MoS_2 to $MoSe_2$ the X–Mo–X sandwich thickness[1] changes hardly at all, viz., from 3.19 to 3.23 Å. However, the van der Waals gap between sandwiches increases significantly, i.e., from 2.96 for MoS_2 to 3.22 Å for $MoSe_2$. Apparently, lone-pair repulsion across the van der Waals gap is greater between selenium atoms than between sulfur atoms, thus making the gap in $MoSe_2$ relatively wider. In the mixed solid solutions $MoS_{2-x}Se_x$ it is believed that the first substitution of Se for S rapidly widens the gap but that subsequent replacement of more Se for S has less effect—hence, the peak in c/a vs. x. What remains a puzzle is how the peak in c/a affects the energy band structure. It is a curious fact that in the series 2H-$MoS_{2-x}Se_x$ the end members are fine, dull-grey powders, whereas the middle members form sparkling, silver-grey microcrystallites. Unfortunately, it has so far been impossible to grow big enough crystals of the middle members to determine their electrical properties.

Acknowledgment. This research was sponsored by the National Science Foundation (Grants CHE 78-12238 and MRL 72-03020) and was supported in part by the Air Force Office of Scientific Research. We also thank the American Association of University Women for awarding the Marion Talbot Fellowship to L.F.S. for 1977–1978.

Registry No. MoS_2, 1317-33-5; $MoSe_2$, 12058-18-3.

Contribution from the Laboratoire de Chimie de l'Ecole
Normale Supérieure, Associé au CNRS,
75231 Paris Cedex 05, France

A New Route to Selenocarbonyl–Transition-Metal Complexes: Preparation of the (5,10,15,20-Tetraphenylporphinato)iron(II)–Selenocarbonyl Complex, Fe(TPP)(CSe), from the Carbenic Fe(TPP)(C(Cl)SeCH$_2$C$_6$H$_5$) Complex

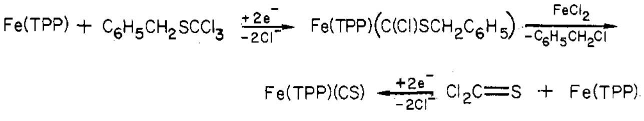
Jean-Paul Battioni, Daniel Mansuy,* and Jean-Claude Chottard

Received July 24, 1979

The preparation of thiocarbonyl–iron(II) porphyrin complexes upon reduction of thiophosgene (Cl_2CS) by iron(II) porphyrin in the presence of a reducing agent in excess has been reported.[1,2] More recently we have found a new indirect method[3] to prepare the same thiocarbonyl complexes by decomposition of the iron(II) porphyrin–carbene complexes obtained by reduction of benzyl trichloromethyl thioether ($C_6H_5CH_2SCCl_3$) (Scheme I).

Whereas numerous examples of carbonyl– and thiocarbonyl–transition-metal complexes have been synthesized by different ways,[4] selenocarbonyl–metal complexes are still rare, and only few methods are available for their synthesis, probably because neither carbon monoselenide (CSe) nor selenophosgene (Cl_2CSe) is stable.[4] Moreover very few carbene–transition-metal complexes with a selenium atom directly bound to the carbenic carbon have been reported, and they have been prepared by indirect methods.[5]

Scheme I



$$\mathrm{Fe(TPP)} + \mathrm{C_6H_5CH_2SCCl_3} \xrightarrow[-2\mathrm{Cl}^-]{+2e^-} \mathrm{Fe(TPP)(C(Cl)SCH_2C_6H_5)} \xrightarrow[-\mathrm{C_6H_5CH_2Cl}]{\mathrm{FeCl_2}}$$

$$\mathrm{Fe(TPP)(CS)} \xleftarrow[-2\mathrm{Cl}^-]{+2e^-} \mathrm{Cl_2C{=}S} + \mathrm{Fe(TPP)}$$

This prompted us to try to prepare selenocarbonyl complexes by reduction of the readily available benzyl trichloromethyl selenoether ($C_6H_5CH_2SeCCl_3$) by an iron(II) porphyrin, by analogy to Scheme I. This paper reports the isolation and characterization of the Fe(TPP)(C(Cl)SeCH$_2$C$_6$H$_5$)[6] and Fe(TPP)(CSe) complexes and compares their properties with those of the corresponding Fe(TPP)–carbonyl,[7] –thiocarbonyl,[1] and –carbene[8] complexes.

