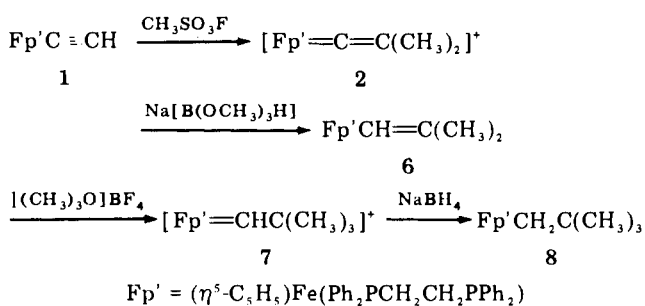


## Scheme I



$^1J_{\text{PC}} = 20.5$  Hz, PCH<sub>2</sub>, 28.8 ppm (s, (CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR ( $^1\text{H}$  gated decoupled,  $^1J_{\text{CH}}$  only): 126.0 Hz (C<sub>α</sub>), 178.8 (C<sub>β</sub>), 130.4 (PCH<sub>2</sub>), 128.0 ((CH<sub>3</sub>)<sub>3</sub>). The preparation of [Fp' = CHC(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**7**) from **6** represents the first instance of the preparation of a nonheteroatom-substituted alkylidene complex from an alkenyl precursor.<sup>7</sup> The infrared spectrum (mull) of **7** did not display the low-frequency C-H stretching mode (~2500 cm<sup>-1</sup>) found in neopentylidene complexes with less than 18 valence electrons, such as CpTa[CHC(CH<sub>3</sub>)<sub>3</sub>]-Cl<sub>2</sub>.<sup>8</sup>

The reaction of [Fp'CH(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> with excess NaBH<sub>4</sub> in THF gave an ~2:3 mixture of the neopentyl complex **8** and Fp'H as shown by  $^1\text{H}$  NMR. Fp'CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub> (**8**) could be isolated in ~8% yield by column chromatography on silica gel. It was characterized by its  $^1\text{H}$  NMR spectrum (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.85–7.45 (m, 4 H, Ph), 7.4–6.7 (m, 30 H, Ph + C<sub>6</sub>D<sub>5</sub>H), 4.40 (br s, 5 H, Cp), 2.00 (1:1:1 t,  $J = 10$  Hz, 4 H, PCH<sub>2</sub>), 1.30 (t,  $^3J_{\text{PH}} = 10$  Hz, 2 H, FeCH<sub>2</sub>), 0.84 (s, 9 H, (CH<sub>3</sub>)<sub>3</sub>).

The significance of the reaction sequence in Scheme I lies in its elucidation of the nucleophilicity of C<sub>β</sub> and the electrophilicity of C<sub>α</sub> in unsaturated ligands of late<sup>9</sup> transition metal complexes. Similar polarizations have been demonstrated for thiocarbonyl<sup>10</sup> and dinitrogen<sup>11</sup> complexes.

