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New Ferrocenyl Sulfides and Selenides: Preparation and Application as Efficient Selective Hydrogenation Catalysts

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A series of ferrocenyl sulfides and selenides, $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}ER)$ (E = S, Se; R = *n*-Pr, *n*-Bu, *s*-Bu, *t*-Bu, Bz, 4-tolyl, 4-ClPh), have been made from the appropriate ferrocene precursors via lithiation and reaction with RSSR or RSeSeR. The following techniques were used for characterization: ^1H and ^{13}C NMR, IR, HS, and elemental analysis. The ferrocenyl sulfide derivatives readily chelate platinum(II) and palladium(II) dichloride to form heterobimetallic complexes, $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SeMe)PtCl_2$ and $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}Sr)PdCl_2$ (R = Me, *n*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *i*-Pent, Ph, Bz, 4-tolyl, 4-ClPh). ^1H and ^{13}C NMR spectra were obtained, and IR, MS, melting point, and elemental analysis data of these bimetallic complexes are presented. The palladium(II) ferrocenyl sulfide complexes are good selective homogeneous and heterogenous hydrogenation catalysts for the reduction of conjugated dienes to monoenes at room temperature.

Introduction

The preparation, characterization, and use in catalytic processes of ferrocenyl sulfide complexes of palladium and platinum has been reported by this laboratory.[1-5] In this work we report the preparation of new ferrocenyl sulfide and selenide complexes such as $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}ER)PdCl_2$ (E = S, Se; R = Pr, *n*-Bu, *s*-Bu, *t*-Bu, Bz, 4-tolyl, 4-ClPh). These chiral complexes have been used in selective hydrogenation of conjugated dienes to monoenes at ambient temperatures.

Experimental Section

Proton ^1H NMR spectra were obtained by use of a Bruker WM 250 spectrometer at 250 MHz. Unless otherwise noted, all NMR spectra were recorded in chloroform-d_1 solutions with chemical shifts reported in parts per million downfield from a TMS internal standard. The ^{13}C NMR spectra (broad-band proton decoupled and off-resonance decoupled) were obtained by use of a Bruker WM 250 spectrometer at 62.99 MHz. A pulse width (PW) of 8 s and a relaxation delay (RD) of 6 s were generally used.

Infrared spectra (IR) were obtained by use of a Perkin-Elmer 599 grating spectrophotometer by using neat films for liquid samples and Nujol or Fluorolube mulls between CsBr plates or in KBr pellets for solid samples. Mass spectra (MS) were obtained by means of a Finnigan 4021 instrument with INCOS data system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gas chromatography (GC) was carried out by using a Hewlett-Packard 5880A instrument. All melting points were determined by using a Thomas-Hoover capillary melting point apparatus. Air-sensitive reagents were manipulated in a prepurified Ar or N_2 flush or in a glovebox. [(Dimethylamino)methyl]ferrocene was made by the standard method[6] or was purchased. Bis(benzonitrile) complexes $[(PhCN)_2MCl_2]$ (M = Pd, Pt) were prepared according to published procedures.[7-9] All of the reagents and the solvents were purified by standard methods.[10] The (1,3-cyclooctadiene + cyclooctene):cyclooctane and the 1,3-cyclohexadiene:cyclooctadiene:cyclooctene ratios were determined by integration of the olefinic region of the ^1H NMR spectra. 1-[(Dimethylamino)methyl]-2-ferrocenyl selenides, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SeR)$, where R = Me (**1**), Ph (**2**), and 4-ClPh (**3**), and their palladium complexes, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SeR)]PdCl_2$, where R = Me (**4**) and 4-ClPh (**5**), were obtained previously in this laboratory.[4] 1-[(Dimethylamino)methyl]-2-ferrocenyl sulfides, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)$, where R = Me (**6**), Et (**7**), *i*-Pr (**8**), *i*-Bu (**9**), *i*-Pent (**10**), and Ph (**11**), were obtained in high yields (80%) by a modified method of Honeychuck.[5]

1-[(Dimethylamino)methyl]-2-(propylthio)ferrocene (12, R = *n*-Pr). A 2.7 M solution of *n*-BuLi in hexane (4.1 mL, 11.1 mmol) was added over a half-hour period to a solution of [(dimethylamino)methyl]ferrocene (2.3 g, 8.7 mmol) in 50 mL of dry ether under argon in a 250-mL round-bottomed Schlenk flask equipped with a magnetic stirring bar at −78 °C. The suspension was stirred for 20 h at room temperature under argon, and then 3.8 mL (25.0 mmol) of dipropyl disulfide was added via a cannula at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperaure and stirred for 20 h. The mixture was slowly added to $NaHCO_3(aq)$ and was cooled in an ice bath, and the cloudy solution was filtered. The resulting organic layer and ether extracts from the aqueous layer was combined, washed with ice water, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford a dark brown oil that was chromatographed on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil: yield 82.0%; IR (neat, CsI) 458, 500, 530, 820, 1002, 1022, 1108, 1181, 1240, 1260, 1378, 1458, 2770, 2820, 2860, 2950, 2972 cm^{-1}; MS, *m/e* (relative intensity) 43 (40, *n*-Pr), 44 (17, NMe_2), 56 (71, Fe), 58 (74, CH_2NMe_2), 65 (8, C_5H_5), 121 (100, C_5H_5Fe), 196 (6, $M^+ - C_5H_5Fe$), 242 (38, $M^+ - S\text{-}n\text{-}Pr$), 273 (12, $M^+ - NMe_2$), 274 (6, $M^+ - n\text{-}Pr$), 317 (40, M^+). Anal. Calcd for $C_{16}H_{23}NSFe$: C, 60.57; H, 7.31. Found: C, 60.17; H, 7.52.

