Synthesis and X-ray Structure of Selenasapphyrin

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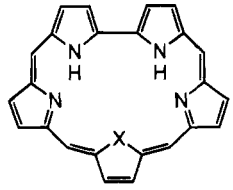
Introduction

Sapphyrins, oxasapphyrins, and thiasapphyrins, represented by generalized structures **1-3**, were first reported more than 20



1. X = NH 3. X = S
2. X = O 4. X = Se

years ago.[1] They are potentially pentadentate aromatic macrocycles related to the porphyrins. Despite their interesting properties, however, the chemistry of sapphyrins and heterosapphyrins has not been explored extensively, in part because the synthesis of these molecules is long and tedious. Recently, improved syntheses of these compounds have been reported[2] and the novel properties of sapphyrins as anions carriers demonstrated.[3] This has led to something of a renaissance in the area of sapphyrin-related chemistry.[1-5] In spite of this resurgence in interest, selenasapphyrins, sapphyrin-like compounds (e.g., **4**) wherein one or more of the central nitrogen atoms is replaced by a selenium atom, remain unknown at present. Such systems, which have their antecedents in the porphyrin series,[6] would be of interest in view of the smaller central cores they would presumably possess and the modified anion and cation chelation chemistry they might display.

In this paper we report the synthesis and characterization of the first selenium-containing sapphyrin, the monoselensapphyrin **5** (corresponding to generalized structure **4** above) as well an improved synthesis of monothiasapphyrins. Compound **5** (Scheme 1), like its pentaaza sapphyrin "parents", both forms out-of-plane complexes with certain low-valent transition metal fragments and binds halide-type anions in its diprotonated state.

Results and Discussion

The key element in the selenasapphyrin synthesis (Scheme 1) and improved preparation of thiasapphyrin is a metathesis reaction wherein furan derivatives are converted into their respective thiophene or selenophene analogs. This transformation, which was first introduced by Russian workers,[7] has been successfully employed by Vogel and co-workers to prepare both tetrathia- and tetraselenaporphyrins.[6b] In our case (Scheme 1), the key starting material is 2,5-bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)furan (**10**), a material that is readily obtainable in two steps from commercially available 2,5-furandimethanol[8] (**8**). Treatment with H_2S or H_2Se under anaerobic acidic conditions then gives the corresponding monothiophene and monoselenophene tripyrrane analogues **12** and **11**, respectively. These metatheses thus generate species that may be carried on in the usual way[2b] to produce the target thia- and selenasapphyrins **6** and **5** (cf. Scheme 1). In the particular case of selenasapphyrin **5**, this follow-up chemistry involves acid-catalyzed removal of the ester group and condensation of the resulting α-free tripyrrane analog **13** and 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-bipyrrole (**15**).[2a] Following molecular oxygen-based oxidation and purification, the product is obtained in the form of dark green microcrystals in ca. 25% overall yield based on **10**.

Analysis of the 2D ROESY spectrum of **5** not only serves to confirm the identity of this new substance unequivocally but also allows for a full ^{1}H NMR spectral assignment (Figure 1). Specifically, the three most downfield shifted signals, labeled as "b", "f", and "a", respectively, were found to integrate to 2 protons each. Taken together, they must therefore correspond to the β-hydrogens of the selenophene fragment and the two sets (2H each) of independent *meso* protons. Two of these signals, namely pair "a" and "b", are NOE correlated with each other (Figure 1) and, therefore, belong individually *either* to the β-hydrogens on the selenophene *or* to the *meso* hydrogens nearest this fragment. Since signal "b" is also cross correlated with the methyl signal "c", it is assignable to the *meso* position, while signal "a", by process of elimination, becomes assigned to the β-selenophene protons.

Consistent with this assignment is the finding that the third original downfield signal, namely "f", shows an NOE to two ethyl groups; this is just as would be expected for the two equivalent *meso* hydrogens farthest from the selenophene fragment. Crosspeaks are also observed between the methyl protons "c" and the ethyl signals "d" and "e". This not only supports the assignment for "c" but also allows for an

(1) (a) Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6529. (b) Broadhurst, M. J.; Grig, R.; Johnson, A. W. *J. Chem. Soc. Perkin 1*, **1972**, 2111. (c) Sessler, J. L.; Cyr, M. J.; Burrell, A. K. *Synlett* **1991**, *3*, 127.

