metal center, followed by loss of an olefin, has been obtained in phenyltungsten trichloride–aluminum chloride mixtures.[21] The results reported here confirm that each of these reactions can provide metal carbene complexes.

Several metal carbenes have been suggested as active catalytic species in solution, among these $(CO)_4WCPh_2$[22] and $(CO)_4ReCHCH_2CH_3^+$.[23] It was expected that $(CO)_4MnCH_2^+$ would exhibit similar chemistry, but the activated complex formed in its reaction with olefins only loses CO.

Olefin homologation processes (e.g. reaction 10) are documented for $(\eta^5\text{-}C_5H_5)_2TiCH_2AlCl(CH_3)_2$[3a] and several tantalum alkylidenes,[3b] as well as being observed in systems catalyzing the metathesis reaction.[5] The results reported here show that the carbene complex $MnCH_2^+$ undergoes competing metathesis and homologation reactions.

The present results include the first experimental determinations of metal–carbene bond dissociation energies. Important points are that (a) metal–methylene bond energies are extremely strong and (b) the Mn^+-methylene bond energy is decreased substantially on addition of five carbonyls to the metal center.[24] There is no obvious requirement that an effective metathesis catalyst possess a strong metal–carbene bond. However, if the metal–carbene bond energy exceeds 100 kcal/mol, then transfer of the carbene to an olefin to give a cyclopropane or new olefin will be endothermic and thus will not compete with the metathesis reaction. In order to avoid low turnover numbers resulting from consumption of carbene intermediates, strong metal–carbene bonds are a desirable feature of practical metathesis catalysts.

We are continuing to explore the effects of a variety of ligands on metal–carbene bond strengths, as well as periodic trends in reactivities and thermochemistry of these species.

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(9) Mn^+ was produced by 100-eV electron impact ionization of $Mn_2(CO)_{10}$ (obtained from Alfa Products).

(10) All reactions are identified by double resonance techniques.[7] In reaction 3, for example, a decrease in abundance of MnO^+ is observed on irradiating Mn^+. In addition, double resonances were repeated with and without neutral reactants present, as well as with manganese ions absent.

(11) Deuterium transfer is consistent with alkylidene units remaining intact; for example no $MnCHD^+$ is observed from reaction of $MnCH_2^+$ with CD_2CD_2.

(12) This type of rearrangement is observed for $(CO)_5WC(C_6H_5)(CH_3)$ in solution: Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533.

(13) Owing to the complexities of the reaction pathways, rates of reactions were not measured; we estimate rate constants to be on the order of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Comparable product intensities resulted from the competing reactions 4 and 9, and 8 and 10.

(14) Thermochemical data is taken from Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds", Academic Press: New York, **1975**. Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, No. 37. An exception is $\Delta H_f°(CH_2)$ = 92.4 kcal/mol: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1975**, *4*, No. 1. Another is $\Delta H_f°(CH_2F)$ = −4.9 kcal/mol: Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269. All data are at 298 K.

(15) The method of obtaining Mn^+ ions[9] raises the possibility of producing manganese ions in excited states. However, the appearance potential curve for $MnCH_2^+$ produced by reaction 5 is superimposable on that of Mn^+, consistent with reaction of ground state Mn^+ ions (s^1d^5, ^7S).

(16) Exothermicity of reactions 6, 9, and 4 similarly requires 84 kcal/mol $\leq$ $D(Mn^+\text{–}O)$ $\leq$ 106 kcal/mol.

(17) Pentacarbonyl(fluoromethyl)manganese was prepared by decarbonylation of $(CO)_5MnC(O)CH_2F$ and purified by sublimation: Noack, K.; Schaerer, U.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *8*, 517. Traces of $(CO)_5MnC(O)CH_2F$ remained in the sample, as evidenced by the presence of $(CO)_6Mn^+$ in the mass spectrum.

(18) These reactions are similar to those used to generate molybdenum perfluorocarbene complexes in solution: Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67.

(19) The bond energy $D[(CO)_5Mn^+\text{–}CH_2]$ is calculated from the ~1.7-eV difference in appearance potentials of the two fragments $(CO)_5MnCH_2^+$ and $(CO)_5Mn^+$. The thresholds for these reactions are being determined more precisely using photoionization mass spectrometry.