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

**Acknowledgment.** We thank the National Science Foundation for a graduate fellowship to J.P.S.

## References and Notes

- (1) (a) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8–C12. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765.
- (2) The  $^{13}\text{C}$  NMR spectrum<sup>3</sup> of vinylidene complex **3** was not previously reported (15 MHz, CDCl<sub>3</sub>): 354.5 (AXY,  $^2J_{\text{PC}} = 35.1$ ,  $^2J_{\text{PC}} = 33.7$  Hz, C<sub>α</sub>), 136.9–128.0 (complex multiplets, Ph), 106.8 (s, C<sub>β</sub>), 88.9 (s, Cp), 28.5 ppm (t,  $^1J_{\text{PC}} = 22.7$  Hz, PCH<sub>2</sub>).
- (3)  $^{13}\text{C}$  NMR spectra were recorded on a HEOL FX-60Q spectrometer with internal deuterium lock and complete proton decoupling, at ambient probe temperature. Shifts are reported in parts per million downfield from Me<sub>4</sub>Si.
- (4) (a) Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1873. (b) Sellmann, D.; Kleinschmidt, E. *J. Organomet. Chem.* **1977**, *140*, 211–219.
- (5) Similar low-field resonances have been observed for H<sub>α</sub> in other secondary alkylidene complexes of the later transition metals.<sup>6</sup>
- (6) (a) Brookhart, M.; Nelson, G. L. *J. Am. Chem. Soc.* **1977**, *99*, 6099–6101. (b) Casey, C. P.; Polichnowski, S. W. *Ibid.*, **1977**, *99*, 6097–6099.
- (7) The reaction of CpFe(CO)(PPh<sub>3</sub>)[C(OC<sub>2</sub>H<sub>5</sub>)=CH<sub>2</sub>] with HBF<sub>4</sub> produces [CpFe(CO)(PPh<sub>3</sub>)[C(OC<sub>2</sub>H<sub>5</sub>)CH<sub>3</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, a carbenoid species: Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237–9238.
- (8) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.*, **1979**, *101*, 3210–3222. (b) Schultz, A. J.; Williams, J. F.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *Ibid.*, **1979**, *101*, 1593–1595.
- (9) It has been amply demonstrated that alkylidene complexes of the early transition metals, e.g., tantalum, are nucleophilic at C<sub>α</sub>: Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578.
- (10) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73–89.
- (11) Sellman, D.; Weiss, W. *J. Organomet. Chem.* **1978**, *160*, 183–196.

Alan Davison,\* John P. Selegue

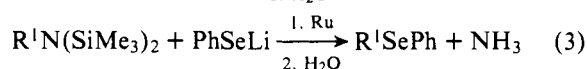
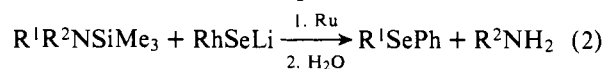
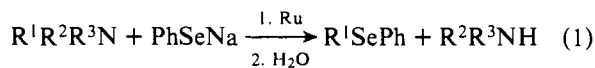
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received February 12, 1979

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

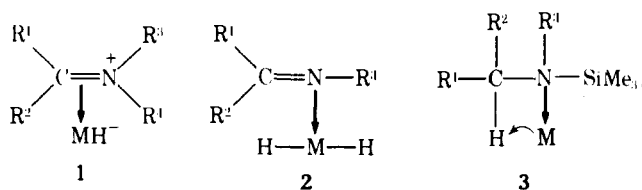
Sir:

The transformation of amine compounds which are easily prepared<sup>1</sup> and naturally occurring<sup>2</sup> would appear to possess tremendous potential. However, known methods for these transformations are limited to a few reactions<sup>3</sup> which include oxidations of a tertiary amine with a stoichiometric oxidant.<sup>4</sup> 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,<sup>5</sup> 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.

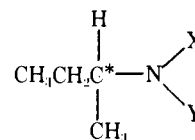


Treatment of a wide variety of amines with an equivalent of benzeneselenolates in diglyme in the presence of ruthenium catalyst results in formation of phenyl selenides uniformly in excellent yields. The scope of this operationally simple, highly selective, and efficient transformation is illustrated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

Primary and secondary amines do not undergo the transformation since these amines produce a Schiff-base complex (**2**)<sup>6</sup> 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,<sup>5</sup> an electron-donating group such as a trimethylsilyl group should be a good protecting group (**3**).<sup>7</sup> To clarify this point, the reaction of an equimolar mixture of (+)-*N,N*-dimethyl-, (+)-*N*-methyl-*N*-trimethylsilyl-, and (+)-*N,N*-bis(trimethylsilyl)-*sec*-butylamine (**6**) was carried out in the



