text{W}(\text{D})\text{CHD}_2$ by the same process that transfers deuterium from one molecule to another and converts $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3$ into $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_2\text{D}$.

The tungsten hydride in $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$ can thus exchange with the C-H bonds in the methyl ligand of another molecule of the same material—at a rate that competes successfully with intramolecular methane elimination except in very dilute solution. Preliminary ^2D NMR experiments show similar exchange between $\text{Cp}_2\text{W}(\text{D})\text{CD}_3$ and Cp_2WH_2 . Similar exchange between arene hydrogens and M-H bonds of the early transition metals is common,¹⁶ but the tungsten hydrides discussed herein are the first hydrides for which intermolecular exchange with an *aliphatic ligand* has been reported.

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Registry No. $\text{Na}[\text{D}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$, 94370-28-2; $\text{Cp}_2\text{W}(\text{CH}_3)(\text{OCOPh})$, 73210-66-9; $(\eta^5\text{-C}_5\text{H}_4\text{D})(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{H})\text{CH}_3$, 94370-29-3; $\text{Cp}_2\text{W}(\text{D})\text{CH}_3$, 94370-30-6; $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$, 72415-89-5; $\text{Cp}_2\text{W}(\text{H})\text{CD}_3$, 94370-31-7; $\text{Cp}_2\text{W}(\text{H})^{13}\text{CH}_3$, 94370-32-8; $\text{Cp}_2\text{W}(\text{D})\text{CD}_3$, 94370-33-9; $\text{Cp}_2\text{W}(\eta^2\text{-CD}_3\text{CN})$, 94370-34-0; D_2O , 7789-20-0; CH_3D , 676-49-3; CD_3H , 676-80-2; $^{13}\text{CH}_4$, 6532-48-5; CD_4 , 558-20-3; CD_2H_2 , 676-55-1; CH_4 , 74-82-8.

Supplementary Material Available: Determination of the equilibrium constant K for eq 5 from ^1H and ^2D NMR relative intensity measurements and determination of the equilibrium fraction of ^{13}C present in undeuterated methyl groups and the equilibrium fraction of ^1H present in ^{12}C methyl groups (4 pages). Ordering information is given on any current masthead page.

(16) See footnote 13 of ref 3f for a list of leading references on this topic; see especially: Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

Formyl, Acyl, and Carbene Derivatives of $\text{Fe}_3(\mu_3\text{-EPh})_2(\text{CO})_9$ (E = N, P). Unique Examples of Carbene-Nitrene and Carbene-Phosphinidene Coupling

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The chemistry of phosphinidene-bridged ($\mu_3\text{-PR}$) compounds is currently under active exploration.¹ Comparatively fewer nitrene-bridged ($\mu_3\text{-NR}$) clusters have been prepared, and little is known about the chemistry of this bridging ligand.² The few

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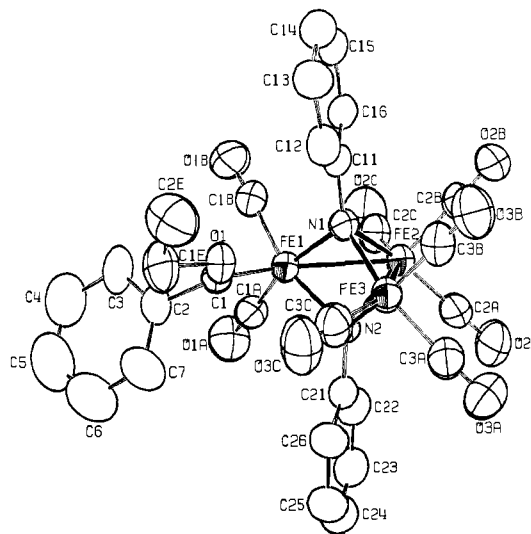
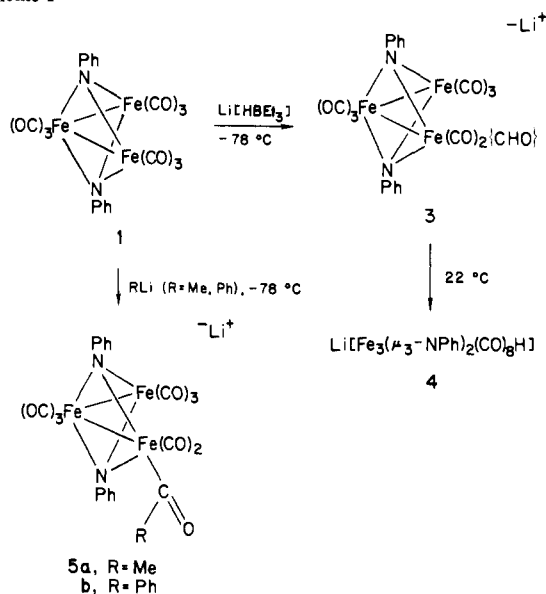


Figure 1. ORTEP drawing of $\text{Fe}_3(\mu_3\text{-NPh})_2(\text{CO})_8[\text{C}(\text{OEt})\text{Ph}]$ (6). Relevant bond distances (Å) and angles (deg): Fe(1)-Fe(2), 2.498 (1); Fe(2)-Fe(3), 2.419 (1); Fe(1)-N(1), 1.937 (4); Fe(1)-N(2), 1.929 (4); Fe(2)-N(1), 1.980 (4); Fe(2)-N(2), 1.988 (4); Fe(3)-N(1), 1.944 (4); Fe(3)-N(2), 1.939 (4); Fe(1)-C(1), 1.856 (5); Fe(1)-Fe(2)-Fe(3), 77.04 (3).

Scheme I



studies do indicate that μ_3 -nitrene ligands are relatively inert since they are not easily removed by hydrogenation to give amines or carbonylation to give isocyanates.³ In our studies of the derivative chemistry of the μ_3 -nitrene cluster $\text{Fe}_3(\mu_3\text{-NPh})_2(\text{CO})_9$ (1)⁴ and its phosphinidene analogue $\text{Fe}_3(\mu_3\text{-PPh})_2(\text{CO})_9$ (2)⁵ we have discovered unique examples of carbene-nitrene and carbene-phosphinidene coupling, details of which are described herein.

Complex 1 reacts with $\text{Li}[\text{BHET}_3]$ to give a relatively stable formyl derivative $\text{Li}[\text{Fe}_3(\mu_3\text{-NPh})_2(\text{CO})_8(\text{CHO})]$ (3),⁶ which at

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(6) 3: IR (THF) 2050 m, 2004 s, 1997 s, 1975 m, 1938 m, 1595 cm^{-1} ; ^1H NMR δ 14.52 (s, CHO).