excess of imidazole to the protein sample. The 483-ppm peak now reappears at 519 ppm and the 751-ppm peak is still unshifted. Since imidazole is not known[5] to coordinate to the noncatalytic site, this directly identifies the 483-ppm resonance as the catalytic Cd(II).

There has been some discrepancy between solid and solution experiments in regard to first- or second-sphere imidazole coordination to the catalytic metal ion. Crystal studies indicate direct coordination to zinc,[14] while imidazole proton relaxation studies with completely cobalt substituted LADH have been interpreted in terms of second-sphere coordination.[17] Our solution data indicated first-sphere coordination. In a titration of $CdSO_4$ at pH 7.4 with 0.5-10 equiv of imidazole we observe a continuously shifted resonance, and we can calculate the average number of imidazoles bound per cadmium from published equilibrium constants.[18] The positions of these $^{113}Cd$ NMR resonances yield downfield shifts for one imidazole replacing an $H_2O$ ranging from 41 to 30 ppm. The downfield shift of the catalytic cadmium resonance is within this range at 36 ppm. We do not believe that this shift could be due to conformational changes affecting Cd(II) ligation. Our preliminary coenzyme binding experiments indicate upfield shifts of 42 ppm upon the conformational change with NADH binding. In addition, the X-ray study of the native enzyme-imidazole complex detected no movement in the protein ligands of the catalytic metal ion compared with the native enzyme alone.[14] We believe that the 36-ppm upfield shift upon imidazole binding, assuming insignificant conformational changes, demonstrates direct coordination of imidazole to the catalytic Cd(II).

Further coenzyme and substrate binding studies are under way at various pH values to learn more about the nature of coordination at the catalytic site.

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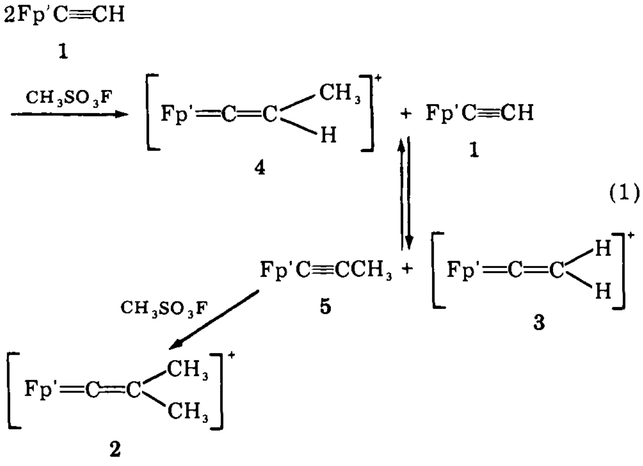
## Stepwise Reduction of an Ethynyl-Iron Complex to a Neopentylidene Complex

*Sir:*

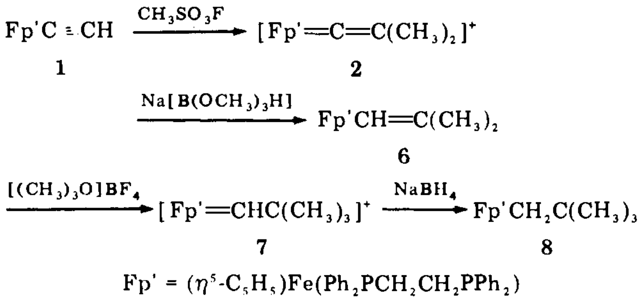
We report here the stepwise reduction of a metal-ethynyl complex to an 18-electron neopentylidene complex. Each intermediate has been isolated and characterized.

The sequence of reactions shown in Scheme I exploits the tendency for monohapto carbon ligands attached to late transition metals to undergo $\alpha$ attack by nucleophiles and $\beta$ attack by electrophiles.[1] The ethynyl complex **1**[1b] reacts rapidly with methyl fluorosulfonate in benzene to give principally a equimolar mixture of the isobutenylidene complex **2**[1b] and the vinylidene complex **3**,[2] along with a small quantity of the propenylidene complex **4**, as shown by $^1H$ NMR and infrared spectroscopy. Evidently, the ethynyl complex **1** is more basic than the propynyl complex **5** ($pK_a = 7.7$).[1b] Thus, equilibrium 1 explains the formation of **2** and **3**.