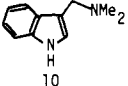
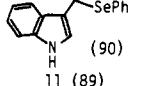
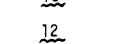
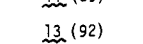
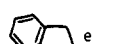
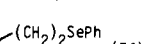
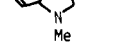
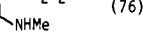
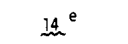
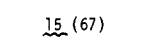
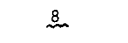
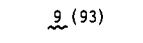
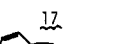
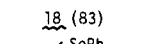
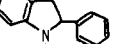
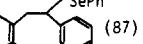
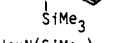
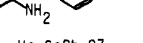
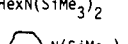
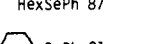
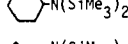
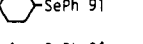
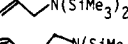
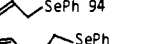
**4**, X = Me, Y = Me

**5**, X = Me, Y = SiMe<sub>3</sub>

**6**, X = SiMe<sub>3</sub>, Y = SiMe<sub>3</sub>

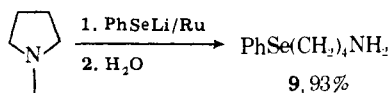
presence of palladium catalyst at 100 °C. The optical activities of the recovered amines, which were each collected by preparative VPC, showed that the relative rate of the racemization of **4**, **5**, and **6** was 1.0:2.0:3.6 (Table II). Actually, *N*-mono(trimethylsilyl)- and *N,N*-bis(trimethylsilyl)amines 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.<sup>8</sup>

**Table I.** The Ruthenium-Catalyzed Reactions of Amines with Benzeneselenolate<sup>a</sup>

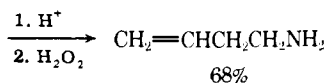
Entry	Amines	Temp. (°C)	Time (hr)	Product <sup>b</sup> and Yield <sup>c</sup> % (isolated) <sup>d</sup>
1	Bu <sub>3</sub> N <sup>e</sup>	150	15	BuSePh 88 Bu <sub>2</sub> NH 89
2		150	15	 (90)
3		100	15	 (89)
4		100	15	 (92)
5		150	20	 (76)
6		100	10	 (67)
7		80	10	 (93)
8	Hex <sub>2</sub> N-SiMe <sub>3</sub>	80	6	HexSePh 94 HexNH <sub>2</sub> 90
9		100	10	 (83)
10		150	20	 (87)
11	HexN(SiMe <sub>3</sub> ) <sub>2</sub>	100	10	HexSePh 87
12		100	10	 91
13		80	6	 94
14		100	10	 (72)
15		100	10	 (81)

<sup>a</sup> A mixture of amine (6 mmol), lithium benzeneselenolate (8 mmol), and ruthenium catalyst (1 mmol) in diglyme (8 mL) was reacted under argon. <sup>b</sup> Identified by IR, NMR, and mass spectral data and elemental analyses. <sup>c</sup> GLC yields based upon the starting amine using an internal standard. <sup>d</sup> Isolated yields by chromatographic separation or distillation.

The efficiency of the transformation of silylamines is augmented by the ease with which it is performed, as typified in the two-step synthesis of homoallylamine, which is obtained with difficulty<sup>9</sup> by other methods (entry 7). The process corresponds to the highly selective Hofmann elimination reaction. A mixture of anhydrous ruthenium trichloride (624 mg, 3 mmol) and potassium (354 mg, 9 mmol) in anhydrous diglyme (10 mL) was reacted with stirring at 120 °C for 3 h under argon. *N*-Trimethylsilylpyrrolidine (**8**, bp 51 °C at 32 mmHg), 3.06 g, 36 mmol), prepared from pyrrolidine (**7**), lithium amide, and trimethylsilyl chloride, and a solution of lithium benzeneselenolate (48 mmol)<sup>10</sup> in diglyme (10 mL), prepared from phenyllithium and selenium, were added at room temperature. The resulting mixture was allowed to react with stirring at 80 °C for 10 h under argon. The reaction mixture was then quenched with water, filtered off, and extracted with ether. Removal of the solvent followed by silica gel chromatography [CHCl<sub>3</sub>-MeCO<sub>2</sub>Et (10:1)] gave aminoselenide (**9**)