(20) Schrock[3b] has estimated $D(Cp_2TaCH_3\text{–}CH_2)$ to be on the order of 75 kcal/mol.

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(24) These results can be compared with a $D(Mn^+\text{–}CH_2)$ of <10 kcal/mol, calculated using an ab initio single-configuration SCF wave function: Brooks, B. R.; Schaeffer III, H. F. *Mol. Phys.* **1977**, *34*, 193.

Amy E. Stevens, J. L. Beauchamp*
Contribution No. 6054
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

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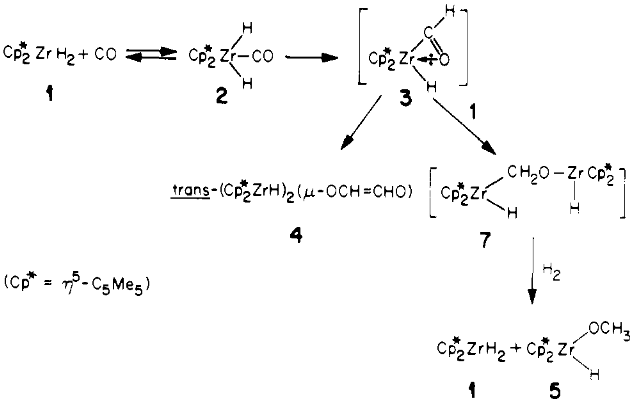
Dihydrogen Reduction of Isocyanides Promoted by Permethylzirconocene Dihydride. A Modeling Study of Carbon Monoxide Reduction

Sir:

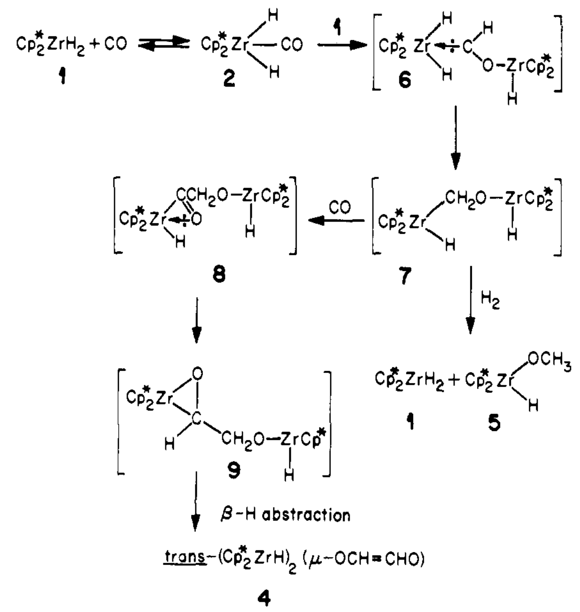
We have reported the stoichiometric reduction of carbon monoxide by $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**1**) leads to *trans*-$[(\eta^5\text{-}C_5Me_5)_2ZrH]_2(\mu\text{-}OCH{=}CHO)$ (**4**) or $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (**5**), depending on the reaction conditions (Scheme I).[1,2] The proposed key intermediate, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^2\text{-}CHO)$ (**3**), generated by migratory insertion of CO into a Zr—H bond, was postulated to exhibit an oxy-carbenoid reactivity undergoing dimerization (**3** → **4**) or insertion into a Zr—H bond of **1** eventually leading to **5**.[2] In light of recent results[3] which indicate that formyl complexes of transition metals from groups 7 and 8 spontaneously decompose in most cases to the corresponding carbonyl hydrides, one might question whether the rearrangement of **2** to **3** is thermodynamically accessible even with a substantial Zr-O interaction for **3**.[4] In addition, our findings that **1** is capable of the facile reduction of coordinated carbon monoxide to "zirconoxy" carbenes[5] suggest an alternative mechanism for the generation

Scheme I



0002-7863/79/1501-6450$01.00/0

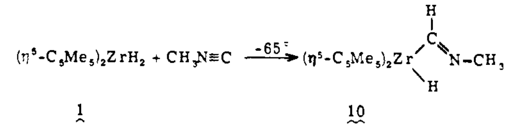
Scheme II



of **4** and/or **5** from **2** (Scheme II). This pathway avoids the need for an intramolecular rearrangement of **2** → **3**, and, furthermore, each step of this alternative mechanism is precedented by analogous steps previously observed in the reactions of zirconium hydrides.[2,5,6]

