

MoS₂ to MoSe₂ the X-Mo-X sandwich thickness¹ 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 MoS₂ to 3.22 Å for MoSe₂. Apparently, lone-pair repulsion across the van der Waals gap is greater between selenium atoms than between sulfur atoms, thus making the gap in MoSe₂ 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.

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Registry No. MoS₂, 1317-33-5; MoSe₂, 12058-18-3.

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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)SeCH₂C₆H₅) Complex

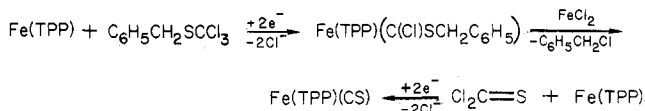
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The preparation of thiocarbonyl-iron(II) porphyrin complexes upon reduction of thiophosgene (Cl₂CS) by iron(II) porphyrin in the presence of a reducing agent in excess has been reported.^{1,2} More recently we have found a new indirect method³ to prepare the same thiocarbonyl complexes by decomposition of the iron(II) porphyrin-carbene complexes obtained by reduction of benzyl trichloromethyl thioether (C₆H₅CH₂SCCl₃) (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 (Cl₂CSe) is stable.⁴ Moreover very few carbene-transition-metal complexes with a selenium atom

Scheme I



directly bound to the carbenic carbon have been reported, and they have been prepared by indirect methods.⁵

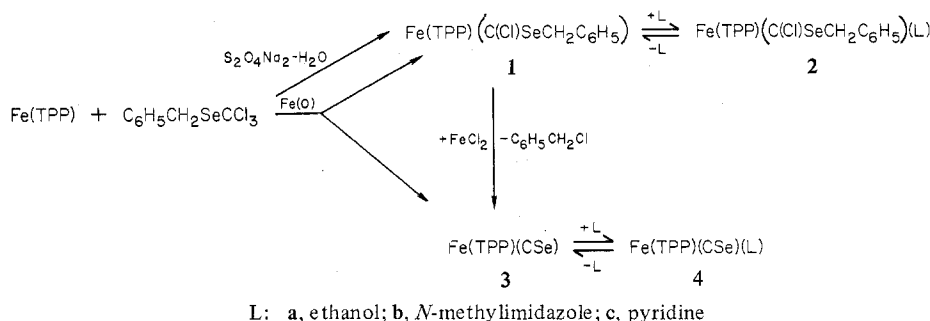
This prompted us to try to prepare selenocarbonyl complexes by reduction of the readily available benzyl trichloromethyl selenoether (C₆H₅CH₂SeCCl₃) by an iron(II) porphyrin, by analogy to Scheme I. This paper reports the isolation and characterization of the Fe(TPP)(C(Cl)SeCH₂C₆H₅)⁶ and Fe(TPP)(CSe) complexes and compares their properties with those of the corresponding Fe(TPP)-carbonyl,⁷ -thiocarbonyl,¹ and -carbene⁸ complexes.

Benzyl trichloromethyl selenoether is easily prepared by reaction between benzyl selenocyanate (C₆H₅CH₂SeCN) and chloroform in the presence of sodium hydroxide and a phase-transfer agent.⁹ C₆H₅CH₂SeCCl₃ (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)SeCH₂C₆H₅): elemental analysis (C, H, N, Cl);¹⁰ electronic spectrum λ(C₆H₆) 411 nm (ε 2.2 × 10⁵), 521 (18 × 10³), and 548 (sh) similar to those of previously reported Fe(TPP)(carbene) complexes;⁸ ¹H NMR δ (CDCl₃, Me₄Si, 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; ¹³C NMR δ (CDCl₃, Me₄Si, 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 ¹³C NMR signals which are also indicative of an axial symmetry. Furthermore the pres-

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- (9) This method of preparation is similar to that used for the analogous sulfur compounds: Makosza, M.; Fedoryński, M. *Synthesis*, **1974**, 274. C₆H₅CH₂SeCCl₃: bp 88 °C (12 mmHg); ¹H NMR δ (CDCl₃, Me₄Si, ppm) 7.45 (5 H), 4.65 (2 H); ¹³C NMR δ (CDCl₃, Me₄Si, ppm) 134.0, 129.4, 128.7, 127.6, 77.7, 37.7; mass spectrum (70 eV, 140 °C) *m/e* 288 (for ⁸⁰Se and ³⁵Cl); elemental analysis (C, H, Cl). C₆H₅CH₂SeCN is prepared from benzyl chloride and potassium selenocyanide in acetone: mp 78 °C; ¹H NMR δ (CDCl₃, Me₄Si, ppm) 7.50 (5 H), 4.18 (2 H); ¹³C NMR δ (CDCl₃, Me₄Si, 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)SeCH₂C₆H₅)(H₂O): 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.

Scheme II



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 $\text{Fe}_{\text{III}}(\text{TPP})(\text{Cl})$ 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 hexacoordinated complexes (Scheme II): **2b** (L = *N*-methylimidazole), $\lambda(\text{C}_6\text{H}_6)$ 430 nm (ϵ 2.4×10^5) and 540 (15×10^3), formation constant at 25 °C $K_b = 9000 \text{ L mol}^{-1}$; **2c** (L = pyridine), which is less stable and decomposed by an excess of pyridine to give $\text{Fe}(\text{TPP})(\text{py})_2$, 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 ^1H 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 ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$). Complex **3** is directly obtained when the reduction of $\text{C}_6\text{H}_5\text{CH}_2\text{SeCCl}_3$ by $\text{Fe}(\text{TPP})$ 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 $\text{Fe}(\text{TPP})$ 40%). Its characteristics are in good agreement with the structure $\text{Fe}(\text{TPP})(\text{CSe})(\text{C}_2\text{H}_5\text{OH})$ (**4a**): elemental analysis (C, H, N); ^{12}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, $J = 6.5 \text{ Hz}$, 2H) and 1.25 (t, $J = 6.5 \text{ Hz}$,

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 ($\delta_{\text{C}=\text{Se}}$ and $\nu_{\text{C}=\text{Se}}$) 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 $\text{Fe}(\text{TPP})(\text{CSe})$.

In solution, **4a**, $\lambda(\text{C}_6\text{H}_6)$ 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 $\text{Fe}(\text{TPP})(\text{CSe})$, **3**, $\lambda(\text{C}_6\text{H}_6)$ 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 hexacoordinated complexes: **4b** (L = *N*-methylimidazole), $\lambda(\text{C}_6\text{H}_6)$ 426 nm (ϵ 2.5×10^5), 547 (16×10^3), and 583 (sh), $K_b = 10000 \text{ L mol}^{-1}$; **4c** (L = pyridine), $\lambda(\text{C}_6\text{H}_6)$ 424 nm (ϵ 2.4×10^5) and 544 (12.3×10^3), $K_c = 3000 \text{ L mol}^{-1}$.

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 $\text{Fe}(\text{TPP})(\text{CO})(\text{L})$ ⁷ complexes. This particular strength is emphasized by the stability of complex **3** toward high dilution ($2 \times 10^{-8} \text{ M}$) 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; $\text{Fe}(\text{TPP})$, 16591-56-3; $\text{C}_6\text{H}_5\text{CH}_2\text{SeCCl}_3$, 72331-79-4; $\text{C}_6\text{H}_5\text{CH}_2\text{SeCN}$, 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 $\text{Fe}(\text{TPP})(\text{CSe}) \cdot 0.25\text{C}_6\text{H}_6$: C, 71.68; H, 3.82; N, 7.19. Found: C, 71.84; H, 4.20; N, 7.07.