**7**, X = H  
**8**, X = SiMe<sub>3</sub>



(7.63 g, 93%). To a solution of **9** (6.84 g, 30 mmol) in THF (50 mL) was added an aqueous hydrogen chloride solution (30

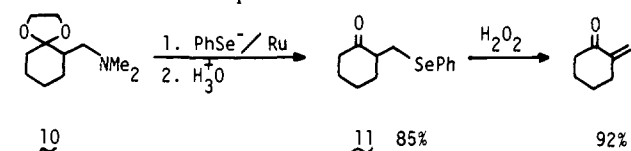
**Table II.** The Reaction of *N,N*-Disubstituted (+)-*sec*-Butylamines (**4–6**) with Palladium Catalyst<sup>a</sup>

amine	[α] <sup>20</sup> <sub>D</sub> of amine, <sup>b</sup> deg	[α] <sup>20</sup> <sub>D</sub> of recovered amine, <sup>c</sup> deg	rel rate
<b>4</b>	+16.1	+12.3	1.0
<b>5</b>	+10.3	+5.16	2.0
<b>6</b>	+7.32	+0.69	3.6

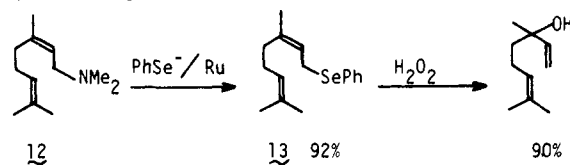
<sup>a</sup> An equimolar mixture of three optically active *N,N*-disubstituted *sec*-butylamines was treated with palladium black at 100 °C for 10 h under argon. <sup>b</sup> Prepared from optically active *sec*-butylamine (optical purity, 98.4%). <sup>c</sup> The recovered *N,N*-disubstituted amines were purified by preparative GLC.

mmol) at 0 °C for 30 min, and then a 30% hydrogen peroxide solution (90 mmol) at 0 °C.<sup>11</sup> The reaction mixture was stirred at the same temperature until the yellow color of the solution became colorless (30 min). After addition of a solution of KOH, the mixture was extracted with methylene chloride. The usual workup followed by distillation (bp 75–76 °C) gave 3-butenylamine (1.45 g, 68%). It is noteworthy that lithium benzeneselenolate prepared by direct selenation of phenyllithium<sup>10</sup> must be used instead of sodium benzeneselenolate,<sup>12</sup> which causes reductive cleavage of the silicon–nitrogen bond of silylamines.

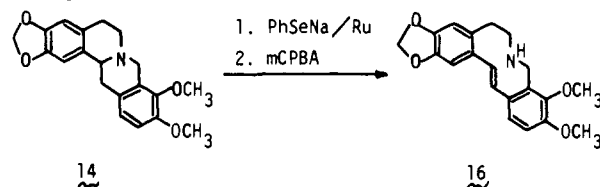
Tertiary amines undergo the transformation without difficulty upon treatment with lithium or sodium benzeneselenolates. In connection with the recently developed organoselenium chemistry, the incorporation of PhSe group permits a variety of modifications to be made to the product.<sup>13</sup> In contrast to the usual selenation of the α position of carbonyl compounds,<sup>13</sup> regioselective β-selenation can be accomplished upon treatment of the ketals of Mannich bases which are readily derived from carbonyl compounds.<sup>14</sup> Thus, the ketal **10** of the well-known Mannich compound was converted into selenide **11**



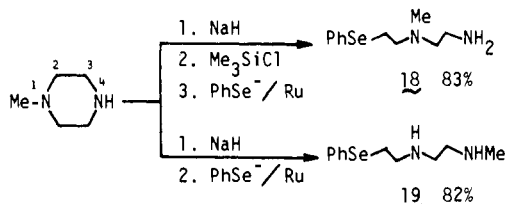
(85% overall yield) after hydrolysis of the ketal. *N,N*-Dimethylnerylamine (**12**), which is readily prepared from the base-catalyzed condensation of isoprene with dimethylamine,<sup>15</sup> was converted into linalool (83% overall yield) by the transformation to give nerylphenyl selenide (**13**),<sup>16</sup> oxidation, and [2,3]-sigmatropic rearrangement.<sup>17</sup>