1-[(Dimethylamino)methyl]-2-(butylthio)ferrocene (13, R = *n*-Bu). The procedure was the same for **12**, except that 4.8 mL (25.0 mL) of di-*n*-butyl disulfide was used. The product was obtained as a brown oil, yield 81.9%. Anal. Calcd for $C_{17}H_{25}NSFe$: C, 61.63; H, 7.61. Found: C, 61.45; H, 7.50.

1-[(Dimethylamino)methyl]-2-(*sec*-butylthio)ferrocene (14, R = *sec*-Bu). The procedure was the same as for **12**, except that 4.8 mL (25.0 mmol) of di-*sec*-butyl disulfide was used. The product was obtained in the form of a yellowish brown oil, yield 21.2%. Anal. Calcd for $C_{17}H_{25}NSFe$: C, 61.63; H, 7.61. Found: C, 61.59 H, 7.43.

1-[(Dimethylamino)methyl]-2-(*tert*-butylthio)ferrocene (15, R = *t*-Bu). The procedure was the same as for **12**, except that 6.0 mL (30.0 mmol) of di-*tert*-butyl disulfide was used. The

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product was obtained as yellowish brown crystals after three recrystallization (CH_2Cl_2/hexane): yield 54.3%; mp 74–75 °C. Anal. Calcd. for $C_{17}H_{25}NSFe$: C, 61.63; H, 7.61. Found: C, 61.55; H, 7.39.

1-[(Dimethylamino)methyl]-2-(isopentylthio)ferrocene (10, R = *i*-pent). The procedure was the same as for **12**, except that 1.8 mL (8.7 mmol) of diisopentyl disulfide was used. Compound **10** was obtained as a brown oil (first band after chromatography), yield 60.6%. Anal. Calcd for $C_{18}H_{27}NSFe$: C, 62.61; H, 7.88. Found: C, 62.70; H, 8.01.

1-[(Dimethylamino)methyl]-2-(phenylthio)ferrocene (11, R = Ph). The procedure was the same as for **12**, except that 1.9 g (8.7 mmol) of diphenyl disulfide in 30 mL of dry ether was used. The compound was obtained by chromatography as yellowish brown crystals of **11** after three recrystallizations (CH_2Cl_2/hexane): yield 66.2%; mp 61–62 °C. Anal. Calcd for $C_{19}H_{21}NSFe$: C, 64.96; H, 6.03. Found: C, 65.01; H, 5.99.

1-[(Dimethylamino)methyl]-2-(benzylthio)ferrocene (16, R = Bz). The procedure was the same as for **12**, except that 2.14 g (8.7 mmol) of benzyl disulfide in 150 mL of dry ether was used. The compound was obtained by chromatography as yellowish orange crystals of **16** after three recrystallizations (CH_2Cl_2/hexane): yield 51.2%; mp 70–71 °C. Anal. Calcd for $C_{20}H_{23}NSFe$: C, 65.76; H, 6.35. Found: C, 65.57; H, 6.25.

1-[(Dimethylamino)methyl]-2-(4-tolylthio)ferrocene (17, R = 4-tolyl). The procedure was the same as for **12**, except that 3.70 g (15.0 mmol) of 4-tolyl disulfide in 50 mL of dry ether was used. The product was obtained as yellowish-brown crystals after three recrystallizations (CH_2Cl_2/hexane): yield 44.0%; mp 82–85 °C. Anal. Calcd for $C_{20}H_{23}NSFe$: C, 65.76; H, 6.35. Found: C, 65.54; H, 6.35.

1-[(Dimethylamino)methyl]-2-[(4-chlorophenyl)thio]ferrocene (18, R = 4-ClPh). The procedure was the same as for **12**, except that 7.5 g (26.0 mmol) of 4-chlorophenyl disulfide in 100 mL of dry ether was used. The product was obtained as a dark brown oil, yield 61.3%. Anal. Calcd for $C_{19}H_{20}NSFeCl$: C, 59.22; H, 5.19. Found: C, 59.68; H, 5.36.

[1-[(Dimethylamino)methyl]-2-(methylseleno)ferrocene]plantinum(II) Dichloride (19). Complex **19** was prepared from a benzene solution of $((PhCN)_2)PtCl_2$ and ferroceryl selenide **1**. The molar ratio of $(PhCN)_2PtCl_2$:**1** was 1:1.1. The reaction mixture was stirred overnight, and the resulting precipitate was filtered, washed with benzene and then petroleum ether, and recrystallized from CH_2Cl_2/hexane or CH_2Cl_2/heptane by slow evaporation to give orange crystals which decomposed at 190 °C: yield 61.2%; IR (KBr pellet) 303, 326, 424, 469, 493, 509, 510, 540, 834, 1000, 1076, 1106, 1191, 1246, 1371, 1414, 1455, 1474, 2930, 3100 cm^{-1}; MS, *m/e* (relative intensity) 44 (100, NMe_2), 56 (6, Fe), 58 (11, CH_2NMe_2), 65 (34, C_5H_5), 66 (55, C_5,H_5), 95 (2, SeMe), 121 (9, C_5H_5, Fe, $M^+ - C_5H_5Fe - SeMe - PtCl_2$), 242 (1, $M^+ - SeMe - PtCl_2$), 336 (1, $M^+ - PtCl_2$). Anal. Calcd for $C_{14}H_{19}Cl_2NSeFePt$: C, 27.91; H, 3.16. Found: C, 28.06; H, 3.23.