(2) (a) Sessler, J. L.; Cyr, M.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810. (b) Sessler, J. L.; Cyr, M. J.; Burrell, A. K. *Tetrahedron* **1992**, *48*, 9661.

(3) (a) Furuta, H.; Cyr, M. J.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 6677. (b) Shinoya, M.; Furuta, H.; Lynch, V.; Harriman, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 5714. (c) Král, V.; Sessler, J. L.; Furuta, H. *J. Am. Chem. Soc.* **1992**, *114*, 8704. (d) Iverson, B. L.; Shreder, K.; Kral, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 11022. (e) Sessler, J. L.; Ford, D. A.; Cyr, M. J.; Furuta, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1733. (f) Iverson, B. L.; Thomas, R. E.; Kral, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2663.

(4) (a) Burrell, A. K.; Sessler, J. L.; Cyr, M. J.; McGhee, E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 91. (b) Burrell, A. K.; Cyr, M.; Lynch, V.; J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1710. (c) Burrell, A. K.; Cyr, M. J.; Lynch, V.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1710.

(5) (a) Regev, A.; Michaeli, S.; Levanon, H.; Cyr, M.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 9121. (b) Sessler, J. L.; Furuta, H.; Kral, V. *Supramol. Chem.* **1993**, *1*, 209.

(6) (a) Diselenaporphyrin and selenathiaporphyrin: Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Tetrahedron. Lett.* **1978**, *2*, 167. (b) Tetraselenaporphyrin and tetrathiaporphyrin: Vogel, E.; Röhrig, P.; Sicken, M.; Knipp, B.; Herrmann, A.; Pohl, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1651. (c) Dithiaporphyrins: Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540. Hill, R. L.; Gouterman, M.; Ulman, A. *Inorg. Chem.* **1982**, *21*, 1450. Stein, P.; Ulman, A.; Spiro, T. G. *J. Phys. Chem.* **1984**, *88*, 369. (d) Monothiaporphyrins: Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc. C* **1971**, 3681. Latos-Grazynski, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428. Latos-Grazynski, L.; Lisowski, J.; Chmielewski, P.; Grzeszczuk, M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1994**, *33*, 192 and references cited therein.

(7) Kharachenko, V. G.; Markushina, I. A.; Voronin, S. P. *Khim. Geterosikl. Soedineni.* **1993**, 219.

(8) Compound **8** was converted into **9** by treating with acetic anhydride: Sessler, J. L.; Hoener, M. Unpublished results.

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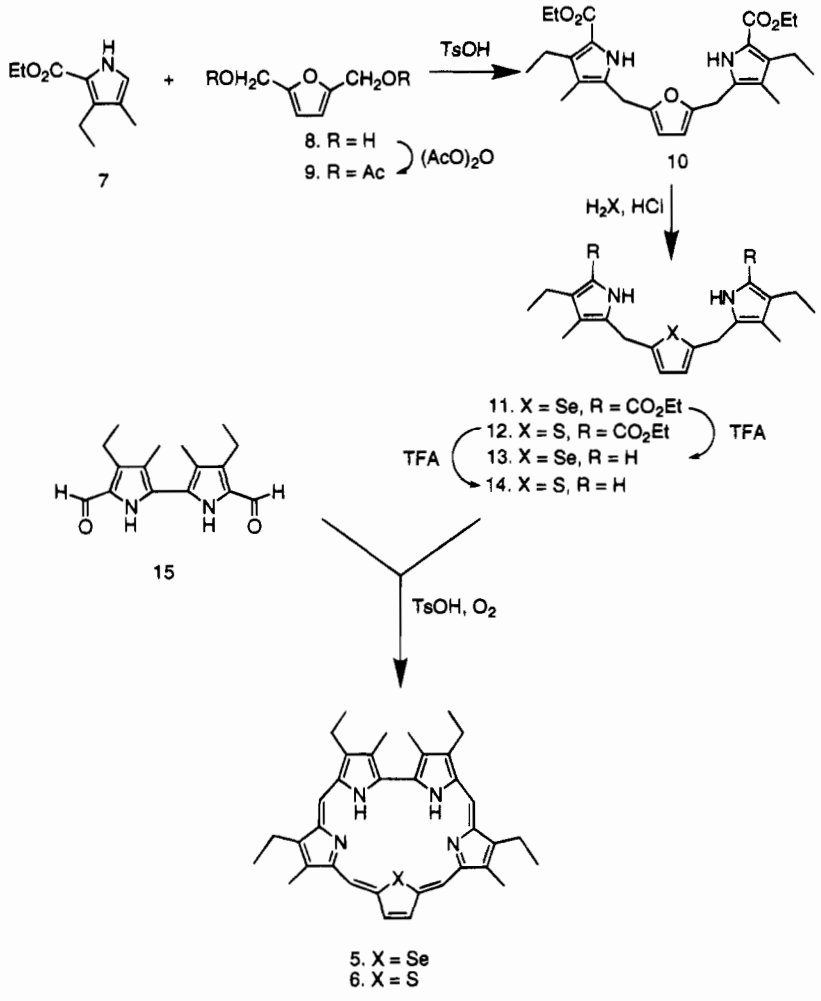
Scheme 1



