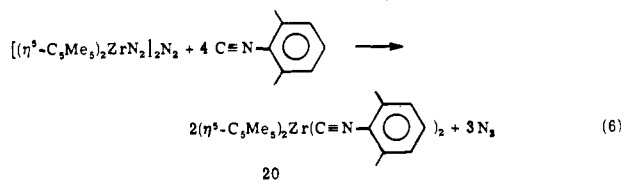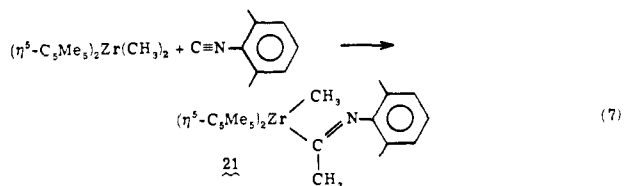isocyanide appears to serve as a viable substitute for carbon monoxide in the displacement of dinitrogen from $[(\eta^5\text{-}C_5Me_5)_2ZrN_2]_2N_2$, affording the green, microcrystalline adduct $(\eta^5\text{-}C_5Me_5)_2Zr(C\equiv NC_8H_9)_2$ **(20)**[19] in 85% isolated yield (eq 6), and in its facile 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).



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]

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(8) $^1$H NMR (toluene-$d_8$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 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): $\nu$(Zr—H) 1510; $\nu$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 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): $\nu$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.94 (30 H); Zr—H, s, 6.41 (1 H); N(CH$_3$)$_2$, s, 2.41 (6 H). IR (Nujol mull): $\nu$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s $\delta$ 1.91 (30 H); N(CH$_3$)$_2$, s, 2.67 (6 H).
(12) $^1$H NMR (toluene-$d_8$) at $-56$ °C; $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.80 (30 H); Zr—H, s, 4.82 (1 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 3.06 (3 H), and s, 2.24 (3 H); N—C$_6$H$_3$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.81 (30 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 2.42 (6 H); N—C$_6$H$_3$(CH$_3$)$_2$, A$_2$B, 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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.71 (30 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 2.86 (3 H), and s, 0.56 (3 H); N—C$_6$H$_3$(CH$_3$)$_2$, m, 6.6–7.1 (3 H); NCH$_2$, s, 2.93 (2 H).
(15) $^1$H NMR (benzene-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.84 (30 H); Zr—H, s, 5.60 (1 H); N—CH$_3$, s, 2.99 (3 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 2.32 (3 H), and s, 2.13 (3 H); N—C$_6$H$_3$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.97 (15 H), and s, 1.64 (15 H); N—CH$_3$, s, 2.98 (3 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 2.37 (3 H), and s, 2.04 (3 H); N—C$_6$H$_3$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.72 (30 H); N—CH$_3$, s, 2.29 (3 H); N—C$_6$H$_3$(C$H_3$)CH$_2$–, s, 2.86 (3 H); N—C$_6$H$_3$(CH$_3$)CH$_2$–, s, 2.86 (3 H); N—C$_6$H$_3$(CH$_3$)CH$_2$–, m, 6.80–7.05 (3 H); N—C$_6$H$_3$(CH$_3$)C$H_2$—Zr, s, 1.92 $\delta$ (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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 1.92 (30 H); N—C$_6$H$_3$(C$H_3$)$_2$, s, 2.46 (12 H); N—C$_6$H$_3$(CH$_3$)$_2$, A$_2$B, 6.86 (6 H). IR (Nujol mull): $\nu$(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-$d_6$): $\eta^5$-$C_5(CH_3)_5$, s, $\delta$ 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): $\nu$(C=N) 1630 cm$^{-1}$.
(21) The question of the coordination mode ($\eta^1$ vs. $\eta^2$) 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 $\eta^1$ coordination. The $\nu$(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.
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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 HO-$CH_2SiMe_3$ and triflic anhydride/pyridine)[4] is far superior in