Benzyl trichloromethyl selenoether is easily prepared by reaction between benzyl selenocyanate ($C_6H_5CH_2SeCN$) and chloroform in the presence of sodium hydroxide and a phase-transfer agent.[9] $C_6H_5CH_2SeCCl_3$ (2 mmol) is added to a stirred benzene solution of Fe(TPP) (1 mmol) in the presence of an aqueous solution of sodium dithionite, as a reducing agent in excess, under argon. After 2-h reaction, washing with deaerated water, evaporation of solvents, and crystallization from benzene–pentane, a purple complex **1** is obtained (80% yield). All of its characteristics are in good agreement with the carbene-complex structure Fe(TPP)(C(Cl)SeCH$_2$C$_6$H$_5$): elemental analysis (C, H, N, Cl);[10] electronic spectrum $\lambda(C_6H_6)$ 411 nm (ϵ 2.2×10^5), 521 (18×10^3), and 548 (sh) similar to those of previously reported Fe(TPP)(carbene) complexes;[8] ^1H NMR δ ($CDCl_3$, Me_4Si, ppm) 8.70 (s, 8 H), 8.08 (m, 8 H), and 7.71 (m, 12 H) for the protons of the porphyrin ring and 6.88 (m, 3 H), 6.01 (m, 2 H), and 2.91 (s, 2 H) for the protons of the benzyl group; ^{13}C NMR δ ($CDCl_3$, Me_4Si, ppm) 144.8, 140.6, 132.2, 126.0, 125.3, 125.1, and 120.3 for the carbons of the porphyrin ring and two sharp, weak peaks at 38.1 and 265.1 corresponding respectively to the methylene and carbene carbons.[11] Complex **1** is a low-spin iron(II) complex as indicated by the positions and shapes of its ^1H NMR and ^{13}C NMR signals which are also indicative of an axial symmetry. Furthermore the pres-

---

(1) Mansuy, D.; Battioni, J.-P.; Chottard, J.-C. *J. Am. Chem. Soc.* **1978**, *100*, 4311.

(2) Buchler, J. W.; Kokisch, W.; Smith, P. D.; Tonn, B. *Z. Naturforsch., B* **1978**, *33*, 1371.

(3) Mansuy, D.; Battioni, J.-P.; Chottard, J.-C.; Chevrier, B.; Weiss, R., in preparation.

(4) For reviews on thiocarbonyl– and selenocarbonyl–transition-metal complexes, see: (a) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161. (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183. (c) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.

(5) (a) Fischer, E. O.; Kreiss, G.; Kreissl, F. R.; Kreiter, C. B.; Müller, J. *Chem. Ber.* **1973**, *106*, 3910. (b) Fischer, E. O.; Kiener, V. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 961. (c) Mente, P. G.; Ress, C. W. *J. Chem. Soc., Chem. Commun.* **1972**, 418. (d) Schrauzer, G. N.; Kisch, H. *J. Am. Chem. Soc.* **1973**, *95*, 2501.

(6) TPP is used for the dianion of *meso*-tetraphenylporphyrin; Me_4Si for tetramethylsilane.

(7) Weyland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379.

(8) (a) Mansuy, D.; Lange, M.; Chottard, J.-C.; Guérin, P.; Morlière, P.; Brault, D.; Rougée, M. *J. Chem. Soc., Chem. Commun.* **1977**, 648. (b) Mansuy, D.; Lange, M. Chottard, J.-C.; Bartoli, J.-F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 171. (c) Mansuy, D.; Guérin, P.; Chottard, J.-C. *J. Organomet. Chem.* **1979**, *171*, 195. (d) Mansuy, D.; Battioni, J.-P.; Chottard, J.-C.; Ullrich, V. *J. Am. Chem. Soc.* **1979**, *101*, 3971.