unambiguous distinction between the two unequivalent ethyl substituents present in **5**.

The X-ray crystal structure of the selenasapphyrin bis(hydrochloride) adduct, **5**·2HCl is shown in Figure 2. The two chloride anions are bound in a symmetrical fashion above and below the N_4Se macrocyclic plane (the Cl···Cl′ distance is 5.337(2) Å). The nitrogen−chlorine distances are similar to each other (3.031(2) and 3.119(2) Å, respectively) and fall within the range expected for N···H−Cl hydrogen bonds. Although the hydrogen bonds connecting each of the chloride counteranions to a pair of nitrogens cause some buckling of the selenasapphyrin, the overall conformation is close to planar. For instance, the mean deviation of the selenasapphyrin core atoms from a root-mean-square (RMS) plane defined by these atoms is 0.203 Å.

It is clear from an inspection of Figure 2 that the structure of selenasapphyrin bis(hydrochloride) resembles that of the analogous diprotonated sapphyrin complex. In both cases the two chloride counteranions are held above and below the macrocyclic plane.[3b] However, in the present instance, the overall structure is more symmetrical, with both chloride atoms being ligated by but two (as opposed to three) hydrogen bonds. This, presumably, is a consequence of the fact that one of the pyrrolic nitrogens is "missing", being replaced by a selenium center, such that one of the hydrogen bonds found in the bis(hydrochloride) adduct of sapphyrin is necessarily absent in the structure of **5**·2HCl.

Apart from obvious, if subtle, anion binding effects, the substitution of Se for NH induces modifications in the solid state structure that can be ascribed to changes in the electronic properties of the overall system. In particular, the incorporation of a selenophene moiety into what is formally an aromatic 22 π-electron periphery changes the π delocalization of this fragment as compared to free (i.e. monomeric) selenophene and its derivatives. For instance, in **5**·2HCl, the selenophene Cα−Cβ and Cβ−Cβ distances are equal to 1.419(4) and 1.364(6) Å, respectively, while Cα−Cβ and Cβ−Cβ distances on the order of 1.356−1.379 and 1.417−1.452 Å, respectively, are seen for selenophene fragments incorporated into nonaromatic frameworks.[9] As a result, the pattern of double bonds in **5**·2HCl is reversed compared to that in selenophene itself and is thus in accordance with the bonding pattern depicted by the dominant resonance structure for selenasapphyrin (see insert to Figure 1).

Although, as noted above, the macrocyclic portion of **5**·2HCl is deformed from planarity, by virtue of interactions with the chloride counteranions, the values of the proton chemical shifts, as well as the presence of a characteristic Soret-type absorption band in the UV−vis spectra, confirm that this species, and its corresponding free-base form, are aromatic. In fact, the UV−vis spectrum of free-base selenasapphyrin, **5**, is very similar to that of free-base thiasapphyrin, **6**.[2b] This, presumably, reflects an underlying similarity in the electronic structure of these two congeneric macrocycles. On the other hand, increasing bathochromic shifts are observed, both for the Soret and Q-bands,

(9) (a) Aurivillius, B. *Chem. Scr.* **1971**, *1*, 25. (b) Dorrity, M. R. J.; Malone, J. F. Morley, C. P.; Vaughan, R. R. *Phosphorus, Sulfur, Silicon* **1992**, *68*, 37. (c) Nardelli, M.; Fava, G.; Giraldi, G. *Acta Crystallogr.* **1962**, *15*, 737.