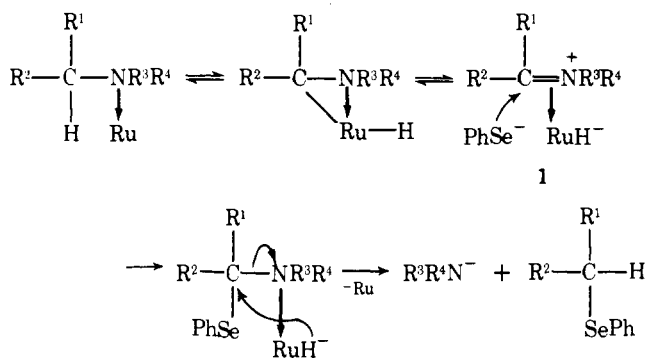
Even more important is the high regio- and chemoselectivities of this transformation. The carbon–nitrogen bonds of a tertiary amine are cleaved more readily in the order of methine > methylene > methyl. Cyclic nitrogen compounds undergo selective ring opening to produce aminoselenides which are often versatile synthetic intermediates. Thus, treatment of (±)-canadine (**14**) with sodium benzene selenolate at 100 °C in the presence of the ruthenium catalyst gave 9,10-dime-



thoxy-2,3-methylenedioxy-14-phenylselenohexahydrodibenz[*c,g*]azecine (**15**) (mp 153 °C)<sup>18</sup> in 67% yield. Oxidation of **15** with *m*-chloroperbenzoic acid (CH<sub>2</sub>Cl<sub>2</sub>, -78 °C) gave azecine **16** (mp 131–132 °C, 61%).<sup>19,20</sup> It is noteworthy that intramolecular cyclization<sup>21</sup> of **16** with PdCl<sub>2</sub>(PhCN)<sub>2</sub> catalyst gave (±)-**14** (mp 169–171 °C)<sup>22</sup> in 83% yield. Furthermore, chemoselective transformation of primary, secondary, and tertiary amines is performed. For instance, *N*-methylpiperazine undergoes either the bond cleavage between N<sub>1</sub>-C<sub>2</sub> or N<sub>4</sub>-C<sub>3</sub> exclusively, depending on the reaction condition employed. Thus, the ruthenium-catalyzed reaction of *N*-methyl-*N'*-trimethylsilylpiperazine (**17**) with lithium benzeneselenolate gave **18** (83% isolated yield), while that of *N*-methylpiperazine sodium amide gave **19** (82%) with no sign of the other possible opening product in either case.



Nucleophilic attack of selenolate anions on the iminium ion complex **1**,<sup>23,24</sup> formed from the insertion of ruthenium into a carbon-hydrogen bond adjacent to the nitrogen,<sup>5,25</sup> and subsequent reductive cleavage seem to operate as key steps.



Work is currently in progress on the extension of potential application of this transformation to other system and of use in the synthesis of natural products.