**Table I.** Sulfur Ylide Generation

| entry | product (% yield)$^a$ |
|---|---|
| 1 | $C_5H_{11}CH(SCH_3)CO_2Me \xrightarrow{b} C_4H_9CH{=}CHCO_2Me$ (81) |
| | $C_5H_{11}CH(SCH_3)CO_2Me \xrightarrow[]{\text{1} \quad (C_3H_7)_4N^+F^-} C_4H_9CH{=}CHCO_2Me$ (42) |
| 2 | (2-dioxolanyl)$(CH_2)_3CH(SCH_3)CO_2Me \xrightarrow{b}$ (2-dioxolanyl)$CH_2CH_2CH{=}CHCO_2Me^c$ (85) |
| 3 | $THPOCH_2CH{=}CH(CH_2)_3CH(SCH_3)CO_2Me \xrightarrow{b} THPOCH_2CH{=}CH(CH_2)_2CH{=}CHCO_2Me^c$ (63) |
| 4 | 2-methylthio-2-methylbutanolactone $\xrightarrow{d}$ 2-methyl-2-butenolactone (64) <br> + 2-methylenebutanolactone (22) |
| 5 | $n\text{-}C_{12}H_{25}SPh \xrightarrow{b}$ 1-dodecene (75) + $PhSCH_3$ (77) |
| 6 | $PhCH{=}CHCH_2SCH_2CO_2Et \xrightarrow{b} PhCH(CH{=}CH_2)CH_2SCH_2CO_2Et^c$ (81) <br> + $PhCH(CH{=}CH_2)CH(SCH_3)CO_2Et^c$ (9) |

$^a$ Yields refer to material isolated by preparative layer chromatography. $^b$ Sulfide alkylation with $Me_3SiCH_2OTf$ in $CH_3CN$ at 20 °C, 1–2 h; dry CsF added after alkylation is complete, 16-h desilylation time at 20 °C. $^c$ Satisfactory exact mass data obtained. $^d$ Alkylation with 1 in $CH_2Cl_2$, 48 h at 20 °C; solvent removed and $CH_3CN$ + CsF added, 16-h desilylation time.

**Table II.** Nitrogen Ylides

| entry | product (% yield)$^a$ |
|---|---|
| 1 | dimethylcyclododecylamine $\xrightarrow{b,c}$ *trans*-cyclododecene$^d$ (70) |
| | dimethylcylododecylamine $\xrightarrow{b:\ KF,\ 18\text{-crown-6}}$ *trans*-cyclododecene$^d$ (27) |
| 2 | $N$-cinnamylpiperidine $\xrightarrow{b,c} PhCH(CH{=}CH_2)CH_2NC_5H_{10}^e$ (54) |
| 3 | $Ph(CH_2)_2CH{=}N\text{-}_t\text{-}Bu \xrightarrow{f}$ **6** (R = H; R' = $CH_2CH_2Ph$; R'' = $t$-Bu$^{e,g}$) (45) |
| 4 | $(PhCH_2)_2C{=}NCH_3 \xrightarrow[CH_3CN]{b \quad CsF}$ **6** (R = R' = $CH_2Ph$; R'' = $CH_3^{e,h}$) (48) |
| 5 | $PhCH{=}NCH_3 \xrightarrow{f}$ **6** (R = H; R' = Ph; R'' = $CH_e^{e,i}$) (70) |

$^a$ Isolated yield after chromatography. $^b$ Alkylation with $Me_3SiCH_2OTf$ (**1**) in $CH_2Cl_2$, 5 h at 20 °C. $^c$ Crystalline ammonium salt + excess CsF in dry diglyme, 16 h, 20 °C. $^d$ >95% trans by $^{13}C$ NMR. $^e$ Satisfactory exact mass data obtained. $^f$ Alkylation with **1** in $CH_3CN$, 5 h, 20 °C; add excess (~5 equiv) dry CsF and $CH_3O_2CC{\equiv}CCO_2CH_3$ (1 equiv), 16 h, 20 °C. $^g$ NMR (CDCl$_3$, $\delta$): 7.24 (5 H, m), 4.44 (1 H, t, $J$ = 4 Hz), 3.94 (2 H, q, $J_{AB}$ = 14 Hz), 3.84 (3 H, s), 3.78 (3 H, s), 3–2.4 (2 H, m), 1.9 (2 H, dt, $J$ = 4, 8 Hz), 1.06 (9 H, s). $^h$ NMR (CDCl$_3$, $\delta$): 7.22 (10 H, s), 3.7 (3 H, s), 3.58 (3 H, s), 3.30 (2 H, s), 3.11 (4 H, q, $J_{AB}$ = 14 Hz), 2.6 (3 H, s). $^i$ NMR (CDCl$_3$, $\delta$): 7.32 (5 H, s), 4.68 (1 H, t, $J$ = 6 Hz), 4.24 (2 H, q, $J_{AB}$ = 14 Hz), 3.72 (3 H, s), 3.56 (3 H, s), 2.14 (3 H, s).

all cases and alkylates, amines, imines, sulfides, phosphines, etc., at room temperature. In most instances, acetonitrile is a convenient solvent because alkylation rates are high and the resulting salts can be desilylated directly without prior isolation. Some interference due to competing alkylation of acetonitrile is observed with sterically hindered or inductively deactivated sulfides (see entry 4, Table I), and it becomes necessary to resort to an inert solvent such as methylene chloride for the alkylation step.