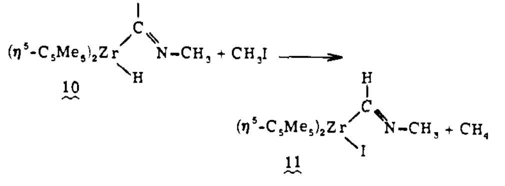
The issue, therefore, centers around the question of *intramolecular* migratory insertion of CO into a Zr—H bond for the carbonyl adduct **2**. Since migratory insertion of isocyanides, which are isoelectronic with CO, into Ru—H, Os—H, and Pt—H bonds has been demonstrated,[7] it appears necessary to establish whether or not this process could be observed for **1**.

Methyl isocyanide does indeed react rapidly with **1** at −65 °C to afford directly the formimidoyl hydride derivative $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH{=}NCH_3)$[8] (**10**) (eq 1) in ~90% yield (NMR). Although the stability of **10** was not sufficient to allow its full characterization, ^{1}H NMR and IR data indicate the *cis*-formimidoyl structure shown in eq 1. The more stable iodo derivative **11** was obtained by treatment of **10** with excess methyl iodide at 25 °C. Concurrent with its formation is the evolution of 0.92 mol of CH_4/mol of **10** (eq 2). Analytical, ^{1}H NMR, and IR data[9] are indicative of a structure for **11** completely analogous to **10**.



$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + CH_3N{\equiv}C \xrightarrow{-65°} (\eta^5\text{-}C_5Me_5)_2Zr(H)(CH{=}NCH_3) \quad (1)$$

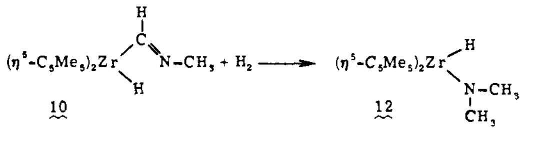
1 10



$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH{=}NCH_3) + CH_3I \longrightarrow (\eta^5\text{-}C_5Me_5)_2Zr(I)(CH{=}NCH_3) + CH_4 \quad (2)$$

10 11

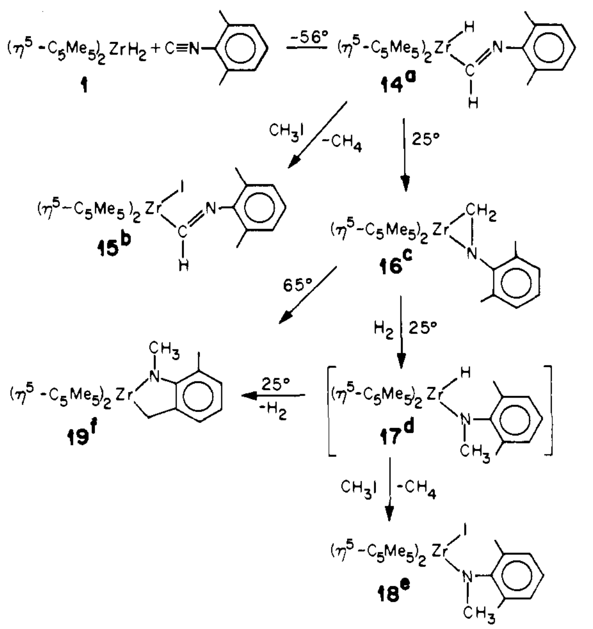
Warming a solution of **10** under H_2 (1 atm) from −80 °C to room temperature results in absorption of 0.73 mol of H_2/mol of **10**. $(\eta^5\text{-}C_5Me_5)_2Zr(H)(NMe_2)$ (**12**)[10] may be recovered by sublimation of the residue in 72% yield (eq 3).