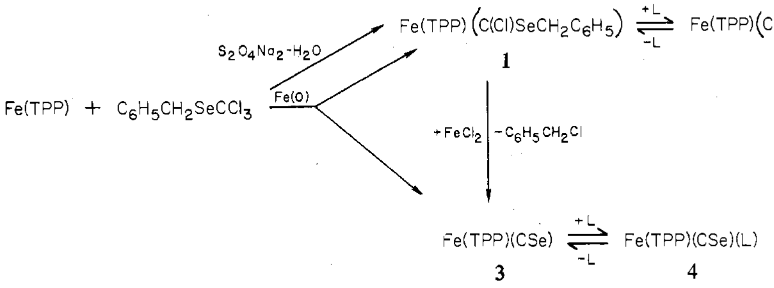
(9) This method of preparation is similar to that used for the analogous sulfur compounds: Makosza, M.; Fedoryński, M. *Synthesis*, **1974**, 274. $C_6H_5CH_2SeCCl_3$: bp 88 °C (12 mmHg); ^1H NMR δ ($CDCl_3$, Me_4Si, ppm)7.45 (5 H), 4.65 (2 H); ^{13}C NMR δ ($CDCl_3$, Me_4Si, ppm) 134.0, 129.4, 128.7, 127.6, 77.7, 37.7; mass spectrum (70 eV, 140 °C) *m/e* 288 (for ^{80}Se and ^{35}Cl); elemental analysis (C, H, Cl). $C_6H_5CH_2SeCN$ is prepared from benzyl chloride and potassium selenocyanide in acetone: mp 78 °C; ^1H NMR δ ($CDCl_3$, Me_4Si, ppm) 7.50 (5 H), 4.18 (2 H); ^{13}C NMR δ ($CDCl_3$, Me_4Si, ppm) 135.3, 128.6, 128.3, 101.7, 32.9; mass spectrum (70 eV, 30 °C) *m/e* 197–195 with the good isotopic ratio for one selenium atom; elemental analysis (C, H, N).

(10) Actually the crystals were found to retain 1 mol of water, in agreement with ^1H NMR determination, even after 10 h under 10^{-2} mmHg. Anal. Calcd for Fe(TPP)(C(Cl)SeCH$_2$C$_6$H$_5$)(H$_2$O): C, 69.08; H, 4.12; N, 6.19; Cl, 3.92. Found: C, 69.32; H, 4.12; N, 6.12; Cl, 4.20.

(11) It is not possible to assign the phenyl carbon signals of the carbene ligand since they are superimposed with those of the porphyrin ring.

0020-1669/80/1319-0791$01.00/0

Scheme II



L: **a**, ethanol; **b**, *N*-methylimidazole; **c**, pyridine

ence of the axial carbene ligand is also supported by the mass spectrum (70 eV, 230 °C) of complex **1** which does not exhibit the molecular ion peak but fragments at *m/e* 795 (for ^{35}Cl and ^{80}Se), 760 (for ^{80}Se), and 668, which correspond to successive loss of the benzyl, chloro, and selenocarbonyl groups.

Complex **1** is stable in deaerated solution but is slowly oxidized to the Fe_{III}(TPP)(Cl) complex in the presence of oxygen ($t_{1/2}$ in benzene at 25 °C ca. 6 h). In solution and in the presence of ligands, complex **1** is in equilibrium with the corresponding hexacoodinated complexes (Scheme II): **2b** (L = *N*-methylimidazole), $\lambda(C_6H_6)$ 430 nm (ϵ 2.4 × 10^5) and 540 (15 × 10^3), formation constant at 25 °C K_b = 9000 L mol^{-1}; **2c** (L = pyridine), which is less stable and decomposed by an excess of pyridine to give Fe(TPP)$(py)_2$, before complete formation of **2c**, its formation constant K_c however being estimated to 1200 L mol^{-1}.

Treated by a catalytic amount of ferrous chloride in acetonitrile, complex **1** is partially (50%) transformed into a new complex, **3**, as shown in ^{1}H NMR spectroscopy by the progressive replacement of the signal of the pyrrolic protons of complex **1** by a signal at 8.88 ppm corresponding to the pyrrolic protons of complex **3** and by the signals of benzyl chloride ($C_6H_5CH_2Cl$). Complex **3** is directly obtained when the reduction of $C_6H_5CH_2SeCCl_3$ by Fe(TPP) is performed in a methylene chloride–methanol solution (20:1) by using iron powder as reducing agent. After 1-h reaction, filtration, evaporation of solvents, and precipitation from chloroform–methanol, a mixture of **1** and **3** (1:1) is obtained (Scheme II).