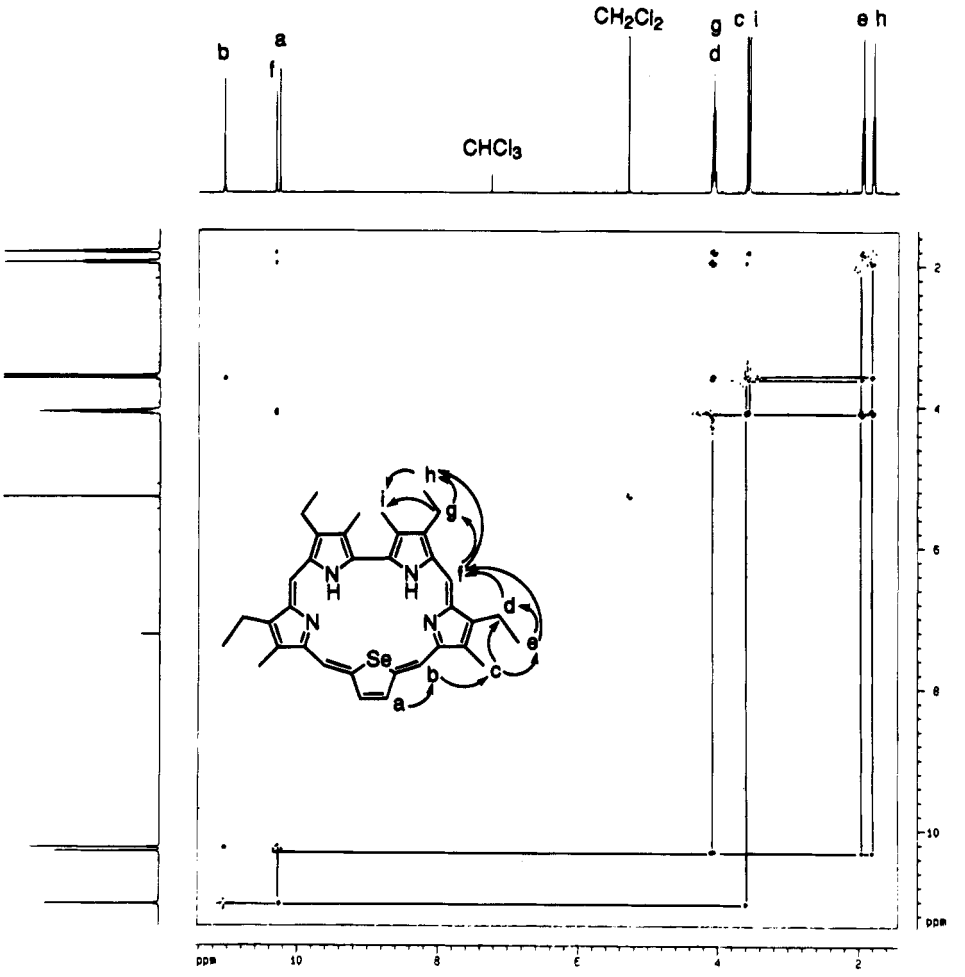


Figure 1. ROESY spectrum of selenasapphyrin **5** solution in $CDCl_3$ (298 K).

when the series of diprotonated macrocycles, sapphyrin, thiasapphyrin, and selenasapphyrin is transversed.[10]

In addition to being a sensitive indicator of protonation state, the UV−vis spectra of protonated derivatives **5**·2HX reflect the specific choice of counteranion, X.[11] This sensitivity, which is something previously seen in the all-aza sapphyrin series,[3b] indicates that the diprotonated form of selenasapphyrin is capable of binding a range of anions.