[1-(Dimethylamino)methyl]-2-(propylthio)ferrocene]palladium(II) Dichloride (20). The procedure was the same as for **19**, except that amine thioether **12** was used. The dark brown solids decomposed at 157–158 °C; yield 75.8%. Anal. Calcd for $C_{16}H_{23}Cl_2NSFePd$: C, 38.86; H, 4.69. Found: C, 38.96; H, 4.72.

[1-(Dimethyl)-2-(butylthio)ferrocene]palladium(II) Dichloride (21). The procedure was the same as for **19**, except that amine thioether **13** was used. The red-brown crystals decomposed at 112–114 °C; yield 78.3%. Anal. Calcd for $C_{17}H_{25}Cl_2NSFePd$: C, 40.15; H, 4.95. Found: C, 40.17; H, 4.98.

[1-[(Dimethylamino)methyl]-2-(isobutylthio)ferrocene]palladium(II) Dichloride (22). The procedure was the same as for **19**, except that amine thioether **14** was used. The red-brown solid decomposed at 110–112 °C; yield 69.8%. Anal. Calcd for $C_{17}H_{25}Cl_2NSFPD$: C, 40.15; H, 4.95. Found: C, 40.39; H, 4.78.

[1-[(Dimethylamino)methyl]-2-(*tert*-butylthio)ferrocene]palladium(II) Dichloride (23). The procedure was the same as for **19**, except that amine thioether **15** was used. The red-brown crystals decomposed at 120–122 °C; yield 62.3%. Anal. Calcd for $C_{17}H_{25}NSFePd$: C, 40.15; H, 4.95. Found: C, 40.42; H, 5.09.

[1-[(Dimethylamino)methyl]-2-(isopentylthio)ferrocene]palladium(II) Dichloride (24). The procedure was the same as for **19**, except that amine thioether **10** was used. The red-brown crystals decomposed at 117–119 °C; yield 89.3%. Anal. Calcd for $C_{18}H_{27}ClNSFePd$: C, 41.37; H, 5.21. Found: C, 41.37; H, 5.19.

[1-[(Dimethylamino)methyl]-2-(phenylthio)ferrocene]palladium(II) Dichloride (25). The procedure was the same as for **19**, except that amine thioether **11** was used. The red-brown sheets decomposed at 151–153 °C; yield 83.7%. Anal. Calcd for $C_{19}H_{21}Cl_2NSFePd$: C, 43.17; H, 4.00. Found: C, 43.00; H, 3.61.

[1-[(Dimethylamino)methyl]-2-(benzylthio)ferrocene]palladium(II) Dichloride (26). The procedure was the same as for **19**, except that amine thioether **16** was used. The dark brown decomposed at 165–167 °C; yield 90.1%. Anal. Calcd for $C_{20}H_{23}Cl_2NSFePd$: C, 44.27; H, 4.27. Found: C, 43.85; H, 4.19.

[1-[(Dimethylamino)methyl]-2-(4-tolylthio)ferrocene]palladium(II) Dichloride (27). The procedure was the same as for **19**, except that amine thioether **17** was used. The red-brown plates decomposed at 145–147 °C; yield 89.3%. Anal. Calcd for $C_{20}H_{23}Cl_2NSFePd$: C, 44.27; H, 4.27. Found: C, 44.38; H, 4.65.

[1-[(Dimethylamino)methyl]-2-[(4-chlorophenyl)thio]ferrocene]palladium(II) Dichloride (28). The procedure was the same as for **19**, except that amine thioether **18** was used. The gray-green powder decomposed at 164–166 °C; yield 61.6%. Anal. Calcd for $C_{19}H_{20}Cl_3NSFePd$: C, 40.57; H, 3.56. Found: C, 40.66; H, 3.61.

Attempted Hydrogenation of 1,3-Cyclooctadiene with 19 and 20 in Acetone at 61.0 psi of Initial Hydrogenation Pressure. Ferrocene–palladium complexes **19** and **20** (2.0×10^{-5} mol), acetone (9.0 mL) and 1,3-cyclooctadiene (1.00 mL, 8.15×10^{-3} mol) were added to a 100-mL pressure bottle equipped with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a pressure of 61.0 psi. No H_2 uptake was seen in 6 days at 27 °C.

Attempted Hydrogenation of 1,3-Cyclooctadiene with 20, 23, and 27 in Methylene Chloride at 61.0 psi of Initial Hydrogen Pressure. Ferrocene–palladium complexes **20**, **23**, and **27** (2.0×10^{-5} mol), methylene chloride (9.0 mL), and 1,3-cyclooctadiene (1.00 mL, 8.15×10^{-3} mol) were added to a 100-mL pressure bottle equipped with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a pressure of 61.0 psi. No H_2 uptake was seen in 6 days at 27 °C.