$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH{=}NCH_3) + H_2 \longrightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)(N(CH_3)CH_3) \quad (3)$$

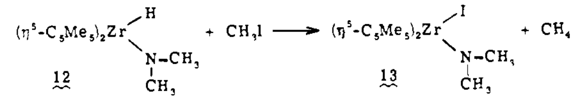
10 12

Scheme III



[a] note 12. [b] note 13. [c] note 14. [d] note 15. [e] note 16. [f] note 17.

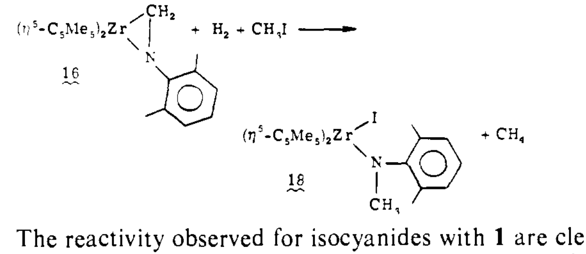
Treatment of **12** with excess methyl iodide yields $(\eta^5\text{-}C_5Me_5)_2Zr(I)(NMe_2)$ (**13**)[11] in good yield concurrent with evolution of 0.89 mol of CH_4/mol of **12** (eq 4).



$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(N(CH_3)CH_3) + CH_3I \longrightarrow (\eta^5\text{-}C_5Me_5)_2Zr(I)(N(CH_3)CH_3) + CH_4 \quad (4)$$

12 13

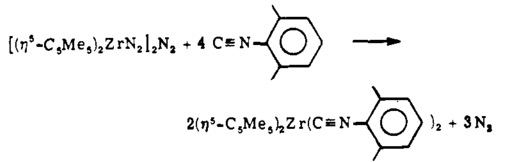
The reactions of 2,6-dimethylphenyl isocyanide with **1** parallel those of methyl isocyanide (Scheme III), although here the formimidoyl hydride derivative[12] rearranges spontaneously at room temperature to the methylene imine adduct **16**,[14] which could be isolated from hexane as a brown microcrystalline material in ~80% yield. When solutions of **16** were warmed to 65 °C, a quantitative conversion (NMR) into the zirconacycle **19**[17] was observed. Apparently the propensity for permethylzirconcene derivatives to insert into ligand C—H bonds provides a rather facile pathway to this isomer with the less strained five-membered ring.[18] Interestingly, the isomerization of **16** to **19** is catalyzed by H_2: by monitoring the reaction by ^{1}H NMR spectrometry, a clean conversion of **16** into **19** is observed to proceed readily under 1 atm of H_2 at 25 °C. Whereas no *net* H_2 evolution or uptake occurs in this process, the catalysis appears to involve the amido hydride **17**, as would be expected by analogy to the reactivity of methyl formimidoyl hydride complex **10** with H_2. Thus by carrying out the reaction of **16** with H_2 (1 atm) in the presence of CH_3I, intermediate **17** is trapped as the iodo derivative; concurrently, H_2 (0.91 mol/mol of **16**) is absorbed, and CH_4 (1.00 mol/mol of **16**) is evolved (eq 5).



(5)

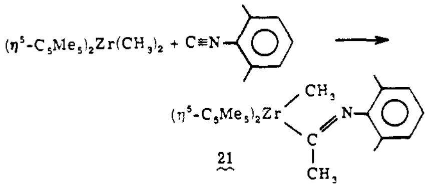
16 18

The reactivity observed for isocyanides with **1** are clearly similar to that for CO. Furthermore, 2,6-dimethylphenyl isocyanide appears to serve as a viable substitute for carbon monoxide in the displacement of dinitrogen from $[(\eta^5\text{-}C_5Me_5)_2ZrN_2]_2N_2$, affording the green, microcrystalline adduct $(\eta^5\text{-}C_5Me_5)_2Zr(C{\equiv}NC_8H_9)_2$ (**20**)[19] in 85% isolated yield (eq 6), and in its facile insertion into Zr—C bonds of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$ leading in >95% yield (NMR) to the acetimidoyl methyl complex **21**[20] (eq 7).