Generation of intermediates having ylide reactivity is achieved by stirring the acetonitrile solution of $\alpha$-silyl salts with anhydrous cesium fluoride[5] at room temperature. Although CsF is more expensive than KF, the reagent is significantly soluble in polar organic solvents and requires no additives (crown ethers, etc.) for solubilization. In our experience, the KF-18-crown-6 reagent gives relatively poor yields of ylide-derived products (see Table II). Tetraalkylammonium fluorides also give low yields in our system, presumably because of difficulties in removing traces of water from the salt. All desilylation experiments involve intra- or intermolecular ylide trapping agents, and no attempt has been made to prove that free ylides accumulate in solution in the absence of such traps.

**Sulfur Ylides.** Table I summarizes results from desilylation of $\alpha$-trimethylsilylsulfonium salts.[6] In entries 1–5, intermediates are generated which undergo apparent five-center fragmentation[7] to alkenes at 20 °C. It is noteworthy that fragmentation involves a nonstabilized methylide even though an ester-stabilized ylide could be formed by proton transfer in entries 1–3. To determine whether such interconversion occurs, a system has been studied where either ylide isomer can rearrange by 2,3-sigmatropic shift (entry 6). The major product **4** is derived from the initial methylide **2**, while **5** (minor) is formed from ester-stabilized ylide **3**. Since **4** predominates over
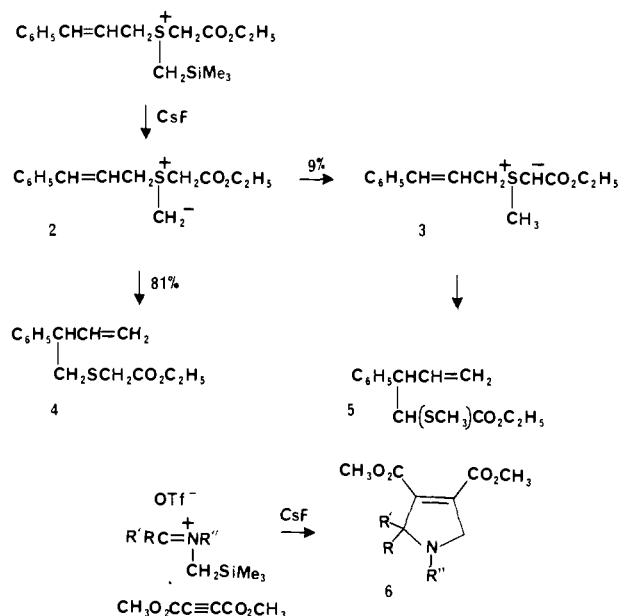
**5** by a 9:1 ratio, ylide equilibration does not lay an important role in desilylation experiments.

**Nitrogen Ylides.** Desilylation of salts $Me_3SiCH_2N^+R_3$ under the usual conditions ($CsF$, $CH_3CN$) is unsatisfactory because the major product is the parent methylammonium salt $CH_3N^+R_3$. The undesired protiodesilylation is due to proton transfer from acetonitrile and can be avoided by using diglyme as solvent. Two representative cases of nonstabilized ammonium ylide trapping have been demonstrated (Table II): entry 1, fragmentation to an alkene; entry 2, rearrangement by 2,3-sigmatropic shift. Previously, such reactions have been possible only under strongly basic conditions ($R'Li + CH_3N^+R_3$).[8]