Hydrogenation of 1,3-Cyclooctadiene with 20–27 in Acetone at 61.0 psi of Initial Hydrogen Pressure. Ferrocene–palladium complex **20–27** (2.0×10^{-5} mol), acetone (9.0 mL), and 1,3-cyclooctadiene (0.91 mL, 7.45×10^{-3} mol) were added to a 100-mL pressure bottle equipped with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a pressure of 61.0 psi. The induction time was dependent on the catalyst. As soon as the system passed the induction period, uptake began and slowed after absorption of 5×10^{-3} mol of H_2. The initial turnover rate, product analysis at the end of reactions, and the selectivity were determined.

The Effect of Additives in Selective Hydrogenation of 1,3-Cyclooctadiene in Acetone at 61.0 psi of Initial Hydrogen Pressure. Ferrocene–palladium complexes **23** and **27** (2.0×10^{-5} mol), acetone (9.0 mL), 1,3-cyclooctadiene (0.91 mL, 7.45×10^{-3} mol), and some different additives (water, silver nitrate, silver 4-toluenesulfonate, and pyridine) were added to a 100-mL pressure bottle equipped with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a pressure of 61.0 psi. The different results were studied.

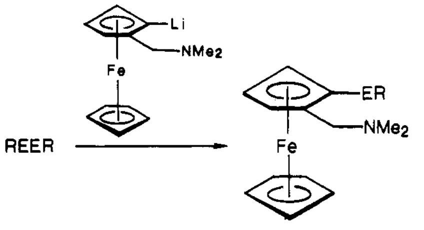
Hydrogenation of 1,3-Cyclohexadiene at Room Temperature. Ferrocene–palladium complexes **23**, **25**, and **27** (2.0×10^{-5} mol), 1,3-cyclohexadiene (7.40×10^{-3} mol), and 9.0 mL of various solvents (acetone, acetone/methylene chloride (1:2), and methylene chloride) were added to a 100-mL pressure bottle equipped with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a predetermined pressure. No H_2 uptake was observed in 3 days. Before the hydrogenation, the substrate was a white precipitate in a brown catalyst/acetone solution. Throughout the induction time, the precipitate dissolved completely, giving an orange solution, and H_2 uptake began immediately and then slowed after absorption of 7×10^{-3} mol of H_2. The color of the solution at the end of the reaction was orange. The hydrogenation was also dependent on the catalyst and initial H_2 pressure; some sensitivity to the catalyst was observed at 102.0

Table I. 250-MHz ^{1}H NMR Data for (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$-1-CH$_2$NMe$_2$-2-ER)(MCl)^a in CDCl$_3$/TMS at Room Temperature Unless Otherwise Noted [δ (J, Hz)]

	ECH$_3$, ER, PhCH$_3$			NMe$_2$		SCH$_2$, SCH		NCH$_2$				
compound	δ-CH$_3$	γ-H	β-H	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	C$_5$H$_5$	C$_5$H$_3$	Ph^g
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SeMe)PdCl$_2$ (**4**)	2.75 s			0.79	2.32 s 3.11 s			1.20	2.80 d (13) 4.00 d (13)	4.24 s	4.38 m^{b,c} 4.50 m^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SeMe)PtCl$_2$ (**19**)	2.75 t			0.71	2.53 t 3.24 t			1.10	3.25 d (13) 4.35 d (13)	4.25 s	4.36 m^{b,c} 4.52 m^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[Se(4-ClPh)]-PdCl$_2$ (**5**)				0.67	2.39 s 3.06 s			1.21	2.85 d (14) 4.06 d (14)	4.32 s	4.16 m^d 4.34 t^b 4.46 m^c	7.42 d (8.5)^m 7.81 d (8.5)^o
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(n-Pr)]PdCl$_2$ (**20**)		1.14 t (7)	1.97 m 2.34 m	0.74	2.31 s 3.08 s	0	3.28 m	1.21	2.77 d (13) 3.98 d (13)	4.25 s	4.38 m^{b,c} 4.53 m^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(n-Bu)]PdCl$_2$ (**21**)	1.01 t (7)	1.56 m	1.56 m 1.93 m	0.75	2.34 s 3.09 s	0	3.30 m	1.19	2.79 d (13) 3.98 d (13)	4.26 s	4.38 m^b 4.40 m^c 4.53 m^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(i-Bu)]PdCl$_2$ (**22**)		1.18 d (7) 1.21 d (7)	2.34 m	0.70	2.39 s 3.09 s	0.68	2.95 m 3.63 m	1.62	2.26 d (13) 3.88 d (13)	4.25 s	4.38 m^{b,c} 4.47 m^D	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(t-Bu)]PdCl$_2$ (**23**)			1.51 s	0.17	3.11 s 3.28 s			0.66	2.70 d (14) 3.36 d (14)	4.66 s	4.33 dd^c 4.52 t^b 4.82 dd^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(i-Pent)]-PdCl$_2$ (**24**)	1.01 d (6.2)	1.82 m	1.82 m 2.25 m	0.74	2.34 s 3.08 s	0	3.33 m	1.20	2.76 d (13) 3.96 d (13)	4.25 s	4.38 m^{b,c} 4.52 m^d	
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SPh)PdCl$_2$ (**25**)^e				0.63	2.52 s 3.15 s			0.87	2.82 d (13.4) 3.96 d (13.4)	4.31 s	4.36 m^b 4.38 m^c 4.43 m^d	7.46 m^{p,m} 7.92 m^o
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SBz)PdCl$_2$ (**26**)				0.95	2.04 s 2.99 s	0.23	4.40 d (14) 4.63 d (14)	1.24	2.52 d (14) 3.76 d (14)	4.04 s	4.26 dd^c 4.34 t^b 4.63 dd^d	7.25 m^{p,m} 7.68 m^o
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(4-tolyl)]-PdCl$_2$ (**27**)^f	2.37 s			0.66	2.50 s 3.16 s			0.92	2.85 d (13.5) 3.77 d (13.5)	4.24 s	4.32 t^b 4.38 m^c 4.41 m^d	7.25 m^m 7.83 m^o
FeCpC$_5$H$_3$(CH$_2$NMe$_2$)[S(4-ClPh)]-PdCl$_2$ (**28**)				0.61	2.52 s 3.13 s			0.86	2.83 d (14) 3.69 d (14)	4.35 s	4.48 t^b 4.58 m^c 4.65 m^d	7.60 m^m 8.08 m^o