In addition to binding anions in its diprotonated state, selenasapphyrin forms a stable η^2-Ir(I) complex, [**5**-2H$^+$]·2Ir(CO)$_2$, upon reaction with $IrCl(CO)_3$ and net loss of two protons. (Here the abbreviation **5**-2H$^+$ refers to the doubly deprotonated form of **5**.) The structure of this neutral complex (Figure 3) is similar to that of the corresponding monovalent rhodium and iridium complexes of sapphyrins[4a] and porphyrins.[12] It possesses overall C_2 symmetry and does not involve the central heteroatom, in this case selenium, in metal coordination. Thus, to a first approximation the structure of complex [**5**-2H$^+$]·2Ir(CO)$_2$ resembles not only that of bis(iridium) tetracarbonyl sapphyrin but also that of **5**·2HCl. In the case of [**5**-2H$^+$]·2Ir(CO)$_2$, however, the basic selenasapphyrin skeleton is ruffled to a considerably greater extent than it is in **5**·2HCl. In particular, the pairs of nitrogens are bent toward the Ir(I) ions to which they are coordinated and the respective pyrrole rings are twisted from the main macrocycle plain. The mean deviation from RMS planarity for the selenasapphyrin core atoms is thus equal to 0.417 Å (compared to a similar value of 0.203 Å for **5**·2HCl). Similarly, the dihedral angle between the two pyrrole rings (defined by the respective RMS planes) in the bipyrrole fragment is equal to 46.0° for [**5**-2H$^+$]·2Ir(CO)$_2$ and 23.3° for **5**·2HCl. The Ir···Ir′ distance is 4.233(1) Å, and the Ir−N distances in **5**-2H$^+$]·[Ir(CO)$_2$]$_2$ are 2.100(5) and 2.076(6) Å with the coordination geometry around each of the Ir(I) ions being close to square planar. Interestingly, as is true in the case of **5**·2HCl, the double-bond pattern within the selenophene fragment itself is altered compared to that found within simple monomeric selenophene derivatives. This time, however, the Cα−Cβ and Cβ−Cβ bonds, equal to 1.421(10) and 1.412(15) Å, respectively, are almost the same length.

In addition to the above, UV−vis studies indicate that **5** can also coordinate other metal ions such as Co^{2+} and Cd^{2+} in solution. Unfortunately, the resulting complexes are unstable and are easily demetalated in the presence of acids, bases, or competing ligands. As a result, these complexes have yet to be isolated in the solid state or characterized fully. Nonetheless, these preliminary results lead us to suggest that the metal

(10) Interestingly, a similar trend was observed in the corresponding porphyrin series, *viz.* tetraphenylporphyrin, dithiatetraphenylporphyrin, and diselenatetraphenylporphyrin.[6a] As a result, we feel confident that the changes seen in the present case reflect inherent differences in electronic structure, rather than changes due to, for instance, degree of distortion caused by anion binding.

(11) For dichloromethane solutions of **5**·2HX containing chloride, bromide, fluoride, perchlorate, acetate, and phosphate as counteranions X, the Soret band is observed at 474, 478, 470, 472, 468, and 472 nm, respectively.

(12) (a) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z.-I. *Acta Crystallogr., Sect. B* **1975**, *31*, 1. (b) Ogoshi, H.; Setsune, J.-I.; Omura, T.; Yoshida, Z.-I. *J. Am. Chem. Soc.* **1975**, *97*, 6461. (c) Ogoshi, H.; Setsune, J.-I.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 317.