20

(6)



21

(7)

Direct observation of the formimidoyl hydride species **10** and **14**, undoubtedly formed by facile migratory insertion of isocyanide into a Zr—H bond of the unstable adduct $(\eta^5\text{-}C_5Me_5)_2ZrH_2(C{\equiv}NR)$, is supportive of earlier proposals of the analogous intramolecular migratory insertion of CO for **2**. It should be emphasized, however, that similar reactivity has been observed with isocyanides but not with carbon monoxide for ruthenium, osmium, and platinum complex hydrides, so that our findings are more appropriately viewed as necessary but insufficient evidence for Scheme I. Furthermore, an alkyl substituent on the nitrogen atom of coordinated isocyanides would clearly disfavor the bimolecular hydride transfer step analogous to that for ligated CO in Scheme II owing to steric crowding.

The close structural similarities of the formimidoyl hydrides,[21] methylene imine complex **16**, and amide hydrides to some proposed intermediates and products obtained from $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ with carbon monoxide are nonetheless in line with earlier suggestions.[1,2]

Acknowledgment. This work has been supported by the National Science Foundation (Grant Nos. CHE-75-03056 and CHE-78-06659) to whom grateful acknowledgment is made.

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(8) ^{1}H NMR (toluene-d_8): η^5-$C_5(CH_3)_5$, s, δ 1.79 (30 H); ZrH, s, 3.97 (1 H); N═CH, q, 9.87 (1 H); N—CH_3, d, 3.14 (3 H) (^4J = 1.4 Hz). IR (Nujol mull): ν(Zr—H) 1510; ν(C═N) 1617 cm^{-1}.

(9) Calcd for $ZrC_{22}H_{34}NI$: C, 49.80; H, 6.46; N, 2.64. Found: C, 49.94; H, 6.45; N, 2.55. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.76 (30 H); N═CH, q, 9.16 (1 H); N—CH_3, d, 3.11 (3 H) (^4J = 1.3 Hz). IR (Nujol mull): ν(C═N) 1628 cm^{-1}.

(10) Calcd for $ZrC_{22}H_{37}N$: C, 64.96; H, 9.17; N, 3.44. Found: C, 64.82; H, 8.98; N, 3.28. ^{1}H NMR (benzene-d_6); η^5-$C_5(CH_3)_5$, s, δ 1.94 (30 H); Zr—H, s, 6.41 (1 H); $N(CH_3)_2$, s, 2.41 (6 H). IR (Nujol mull): ν(Zr—H) 1550 cm^{-1}.

(11) Calcd for $ZrC_{22}H_{36}NI$: C, 49.61; H, 6.81; N, 2.63. Found: C, 49.41; H, 6.95; N, 2.53. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s δ 1.91 (30 H); $N(CH_3)_2$, s, 2.67 (6 H).

(12) ^{1}H NMR (toluene-d_8) at −56 °C; η^5-$C_5(CH_3)_5$, s, δ 1.80 (30 H); Zr—H, s, 4.82 (1 H); N—$C_8H_3(CH_3)_2$, s, 3.06 (3 H), and s, 2.24 (3 H); N—$C_6H_3(CH_3)_2$, m, 6.9–7.1 (3 H); N═CH, s, 10.61 (1 H).

(13) Calcd for $ZrC_{29}H_{40}NI$: C, 56.11; H, 6.49; N, 2.26. Found: C, 56.29; H, 6.59; N, 2.21. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.81 (30 H); N—$C_6H_3(CH_3)_2$, s, 2.42 (6 H); N—$C_6H_3(CH_3)_2$, A_2B, 6.8 (3 H); N═CH, s, 10.03 (1 H).

(14) Calcd for $ZrC_{29}H_{41}N$: C, 70.39; H, 8.35; N, 2.83. Found: C, 70.26; H, 8.41; N, 2.77. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.71 (30 H); N—$C_6H_3(CH_3)_2$, s, 2.86 (3 H), and s, 0.56 (3 H); N—$C_6H_3(CH_3)_2$, m, 6.6–7.1 (3 H); NCH_2, s, 2.93 (2 H).

(15) ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.84 (30 H); Zr—H, s, 5.60 (1 H); N—CH_3, s, 2.99 (3 H); N—$C_6H_3(CH_3)_2$, s, 2.32 (3 H), and s, 2.13 (3 H); N—$C_6H_3(CH_3)_2$, m, 6.85–7.15 (3 H).