Complex **2** reacts with the sodium trimethoxyhydridoborate in THF to give an ~4:1 mixture (by $^1H$ NMR) of the isobutenyl complex **6** and Fp′H.[4] The complex **6** can be isolated in 20% yield by fractional crystallization. Anal. ($C_{35}H_{36}FeP_2$), C, H, P. Mass spectrum: parent ion *m/e* 574. $^1H$ NMR (60 MHz, $C_6D_6$): $\delta$ 7.60, 7.15 (m, 20 H, Ph), 5.33 (t, $^3J_{PH} = 8.5$ Hz, 1 H, $H_\alpha$), 4.30 (t, $^3J_{PH} = 1.1$ Hz, 5 H, Cp), 2.3–1.7 (br m, 4 H, $PCH_2$), 2.05 (s, 3 H, $CH_3$), 1.08 (s, 3 H, $CH_3$). $^{13}C$ NMR (15 MHz, $C_6D_6$): 144.5–131.0 (complex, Ph), 128.6 (br s, $C_\beta$), 127.7 (t, $^2J_{PC} = 3.9$ Hz, $C_\alpha$), 78.4 (s, Cp), 33.7 (s, $CH_3$), 27.0 (t, $^1J_{PC} = 21.5$ Hz, $PCH_2$), 21.9 ppm (s, $CH_3$).

$Fp'CH{=}C(CH_3)_2$ (**6**) reacts with trimethyloxonium tetrafluoroborate in dichloromethane to give the neopentylidene complex **7** in ~60% crude yield. Recrystallization of **7** from acetone gave a mixture of black crystals of [Fp′(acetone)]-[$BF_4$] ($\nu_{CO}$ 1700–1710 $cm^{-1}$; lit.[4b] for $PF_6^-$ salt, $\nu_{CO}$ 1710 $cm^{-1}$) and orange crystals of **7**. Anal. ($C_{36}H_{39}BF_4FeP_2$) C, H, P. $^1H$ NMR (60 MHz, $CD_2Cl_2$): $\delta$ 13.68[5] (t, $^3J_{PH} = 14.0$ Hz, 1 H, $C_\alpha$), 7.6–6.9 (m, 20 H, Ph), 5.13 (br s, 5 H, Cp), 3.18 (d, $^2J_{PH} = 11.0$ Hz, 4 H, $PCH_2$), 0.71 (s, 9 H, $(CH_3)_3$). $^{13}C$ NMR (15 MHz, $CD_2Cl_2$): 359.5 (t, $^2J_{PC} = 26.4$ Hz, $C_\alpha$), 137.0–129.3 (complex, Ph), 88.4 (s, Cp), 63.0 (s, $C_\beta$), 28.3 (t, Scheme I



$$\underset{\mathbf{1}}{\mathrm{Fp'C{\equiv}CH}} \xrightarrow{\mathrm{CH_3SO_3F}} \underset{\mathbf{2}}{[\mathrm{Fp'{=}C{=}C(CH_3)_2}]^+}$$

$$\xrightarrow{\mathrm{Na[B(OCH_3)_3H]}} \underset{\mathbf{6}}{\mathrm{Fp'CH{=}C(CH_3)_2}}$$

$$\xrightarrow{\mathrm{[(CH_3)_3O]BF_4}} \underset{\mathbf{7}}{[\mathrm{Fp'{=}CHC(CH_3)_3}]^+} \xrightarrow{\mathrm{NaBH_4}} \underset{\mathbf{8}}{\mathrm{Fp'CH_2C(CH_3)_3}}$$

$$\mathrm{Fp'} = (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(Ph_2PCH_2CH_2PPh_2)}$$

${}^1J_{PC} = 20.5$ Hz, $PCH_2$), 28.8 ppm (s, $(CH_3)_3$). $^{13}C$ NMR ($^1H$ gated decoupled, $^1J_{CH}$ only): 126.0 Hz ($C_\alpha$), 178.8 (Cp), 130.4 ($PCH_2$), 128.0 ($(CH_3)_3$). The preparation of $[Fp'{=}CHC(CH_3)_3]BF_4$ (**7**) from **6** represents the first instance of the preparation of a nonheteroatom-substituted alkylidene complex from an alkenyl precursor.[7] The infrared spectrum (mull) of **7** did *not* display the low-frequency C–H stretching mode (~2500 cm$^{-1}$) found in neopentylidene complexes with less than 18 valence electrons, such as $CpTa[CHC(CH_3)_3]Cl_2$.[8]

The reaction of $[Fp'CH(CH_3)_3][BF_4]$ with excess $NaBH_4$ in THF gave an ~2:3 mixture of the neopentyl complex **8** and Fp′H as shown by $^1H$ NMR. $Fp'CH_2C(CH_3)_3$ (**8**) could be isolated in ~8% yield by column chromatography on silica gel. It was characterized by its $^1H$ NMR spectrum (60 MHz, $C_6D_6$): $\delta$ 7.85–7.45 (m, 4 H, Ph), 7.4–6.7 (m, 30 H, Ph + $C_6D_5H$), 4.40 (br s, 5 H, Cp), 2.00 (1:1:1 t, $J$ = 10 Hz, 4 H, $PCH_2$), 1.30 (t, $^3J_{PH}$ = 10 Hz, 2 H, $FeCH_2$), 0.84 (s, 9 H, $(CH_3)_3$).