^{a}M = Pd except **19**, M = Pt. ^{b}H4. ^{c}H$_5$. ^{d}H$_3$. ^{e}330 K. ^{f}331 K. ^{g}p = para; o = ortho; m = meta.

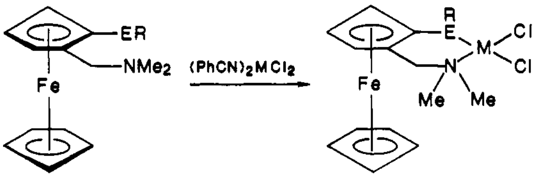
Scheme I



1-3 and **6-17**

E = Se, R = Me (**1**), Ph (**2**), 4 ClPh (**3**); E = S, R = Me (**6**), Et (**7**), Pr (**12**), i-Pr (**8**), Bu (**13**), i-Bu (**9**), sec-Bu (**14**), t-Bu (**15**), i-Pent (**10**), Ph (**11**), Bz (**16**), 4-tolyl (**17**), 4-ClPh (**18**)

Scheme II



19-27

M = Pt, E = Se, R = Me; M = Pd, E = S; R = i-Pr (**20**), Bu (**21**), i-Bu(**22**), t-Bu (**23**), i-Pent (**24**), Ph (**25**), Bz (**26**), 4-tolyl (**27**), 4-ClPh (**28**)

psi of initial H$_2$ pressure. Thus the turnover rate (mol/mol of Pd·h) declined in the order **27** > **25** > **23**.

Results and Discussion

Several new ferrocenyl tertiary amine sulfides and selenides have been synthesized in high yield (80%) by following a modified procedure. Perevalova[11,12] found that quaternary ammonium salts of general formula [C$_5$H$_5$FeC$_5$H$_4$CH$_2$N$^+$(CH$_3$)$_2$CH$_2$R]X$^-$ were prepared in high yields by the reaction of the corresponding alkyl halides on [(dimethylamino)methyl]ferrocene even at low temperatures. Such salt formation will decrease the yield of the ferrocenyl tertiary amine sulfide or selenide; thus ether was used as a solvent in the synthesis. It is necessary to deprotonate the products by use of aqueous NaHCO$_3$

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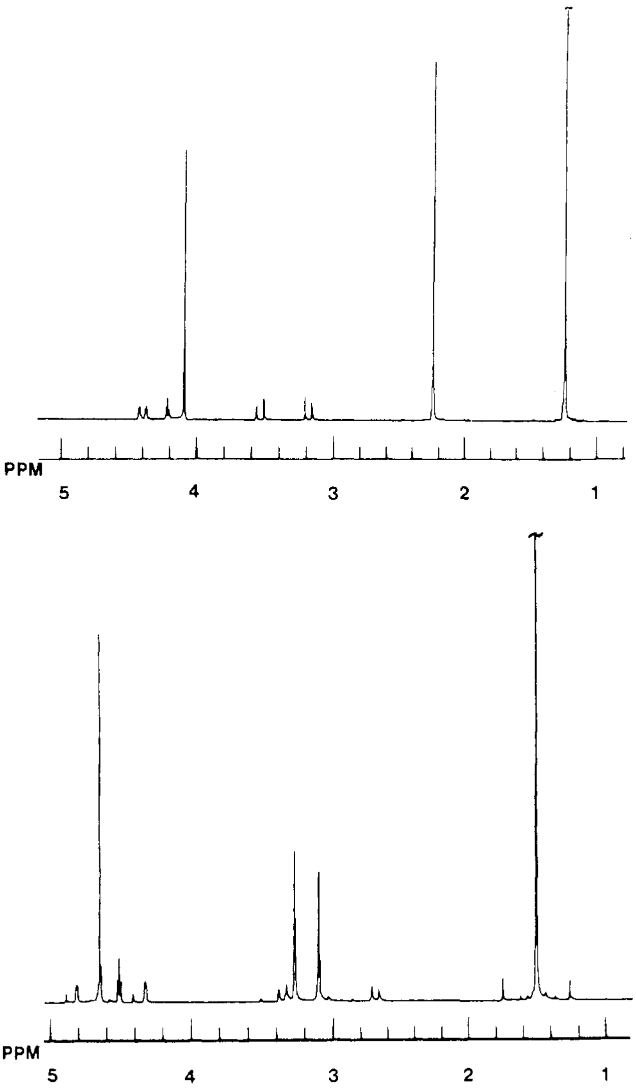
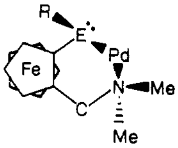