## References and Notes

- (1) (a) Tramontini, M. *Synthesis*, **1973**, 703. (b) Böhme, H.; Viehe, H. G., Ed. *Adv. Org. Chem.* **1976**, *9*. (c) Cook, A. G., Ed. "Enamines"; Marcel Dekker: New York, 1969.
- (2) (a) Nakanishi, K.; Goto, T.; Ito, S.; Natori, S.; Nazoe, S., Ed. "Natural Products Chemistry"; Kodansha Academic Press: Japan, 1975; Vol. 2. (b) ApSimon, J., Ed. "The Total Synthesis of Natural Products"; Wiley: New York, 1977, Vol. 3.
- (3) White, E. H.; Woodcock, D. J. "The Chemistry of the Amino Group", Patai, S., Ed.; Wiley-Interscience: New York, 1962; p 407.
- (4) (a) Modified Polonovski reaction: Potier, P.; Langlois, N.; Langlois, Y.; Guéritte, F. *J. Chem. Soc., Chem. Commun.* **1975**, 670. Langlois, N.; Guéritte, F.; Langlois, Y.; Potier, P. *J. Am. Chem. Soc.* **1976**, *98*, 7017. Mangeney, P.; Andriamialisoa, R. Z.; Langlois, N.; Langlois, Y.; Potier, P. *Ibid.* **1979**, *101*, 2243. (b) Modified von Braun reaction: Kutney, J. P.; Fingendolf, G. K.; Matoe, H.; Murai, A.; Tanaka, K.; Shung, W. L.; Wada, K.; Worth, B. R. *Ibid.* **1978**, *100*, 938. Jeffs, P. W.; Scharver, J. D. *Ibid.* **1976**, *98*, 4301. (c) Mercury acetate: Leonard, N. J.; Hay, A. S.; Fulmer, R. W.; Gash, A. J. *Ibid.* **1955**, *77*, 439.
- (5) Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.*, **1978**, *100*, 348.
- (6) Yoshimura, N.; Moritani, I.; Shimamura, T.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1973**, *95*, 3038. Yoshimura, N.; Moritani, I.; Shimamura, T.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1973**, 307.
- (7) Nöth, H.; Tinhof, W.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 518.
- (8) Other catalysts such as rhodium and palladium gave good results; the conversions of tributylamine were 92, 94, and 79% upon treatment with sodium benzeneselenolate in the presence of ruthenium, rhodium, and palladium catalysts (150 °C, 10 h), respectively.
- (9) Current methods for synthesis of homoallylamines: (a) Ettliger, M. G.; Hodgkins, J. E. *J. Am. Chem. Soc.*, **1955**, *77*, 1831. (b) Bortolussi, M.; Bloch, R.; Conia, J. M. *Bull. Soc. Chim. Fr.* **1975**, 2371. (c) Wille, H.; Goubau, J. *Chem. Ber.* **1972**, *105*, 2156. (d) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 587, 590, 593. (e) Schell, F. M.; Carter, J.-P.; Wiauz-Zamer, C. *J. Am. Chem. Soc.* **1978**, *100*, 2894.
- (10) Sato, M.; Yoshida, T. *J. Organomet. Chem.* **1974**, *67*, 395.
- (11) Generally, selective oxidation of the PhSe group in amino phenyl selenides was performed upon treatment with H<sub>2</sub>O<sub>2</sub> or mcpba after protonation of the amino group to avoid oxidation of the amino group.
- (12) Gunther, W. H. H. *J. Org. Chem.* **1966**, *31*, 1202.
- (13) (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (b) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (c) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singh, and M. W. Young, *Chem. Scr.*, **1975**, *8A*, 9.
- (14) (a) Danishefsky, S.; Kitahara, T.; Mckee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715. (b) Holy, N. C.; Wang, Y. F. *Ibid.* **1977**, *99*, 944. (c) Kinast, G.; Tietze, L.-F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 239.
- (15) Tanabe, K.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1972**, 4009; *Chem. Lett.* **1977**, 1025.
- (16) NMR (CDCl<sub>3</sub>, δ) 1.57 (s, 3 H, (Z)-Me), 1.67 (s, 6 H, (E)-Me), 1.95 (d, 4 H, CH<sub>2</sub>CH<sub>2</sub>, J = 3.5 Hz), 3.50 (d, 2 H, J = 8.0 Hz, CH<sub>2</sub>Se), 4.90–5.60 (m, 2 H, olefin), 7.13 (m, 3 H, Ph), 7.47 (m, 2 H, Ph).
- (17) (a) Reich, H. J. *J. Org. Chem.*, **1975**, *40*, 2570. (b) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.*, **1973**, *95*, 2697.
- (18) NMR (CDCl<sub>3</sub>, δ) 1.25 (s, 1, NH), 2.55–3.38 (m, 6), 3.61 (s, 1, H<sup>6</sup>), 3.80 (s, 6, OCH<sub>3</sub>), 4.08 (s, 1, H<sup>6</sup>), 4.46 (t, 1, H<sup>14</sup>, J = 4.0 Hz), 5.85 (s, 2, OCH<sub>2</sub>O), 6.52 (s, 1, H<sup>4</sup>), 6.67 (s, 1, H<sup>11</sup>), 6.77 (s, 2, H<sup>1</sup>, H<sup>12</sup>), 7.17 (m, 3), 7.50 (m, 2 H); mass (*m/e*) 496, 495, 419, 340, 164, 156, 149, 77.
- (19) NMR (CDCl<sub>3</sub>, δ) 1.29 (s, 1 H, NH), 2.73 (t, 2 H, J = 4.0 Hz, H<sup>6</sup>), 3.57 (t, 2, J = 4.0 Hz, H<sup>5</sup>), 3.78 (s, 6, OCH<sub>3</sub>), 3.90 (d, 2, J = 1.5 Hz, H<sup>6</sup>), 5.85 (s, 3, OCH<sub>2</sub>O), 6.41 (d, 1, J = 16 Hz, H<sup>8</sup>, H<sup>13</sup>), 6.52 (s, 1, H<sup>4</sup>), 6.67 (s, 1, H<sup>11</sup>), 6.77 (s, 2, H<sup>1</sup>, H<sup>12</sup>), 7.07 (d, 1, J = 16 Hz, H<sup>14</sup>).
- (20) Kirby, A. J.; Logan, C. J. *J. Chem. Soc., Perkin Trans. 2* **1978**, 642. Prabhaker, S.; Lobo, A. M. *J. Chem. Soc., Chem. Commun.* **1977**, 419.
- (21) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800.
- (22) Kametani, T.; Noguchi, I.; Saito, K.; Kaneda, S. *J. Chem. Soc. C*, **1969**, 2036.
- (23) Seebach, D.; Meyer, N.; Beck, A. K. *Justus Liebigs Ann. Chem.* **1977**, 846.
- (24) Benzeneselenolate reacts 4.8 times faster than benzenethiolate. See Murahashi, S.-I.; Yano, T. *J. Chem. Soc., Chem. Commun.* **1979**, 270.
- (25) Laine, R. M.; Thomas, D. W.; Cary, L. W.; Buttrill, S. E. *J. Am. Chem. Soc.* **1978**, *100*, 6527.