The significance of the reaction sequence in Scheme I lies in its elucidation of the nucleophilicity of $C_\beta$ and the electrophilicity of $C_\alpha$ in unsaturated ligands of late[9] transition metal complexes. Similar polarizations have been demonstrated for thiocarbonyl[10] and dinitrogen[11] complexes.

Further studies of the chemistry of iron vinylidene complexes will be reported subsequently.

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## Novel Transformation of Primary, Secondary, and Tertiary Amines to Organoselenides with Ruthenium Catalyst

*Sir:*

The transformation of amine compounds which are easily prepared[1] and naturally occurring[2] would appear to possess tremendous potential. However, known methods for these transformations are limited to a few reactions[3] which include oxidations of a tertiary amine with a stoichiometric oxidant.[4] As a consequence of studies directed to using a strategy for the generation of an iminium ion-metal complex (**1**) from a tertiary amine with metal catalysts,[5] a new general method has been developed for the catalytic transformation of tertiary, secondary, and primary amines to the corresponding phenyl selenides as depicted in eq 1–3.

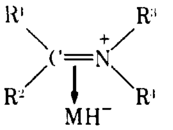
$$\mathrm{R^1R^2R^3N + PhSeNa \xrightarrow[2.\ H_2O]{1.\ Ru} R^1SePh + R^2R^3NH} \quad (1)$$

$$\mathrm{R^1R^2NSiMe_3 + RhSeLi \xrightarrow[2.\ H_2O]{1.\ Ru} R^1SePh + R^2NH_2} \quad (2)$$

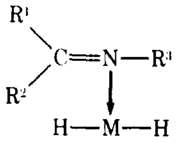
$$\mathrm{R^1N(SiMe_3)_2 + PhSeLi \xrightarrow[2.\ H_2O]{1.\ Ru} R^1SePh + NH_3} \quad (3)$$

Treatment of a wide variety of amines with an equivalent of benzeneselenolates in diglyme in the presence of ruthenium catalyst results in formation of phenyl selenides uniformly in excellent yields. The scope of this operationally simple, highly selective, and efficient transformation is illustrated in Table I.

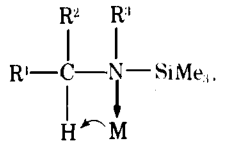
Primary and secondary amines do not undergo the transformation since these amines produce a Schiff-base complex (**2**)[6] instead of an iminium ion complex **1** upon treatment with metal catalysts. This difficulty can be overcome by the protection of their nitrogen–hydrogen bonds. In view of the key step of the initial activation of the carbon–hydrogen bond adjacent to nitrogen with the metal coordinating to the nitrogen,[5] an electron-donating group such as a trimethylsilyl group should be a good protecting group (**3**).[7] To clarify this point, the reaction of an equimolar mixture of (+)-*N*,*N*-dimethyl- (**4**), (+)-*N*-methyl-*N*-trimethylsilyl- (**5**), and (+)-*N*,*N*-bis(trimethylsilyl)-*sec*-butylamine (**6**) was carried out in the presence of palladium catalyst at 100 °C. The optical activities of the recovered amines, which were each collected by preparative VPC, showed that the relative rate of the racemization of **4**, **5**, and **6** was 1.0:2.0:3.6 (Table II). Actually, *N*-mono(trimethylsilyl)- and *N*,*N*-bis(trimethylsilyl)amines undergo the same transformation efficiently under considerably milder conditions (80–100 °C) as shown in Table I. Ruthenium catalyst, prepared by the reduction of ruthenium trichloride with potassium, gave excellent results.[8]



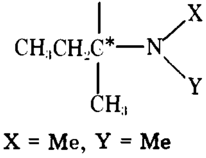
**1**



**2**



**3**



**4**, X = Me, Y = Me
**5**, X = Me, Y = SiMe$_3$
**6**, X = SiMe$_3$, Y = SiMe$_3$

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