(16) Calcd for $ZrC_{29}H_{42}NI$: C, 55.93; H, 6.80; N, 2.25. Found: C, 55.89; H, 6.84; N, 2.17. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.97 (15 H), and s, 1.64 (15 H); N—CH_3, s, 2.98 (3 H); N—$C_6H_3(CH_3)_2$, s, 2.37 (3 H), and s, 2.04 (3 H); N—$C_6H_3(CH_3)_2$, m, 6.85–6.95 (3 H).

(17) Calcd for $ZrC_{29}H_{41}N$: C, 70.39; H, 8.35; N, 2.83. Found: C, 70.15; H, 8.21; N, 2.75. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.72 (30 H); N—CH_3, s, 2.29 (3 H); N—$C_6H_3(CH_3)CH_2$–, s, 2.86 (3 H); N—$C_6H_3(CH_3)CH_2$–, s, 2.86 (3 H); N—$C_6H_3(CH_3)CH_2$–, m, 6.80–7.05 (3 H); N—$C_6H_3(CH_3)CH_2$—Zr, s, 1.92 δ (2 H).

(18) Treatment of $(\eta^5\text{-}C_5Me_5)_2ZrD_2$ with 1,6-dimethylphenyl isocyanide yielded after heating to 65 °C **19**-d_2 with the two deuteriums located exclusively in the *N*-methyl group (NMR).

(19) Calcd for $ZrC_{36}H_{48}N_2$: C, 73.14; H, 7.75; N, 4.49. Found: C, 72.89; H, 7.85; N, 4.33. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.92 (30 H); N—$C_6H_3(CH_3)_2$, s, 2.46 (12 H); N—$C_6H_3(CH_3)_2$, A_2B, 6.86 (6 H). IR (Nujol mull): ν(C≡N) 1795, 1938 cm^{-1}.

(20) Calcd for $ZrC_{31}H_{45}N$: C, 71.20; H, 8.67; N, 2.68. Found: C, 71.08; H, 8.76; N, 2.55. ^{1}H NMR (benzene-d_6): η^5-$C_5(CH_3)_5$, s, δ 1.91 (30 H); Zr—CH_3, s, −0.3 (3 H); N═CCH_3, s, 1.97 (3 H); N—CH_3, s, 2.67 (3 H). IR (Nujol mull): ν(C═N) 1630 cm^{-1}.

(21) The question of the coordination mode (η^1 vs. η^2) of the formimidoyl ligands of **10,** 11, **14,** and **15** and the acetimidoyl ligand of **21** remains open, although we presently favor the sterically less crowded η^1 coordination. The ν(C═N) frequencies are in accord with this suggestion. See for example: DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979,** *166*, 193. Yamamoto, Y.; Yamasaki, H. *Ibid.* **1970,** *23*, 717.

(22) Camille and Henry Dreyfus Teacher–Scholar, 1977–1982.

Peter T. Wolczanski, John E. Bercaw*[22]
Contribution No. 6039
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

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Methylides from Trimethylsilylmethylsulfonium, -ammonium, -immonium, and -phosphonium Salts

Sir:

Fluoride ion induced cleavage of carbon–silicon bonds has become a useful tool for the generation of nucleophilic carbon species.[1] To date, there is little evidence to determine which of the resulting nucleophiles are true carbanions and which are best described as anionic fluoride adducts[1b] of the starting silane. However, it seems reasonable to assume that sufficiently stabilized carbanions would exist in solution independently of the fluorosilane fragment. In this paper, we report that cesium fluoride induced desilyation occurs readily with a variety of systems $(CH_3)_3SiCH_2X$ where X = positively charged sulfur, nitrogen, or phosphorus. The resulting reactive intermediates undergo characteristic reactions of sulfur, nitrogen, and phosphorus ylides.

An acceptable route to the required phosphonium salts is already available from ICH_2SiMe_3 and the phosphine.[2] However, the analogous reaction of simple amines requires drastic conditions (100–150 °C, several days' reaction time)[3,2a] and alkylation of sulfides fails totally.[2a] We have found that the corresponding triflate **1** ($CF_3SO_3CH_2SiMe_3$, from $HOCH_2SiMe_3$ and triflic anhydride/pyridine)[4] is far superior in

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