Figure 1. 250-MHz ^{1}H NMR spectra of $C_5H_5Fe[C_5H_3$-1-CH_2NMe_2-2-S(*t*-Bu)] (**15**) and $C_5H_5Fe[C_5H_3$-1-CH_2NMe_2-2-S(*t*-Bu)]$PdCl_2$ (**23**).

before separation and isolation by gradient elution chromatography. The reaction of 1-[(dimethylamino)methyl]-2-lithioferrocene with the appropriate diselenide or disulfide is shown in Scheme I. Reaction of a benzene solution of the ferrocenyl selenide and ferrocenylsulfide compounds **1–12** with bis(benzonitrile) adducts of palladium and platinum chloride salts gave rise to the metal complexes **19–27** (Scheme II). The palladium ferrocenyl sulfide complexes **20–28** are good selective homogeneous and heterogeneous hydrogenation catalyst for the reduction of dienes to monoenes at room temperature.

Palladium and Platinum Complexes. Table I presents 250-MHz 1H NMR data for the metal complexes of ferrocenyl tertiary amine sulfides and selenides. The strong deshielding at the α-protons of these metal complexes is due to the magnetic anisotropy and the inductive effect of the metal halide and is also due to the tilting of the cyclopentadienyl rings where the α-protons are farther from the shielding iron atom.[31] Figure 1 indicates that the most striking difference in the ^{1}H NMR spectra of the complexed ligand **23** relative to the free ligand **15** is the large downfield shift of the ring protons (especially H_3) and alkyl protons. Sokolov[32] found that the chemical shifts of two methyl groups in NMe_2 of a 2-[(dimethylamino)methyl]ferrocenyl palladium chloride dimer are different (2.85 and 3.00 ppm, respectively). The chemical shifts of two methyl groups in NMe_2 of the metal ferrocenyl selenide and ferrocenyl sulfide complexes, **19–27**, are much more downfield than those of the corresponding free ligands, and the chemical shift difference of two methyl groups is large because the inversion of the pyrimidal N of these metal complexes is inhibited by a six-member-ring rigid structure as shown.



Selective Hydrogenation of Conjugated Dienes to Monoenes with 19–28 as Catalysts in Organic Solvents and a Hydrogen Atmosphere. Homogeneous hydrogenation[42] by group VIII metals with amines and sulfides have been used with varying degrees of success. $PtCl_2(SPh_2)_2$ was found to be selective for the hydrogenation of dienes to monoenes in the presence of $SnCl_2$.[43] Treatment of $PdCl_2$ or Na_2PdCl_4 with tertiary amines resulted in an active selective catalyst.[44] The same was true of $PdCl_2$ when treated with 2,2-bipyridine and $NaBH_4$.[5] Palladium chloride and thioethers gave complexes that, upon reduction by diisobutylaluminum hydride, are selective catalysts.[46] The sulfide–rhodium complex $RhCl_3(SEt_2)_2$ hydrogenates maleic acid.[47–50]

In view of the selective hydrogenation activity of amine–palladium and sulfide–palladium complexes when treated with hydride-reducing agents,[45,46] a number of similar procedures were tried by using the ferrocenyl–palladium complex **24** and $NaH_2Al(OCH_2CH_2OCH)_2$ in various solvents at various temperatures and pressures in this laboratory,[4] but all of the hydrogenations failed. Pretreatment of Pd complexes with O_2 has given increased

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Table II. Selective Hydrogenation of 1,3-Cyclooctadiene with Sulfide–Palladium Complexes in Acetone at 61 psi[a]

catalyst	inductn time (h)	convn (%)	turnover rate (mol/mol of Pd·h)	products (%) cyclooctene	products (%) cyclooctane	selectivity (%)
$FeCpC_5H_3(CH_2NMe_2)(SMe)PdCl_2$	49.7	100	13.96	94.08	5.82	94.08
$FeCpC_5H_3(CH_2NMe_2)(SEt)PdCl_2$	42.3	100	15.10	98.35	1.65	98.35
$FeCpC_5H_3(CH_2NMe_2)[S(n\text{-}Pr)]PdCl_2$	37.5	100	15.74	90.87	9.13	90.87
$FeCpC_5H_3(CH_2NMe_2)[S(i\text{-}Pent)]PdCl_2$	22.3	100	18.01	93.70	6.30	93.70
$FeCpC_5H_3(CH_2NMe_2)[S(i\text{-}Bu)]PdCl_2$	12.4	100	21.34	93.98	6.03	93.98
$FeCpC_5H_3(CH_2NMe_2)(SBz)PdCl_2$	5.7	100	47.48	92.08	7.92	92.08
$FeCpC_5H_3(CH_2NMe_2)[S(n\text{-}Bu)]PdCl_2$	1.5	100	97.40	90.42	9.58	90.42
$FeCpC_5H_3(CH_2NMe_2)(SPh)PdCl_2$	0.6	100	206.24	89.29	10.71	89.29
$FeCpC_5H_3(CH_2NMe_2)[S(i\text{-}Pr)]PdCl_2$	0.2	86.86	299.16	76.88	9.99	88.50
$FeCpC_5H_3(CH_2NMe_2)[S(t\text{-}Bu)]PdCl_2$	0.0	100	345.46	97.22	2.78	97.22
$FeCpC_5H_3(CH_2NMe_2)[S(4\text{-}tolyl)]PdCl_2$	0.0	100	690.91	78.54	21.46	78.54