Desilylation is especially useful for generation of nonstabilized azomethine ylides which can be trapped by 1,3-dipolar addition.[9,10] Best results are achieved by a one-pot procedure where the imine is alkylated with **1** in acetonitrile and the resulting solution of moisture-sensitive immonium salt is immediately treated with CsF and a dipolarophile. This method allows efficient trapping of azomethines even in cases where deprotonation of the ammonium salt might result in an enamine (entries 3, 4, Table II). Analogous azomethine ylides lacking $\alpha$ substituents to stabilize the carbanionic center ($\alpha$-carbonyl, cyano, phenyl, etc.) are virtually unknown in the literature.[9a,b] Stabilized azomethine ylides are of course much more common and their properties are well understood from the extensive studies by Huisgen[10] and others.[9]

**Phosphorus Ylides.** Trialkylphosphonium ylide generation from reaction of $\alpha$-silylphosphonium salts with alkoxide ion has been demonstrated by Schmidbaur et al.[11] Desilylation by chloride ion has also been demonstrated at elevated temperatures, but fluoride ion is reported to give low yields of Wittig product owing to competing protiodesilylation.[12] We have observed no such complications when the $CsF/CH_3CN$ desilylation method is used. Thus, triphenylphosphine reacts readily with **1** to give a crystalline salt (exothermic). Upon treatment with $CsF/CH_3CN$ in the presence of 4-phenylcyclohexanone (20 °C), the salt undergoes desilylation and in situ Wittig reaction to give 4-phenylmethylenecyclohexane (70% yield).

In summary, CsF-induced desilylation provides access to reactive methylides in synthetically useful yield. The reaction is most important in cases where the molecule contains base-sensitive groups or acidic C–H bonds, substituents which preclude ylide generation by strong base deprotonation of methylsulfonium, methylammonium, or methylimmonium salts. General access to nonstabilized azomethine ylides is possible for the first time, and allows synthesis of 3-pyrrolines of interest in natural products chemistry. Work is continuing in this latter area.

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(4) Trimethylsilylmethanol (1.04 g) was added over 5 min to the complex from pyridine (0.79 g) and trifluoromethanesulfonic anhydride (2.82 g) in methylene chloride (20 mL) at −20 °C. The cooling bath was removed, and stirring was continued for 2 h at 20 °C. Pentane (40 mL) was added, salts were removed by filtration, and the pentane solution was passed through a plug of silica gel (∼15 g) with more pentane. Evaporation (0 °C, aspirator) gave **1**, 1.8 g as a colorless oil (76%): NMR (CDCl₃) δ 0.19 (s, 9 H), 4.27 (s, 2 H). The crude triflate is sufficiently pure for all of the experiments described in Tables I and II. If desired, **1** can be distilled without significant decomposition (bp 156–158 °C (1 atm)). The substance is stable to storage (refrigerator) and is not a potent lachrymator. However, precautions in handling this reactive alkylating agent are recommended.

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### Reversible Loss of Metal Ions from the Zinc Binding Site of Copper–Zinc Superoxide Dismutase. The Low pH Transition

*Sir:*

Copper–zinc superoxide dismutase, $Cu_2Zn_2SOD$,[1] from bovine erythrocytes consists of two identical subunits, each of which contains approximately one Cu(II) and one Zn(II)[2] bridged by an imidazolate anion derived from the side chain of histidine 61.[3,11] A number of metal-substituted derivatives have been prepared and spectroscopic studies have convincingly established the location of the metal ions in each derivative.[11,13] Solutions of $Cu_2Zn_2SOD$ or $Cu_2Co_2SOD$ have been



$M = Cu^{2+}$; $M' = Zn^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Hg^{2+}$, $Cd^{2+}$
$M = Ag^+$; $M' = Cu^{2+}$, $Co^{2+}$
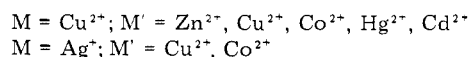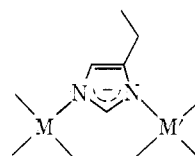
observed to undergo reversible spectral changes below pH 4.5 attributed to a breaking of the imidazolate bridge by protonation of histidine 61.[10,14–16] In the course of our studies of the metal binding properties of this protein,[17,18] we were struck by the resemblance between the spectra of $Cu_2Zn_2SOD$, $Cu_2Cu_2SOD$, and $Cu_2E_2SOD$[1] below pH 4. We have therefore investigated the behavior of these derivatives at low pH and have reexamined the published data concerning the low pH transition in $Cu_2Co_2SOD$. It is our conclusion that the metal ion affinity of the native zinc binding site drops abruptly but reversibly at low pH and that the metal ion is consequently