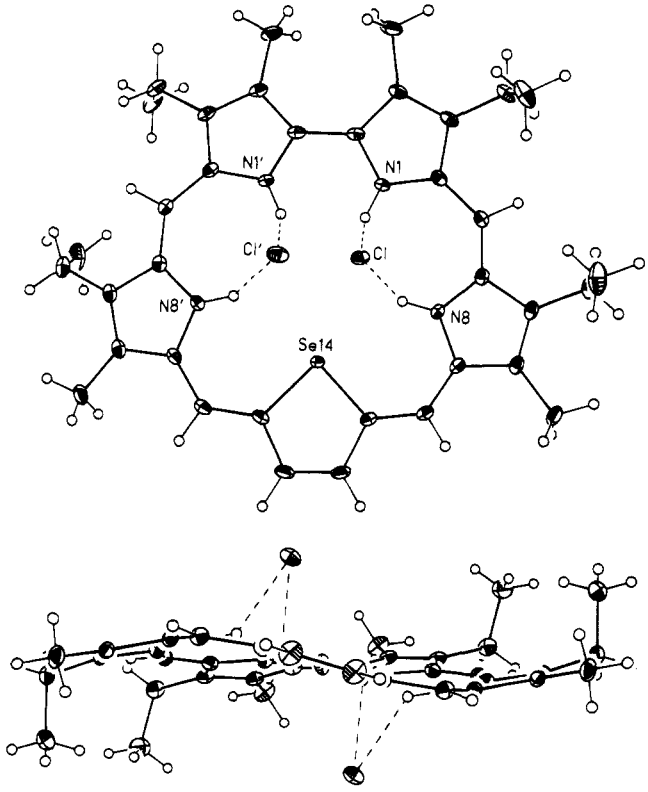


Figure 2. 2. Two views of the molecular structure of the diprotonated selenasapphyrin derivative, **5**·2HCl. Non-hydrogen atoms are drawn using 30% probability ellipsoids; hydrogen atoms are drawn to an arbitrary scale. The Cl^- anions are H-bound to the pyrrolic hydrogens as indicated by the dashed lines; see text for details.

coordination chemistry of selenasapphyrin need not be limited to the coordination of low-valent group 15 metal cations but, rather, could be more general. Therefore, currently, we are exploring further the metal chelation chemistry of **5** with the goals of stabilizing complexes of higher denticity and/or obtaining stable complexes containing selenium-coordinated metal centers.[13]

Experimental Section

General Methods. Proton and carbon NMR spectra were recorded using Bruker AC-250 and AM-500 spectrometers or using General Electric QE-300 and GE GN500 instruments. Observed chemical shifts were referenced to TMS (^{1}H NMR) or to easily identifiable solvent signals (^{13}C NMR). The phase-sensitive (TPPI) ROESY spectrum (100 ms spin lock) was acquired at 500 MHz using 1024 data points in F_1 and 2048 data points in F_2. The data were processed by using a square sine bell window function without zero filling. High-resolution mass spectra (HRMS) were obtained using a VG Analytical ZAB E/SE instrument. Electronic spectra were recorded on a Beckman DU 640 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Inc.

X-ray Diffraction Analyses. $(C_{36}H_{42}N_4Se)^{2+}(Cl^-)_2$ (5·2HCl). Small, almost black, very well-formed crystals were obtained by diffusion diethyl ether into a 10:1 $CH_3OH/CHCl_3$ solution of $(C_{36}H_{42}N_4Se)^{2+}(Cl^-)_2$. The data crystal was a block of approximate dimensions 0.13 × 0.30 × 0.36 mm. Details of crystal data, data collection, and structure refinement are listed in Table 1 and supporting information Table S1. Four reflections (−2,−4,1; 2,0,2; 0,2,−5; −3,1,−3) were remeasured every 96 reflections to monitor instrument and crystal stability.

(13) Preliminary results indicate that palladium(II) actually forms three different complexes with **5**, in which a simple Pd^{2+} ion is coordinated in an η^2 fashion to different adjacent nitrogen pairs or an adjacent nitrogen−selenium pair.