[a] 9.0 mL of acetone, 2.0 × 10^{-5} mol of catalyst, 7.45 × 10^{-3} mol of substrate, at room temperature. [b] Cyclooctene/cyclooctene + cyclooctane.

Table III. Selective Hydrogenation of 1,3-Cyclooctadiene—Effect of Additives[a]

catalyst	additive	convn (%)	turnover rate (mol/mol of Pd·h)	inductn time (h)	products (%) cyclo-octene	products (%) cyclo-octane	selectivity[b] (%)
$FeCpC_5H_3(CH_2NMe_2)$-(SMe)$PdCl_2$		100	13.96	49.7	94.08	5.92	94.08
	2.0 × 10^{-4} mol of H_2O	100	21.68	37.0	90.59	9.41	90.59
$FeCpC_5H_3(CH_2NMe_2)$-[S(4-tolyl)]$PdCl_2$		100	690.91	0.0	78.54	21.46	78.54
	4.0 × 10^{-5} mol of $AgNO_3$	79.08	102.36	2.5	79.08	0.00	100
	4.0 × 10^{-5} mol of $AgNO_3$ and 2.0 × 10^{-4} mol of H_2O	no H_2 uptake					
$FeCpC_5H_3(CH_2NMe_2)$-[S(*t*-Bu)]$PdCl_2$		100	345.46	0.0	97.22	2.78	97.22
	4.0 × 10^{-5} mol $AgNO_3$ and 2.0 × 10^{-4} mol H_2O	no H_2 uptake					
	4.0 × 10^{-5} mol of silver 4-toluenesulfonate	no H_2 uptake					
	4.0 × 10^{-5} mol of pyridine	no H_2 uptake					

[a] 9.0 mL of acetone, 2.0 × 10^{-5} mol of catalyst, 7.45 × 10^{-3} mol of substrate, room temperature, initial hydrogen pressure = 61 psi.
[b] Cyclooctene (cyclooctene + cyclooctane).

rates of hydrogenation,[51,52] but also failed here. When 2.0 × 10^{-4} mol of H_2O was added to dry methylene chloride, hydrogen uptake was observed but only at a slow rate (turnover rate = 27 mol/mol of Pd). In dry methylene chloride, all hydrogenations failed.

Hydrogenation of 1,3-cyclooctadiene became conveniently fast in acetone at 61.0 psi of initial H_2 pressure as shown in Table II. This is a homogeneous system without H_2O or reducing agents, and reaction proceeds at a useful rate (up to 69.9 mol/mol of Pd·h) to obtain a high conversion (up to 100%) and high selectivity (up to 98.35%). The induction time decreases and the turnover rate increases are dependent on the different substituents of the catalysts from **20**–**27**. The hydrogenations that use palladium ferrocenyl selenide catalysts failed in the same hydrogenations that use palladium ferrocenyl selenide catalysts failed in the same reaction conditions because the Pd–Se bond may be stronger than the Pd–S bond in these catalysts. The breaking of the Pd–S bond may thus be important to the selective hydrogenation of the 1,3-cyclooctadiene.

As shown in Table III, the percent conversion, turnover rate, induction time, and selectivity for the selective hydrogenation of 1,3-cyclooctadiene to cyclooctane depend on the effect of the additives being studied. Adding water to the catalyst increases the turnover rate somewhat, but decreases the selectivity of the catalyst, and may be due to hydrolysis of the Pd–Cl bond.[46] The effect of $AgNO_3$ addition, in absence or presence of H_2O, to the catalyst **27** is described below: (1) without added water, the percent conversion and turnover rate decrease, but the selectivity increases from 78.54 to 100% of cyclooctene because the Ag^+ slowly scavenges the Cl^- in dry acetone and inhibits the hydrogenation of the cyclooctene to cyclootane; (2) with added water, the hydrogenation fails completely because the Ag^+ immediately precipitates all the Cl^- from the palladium dichloride complex, before H_2 is oxidatively added to Pd. The hydrogenation reaction also fails with 4-toluenesulfonate addition. The failure of hydrogenation with pyridine added to the catalyst **23** may be due to pyridine's better ability to coordinate to palladium than the thioether or Cl as confirmed by 250-MHz ^1H NMR spectrum. The pyridine–Pd bond is much stronger than S–Pd and Cl–Pd bonds, so the complex is unavailable for hydrogenation.