The corresponding hexacoordinated complex **4a** is obtained as purple crystals after silica-gel thin-layer chromatography of the mixture of **1** and **3** and recrystallization from methylene chloride–ethanol solution (overall yield from Fe(TPP) 40%). Its characteristics are in good agreement with the structure Fe(TPP)(CSe)(C_2H_5OH) (**4a**): elemental analysis (C, H, N);[12] ^{1}H NMR δ ($CDCl_3$, Me_4Si, ppm) 8.88 (s, 8 H), 8.15 (m, 8 H), and 7.75 (m, 12 H) for the protons of the porphyrin ring and 3.78 (q, *J* = 6.5 Hz, 2H) and 1.25 (t, *J* = 6.5 Hz, 3 H) for the protons of ethanol; ^{13}C NMR δ ($CDCl_3$, Me_4Si, ppm) 145.8, 141.6, 133.6, 132.5, 127.8, 126.9, and 122.1 for the carbons of the porphyrin ring, 58.4 and 18.2 for the carbons of ethanol, and a sharp, weak peak at 320.1 for the selenocarbonyl carbon. The presence of the selenocarbonyl ligand is also supported by the intense 1140-cm^{-1} band of the IR spectrum. These two spectroscopic data ($\delta_{^{13}C=Se}$ and $\nu_{C=Se}$) are in good agreement with those reported for selenocarbonyl–transition-metal complexes.[4] Furthermore the mass spectrum (70 eV, 220 °C) of complex **4a** exhibits peaks at *m/e* 760 and 758 (for ^{80}Se and ^{78}Se) corresponding to Fe(TPP)(CSe).

In solution, **4a**, $\lambda(C_6H_6)$ 418 nm (ϵ 1.9 × 10^5) and 535 (13.6 × 10^3), is in equilibrium (K_a(at 25 °C) = 3 L mol^{-1}) with the pentacoordinated complex Fe(TPP)(CSe), **3**, $\lambda(C_6H_6)$ 409 nm (ϵ 2.3 × 10^5), 524 (16 × 10^3), and 550 (sh), and free ethanol. More basic ligands (L) exhibit a greater affinity for **3** and give the corresponding hexacoodinated complexes: **4b** (L = *N*-methylimidazole), $\lambda(C_6H_6)$ 426 nm (ϵ 2.5 × 10^5), 547 (16 × 10^3), and 583 (sh), K_b = 10 000 L mol^{-1}; **4c** (L = pyridine, $\lambda(C_6H_6)$ 424 nm (ϵ 2.4 × 10^5) and 544 (12.3 × 10^3), K_c = 3000 L mol^{-1}.

Like the Fe–CS bond of the previously reported iron porphyrin–thiocarbonyl complexes,[1] the Fe–CSe bonds in complexes **3** and **4** are considerably stronger than the Fe–CO bonds of known Fe(TPP)(CO)(L)[7] complexes. This particular strength is emphasized by the stability of complex **3** toward high dilution (2 × 10^{-8} M) or toward oxidation by oxygen, since it can be handled in air and even purified without decomposition by thin-layer chromatography.

The reported reduction of alkyl trichloromethyl selenoethers should be a good method to directly synthesize carbene complexes stabilized by a selenium atom. Moreover the decomposition of such carbene complexes catalyzed by Lewis acids, such as ferrous chloride, is a new, convenient method to obtain the corresponding selenocarbonyl complexes from a readily available and stable precursor. We are currently investigating the generality of this synthetic route with other transition-metal complexes.

Registry No. **1**, 72347-08-1; **2b**, 72347-09-2; **2c**, 72347-10-5; **3**, 72347-11-6; **4a**, 72347-12-7; **4b**, 72347-13-8; **4c**, 72347-14-9; Fe(TPP), 16591-56-3; $C_6H_5CH_2SeCCl_3$, 72331-79-4; $C_6H_5CH_2SeCN$, 4671-93-6.

---

(12) The elemental analysis was performed on a sample recrystallized from benzene–pentane. It was not possible to completely remove the benzene from the crystals even after 10 h at 80 °C under 10^{-2} mmHg. Anal. Calcd for Fe(TPP)(CSe)·0.25C_6H_6: C, 71.68; H, 3.82; N, 7.19. Found: C, 71.84; H, 4.20; N, 7.07.