Shun-Ichi Murahashi,\* Tsuneo Yano

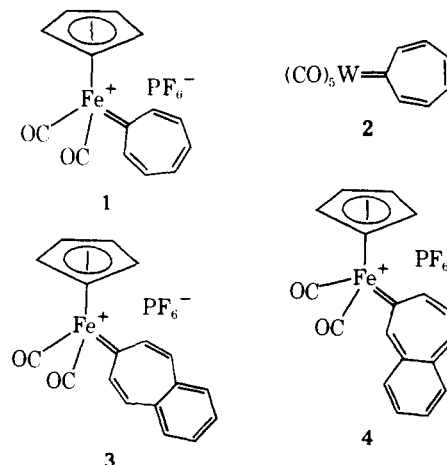
Department of Chemistry  
Faculty of Engineering Science, Osaka University  
Machikaneyama, Toyonaka, Osaka, Japan 560

Received November 29, 1979

## Synthesis and Crystal Structures of Cycloheptatrienylidene Complexes of Iron

Sir:

We recently reported the synthesis of **1** and **2**, the first examples of transition metal complexes of cycloheptatrienylidene (CHT).<sup>1</sup> At this time we report the application of the same method to the synthesis of two benzannulated CHT complexes **3** and **4**, as well as the X-ray crystal structures of **1** and **4**.



Bromide **6**, prepared in accordance with Scheme I and previously successful procedures,<sup>1,2</sup> was converted into **7**, as shown, and then to yellow-brown complex **8**<sup>3</sup> by treatment with