The effect of catalysts, initial hydrogen pressure, and solvents of the selective hydrogenation of 1,3-cyclo-

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Table IV. Selective Hydrogenation of 1,3-Cyclohexadiene—Effect of Catalysts, Pressure, and Solvents[a]

catalyst	solvent	initial H_2 pressure (psi)	inductn time (h)	convn (%)	turnover rate (mol/mol of Pd·h)	products (%) cyclohexene	products (%) cyclohexane	selectivity[b] (%)
$FeCpC_5H_3(CH_2NMe_2)$-[S(*t*-Bu)$PdCl_2$	acetone	102.0	2.8	100	61.0	46.9	53.1	46.9
$FeCpC_5H_3(CH_2NMe_2(SPh)$-$PdCl_2$	acetone	65.0	4.5	100	268.9	66.8	33.2	66.8
	acetone	102.0	1.5	100	936.8	64.3	35.7	64.3
$FeCpC_5H_3(CH_2NMe_2)$-[S(4-tolyl)]$PdCl_2$	acetone	102.0	2.8	100	1005.0	62.1	37.9	62.1
	acetone/methylene chloride (1:2)	102.0	47.3	96.4	18.8	93.5	2.9	97.0
	methylene chloride	102.0		no H_2 uptake				

[a] 9.0 mL of solvent, 2.0×10^{-5} mol of catalyst, 7.40×10^{-3} mol of substrate, room temperature. [b] Cyclohexane (cyclohexane + cyclohexene).

Table V. Homogeneous Selective Hydrogenation of Dienes to Monoenes[a]

initial rate (mol/mol of Pd·H·psi)	substrate	*T*, °C	metal	solv	ref
3.38	1,3-COD	27	Pd^{2+} (**25**)	acetone	this work
4.90	1,3-COD	27	Pd^{2+} (**20**)	acetone	this work
5.66	1,3-COD	27	Pd^{2+} (**23**)	acetone	this work
11.33	1,3-COD	27	Pd^{2+} (**27**)	acetone	this work
10.83	1,3-cyclohexadiene	27	Pd^{2+} (**25**)	acetone	this work
11.82	1,3-cyclohexadiene	27	Pd^{2+} (**27**)	acetone	this work

[a] COD = cyclooctadiene. Ligands vary from case to case.

hexadiene to cyclohexene is shown in Table IV. The catalysts and 1,3-cyclohexadiene dissolved completely in methylene chloride and became a red-brown solution. The solution is catalytically inactive since H_2 is unable to add oxidatively to Pd. When the complexes are dissolved in acetone, acetone may replace the thioether in coordinating to Pd, and the substrate is introduced into solution by coordinating to Pd center of the catalyst–acetone intermediate and then H_2 uptake immediately occurs to induce the hydrogenation. In the mixed-solvent acetone and methylene chloride, the hydrogenation turnover rate decreases but the selectivity increases, so the solvent effect is important in the selective hydrogenation of the 1,3-cyclohexadiene. The turnover rate declined in the order **27** > **25** > **23** because the breaking of the Pd–S bond appears to be important to the selective hydrogenation and the electron-withdrawing effect is stronger than the steric (crowding) effect of the alkyl or aryl substituents of the thioether in the palladium ferrocenyl sulfide catalysts. With the same catalyst and solvent (acetone), the turnover rate at 102.0 psi of initial H_2 pressure is 3 times as large as at 65.0 psi of initial H_2 pressure. The results of the selective hydrogenation of 1,3-cyclooctadiene to cyclooctene are compared with those of 1,3-cyclohexadiene to cyclohexene. The turnover rate of the latter is high, but the selectivity of the monoene is comparatively low.

Promotion of Me/CO Migratory Insertion by Transition-Metal Lewis Acids. Synthesis and Reactivity of a Transition-Metal Heterobimetallic Carbonyl Alkyl Anion, $MeFeW(CO)_9^-$

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The heterobimetallic alkyl anion 1 was prepared by alkylation of $FeW(CO)_9^{2-}$ using MeI or MeOTs. Addition of the monometallic $MeFe(CO)_4^-$ to a solution of $W(CO)_5$·THF produced the same product. Spectroscopic data indicated the structure of 1 to be analogous to that of $HFeW(CO)_9^-$ or $Ph_3AuFeW(CO)_9^-$, i.e., containing octahedral metal centers with a CH_3 group bound to Fe, cis to the Fe–W bond. A comparative rate study of the reaction of with monomeric $MeFe(CO)_4^-$ and with 1 indicated the promotional effect of $W(CO)_5{}^0$ for the Me/CO migratory insertion reaction. There was no reaction of $MeFe(CO)_4^-$ with CO_2, whereas bimetallic 1 readily added CO_2 yielding $MeC(O)OW(CO)_5^-$. With CS_2 a heterobimetallic, formulated as μ-$MeCS_2FeW(CO)_8^-$, was produced.

Introduction

The extent to which an adjacent metal influences the reactivity of a functionalized organometallic is of interest with respect to heterobimetallic complex reactivity and reaction pathways. Herein we report the synthesis, structure, stability, and small molecule reactions of $MeFeW(CO)_9^-$ (**1**).

Complex anion **1** is a member of a family of heterobimetallics containing metal–metal bonds that are best described as metal donor–metal acceptor complexes. Other members of that family are $HFeM(CO)_9^-$, $HFeM(CO)_8PR_3^-$ (M = Cr, Mo, W),[1,2] and $Ph_3PAuFeW(CO)_9^-$.[3] As indi-

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