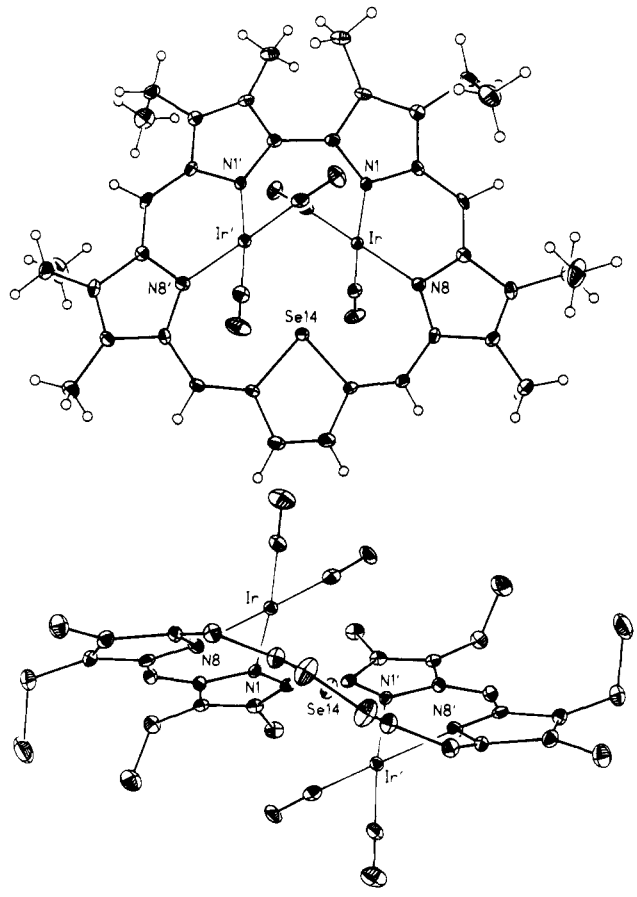


Figure 3. Two views of the molecular structure of the iridium(I) complex, [**5**-2H$^+$]·2Ir(CO)$_2$. Non-hydrogen atoms are drawn using 30% probability ellipsoids; hydrogen atoms are drawn to an arbitrary scale.

$(C_{36}H_{38}N_4Se)Ir_2(CO)_4$ ([5-2H$^+$]·[Ir(CO)$_2$]). Small, almost black, very well-formed square prismatic crystals were obtained by diffusion of CH_3OH into a $CDCl_3$ solution of $(C_{36}H_{38}N_4Se)Ir_2(CO)_4$. The data crystal was a block of approximate dimensions 0.12 × 0.12 × 0.25 mm. Details of crystal data, data collection, and structure refinement are listed in Table 1 and supporting information Table S1. Four reflections (4,−2,−3; 5,3,−2; −4,−2,3; −6,0,0) were remeasured every 96 reflections to monitor instrument and crystal stability. For both compounds the data were collected at 193 K on a Nicolet P3 diffractometer using a graphite monochromator and Mo Kα radiation (λ = 0.710 73Å). A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.992 to 1.01 for **5**·2HCl and from 0.990 to 1.01 for [**5**-2H$^+$]·2Ir(CO)$_2$. The data were corrected for *Lp* effects but not absorption. Data reduction and decay correction were performed using the SHELXTL-PLUS software package.[14] The structures were solved by a combination direct methods[14] and refined on F^2 by full-matrix least-squares methods with anisotropic thermal parameters for the non-H atoms.[15] The hydrogen atoms were calculated in idealized positions (C−H = 0.96 Å, N−H = 0.90 Å) with isotropic U set to $1.2U_{eq}$ of the appropriate atom. Individual molecules of both **5**·2HCl and [**5**-2H$^+$]·2Ir(CO)$_2$ in the lattices lie on crystallographic 2-fold rotation axes at 0, y, $^1/_4$. In both cases, the 2-fold axis passes through the selenium atom and bisects the bipyrrole moiety. For compound **5**·2HCl a total of 195 independent parameters were refined to a final $wR(F^2)$ = 0.0993 using all 3732 reflections, with a goodness of fit = 1.174. The conventional $R(F)$ for 2901 reflections with $F_o > 4\sigma(F_o)$ was equal to 0.0430. In the case of [**5**-2H$^+$]·2Ir(CO)$_2$, a total of 231 independent parameters were

(14) Sheldrick, G. M. SHELXTL-*Plus* (Version 4.11). Siemens X-ray Analytical Instruments, Inc., Madison, WI, 1991.
(15) Sheldrick, G. M. SHELXL-93. *J. Appl. Crystallogr.*, in preparation.

Table 1. Crystallographic Data[a] for $(C_{36}H_{42}N_4Se)^{2+}(Cl^-)_2$ (**5**·2HCl) and $(C_{36}H_{38}N_4Se)(Ir(CO)_2)_2$ ([**5**-2H$^+$]·2Ir(CO)$_2$)

	5·2HCl	[**5**-2H$^+$]·2Ir(CO)$_2$
formula	$C_{36}H_{42}N_4SeCl_2$	$C_{40}H_{38}N_4SeIr_2$
fw	680.62	1102.16
a, Å	12.824(3)	21.319(2)
b, Å	14.172(2)	13.376(1)
c, Å	18.330(4)	13.604(1)
β, deg	102.915(15)	112.74(1)
V, Å^3	3247.1(11)	3577.8(5)
Z	4	4
F(000)	1416	2104
space group	*C*2/*c*	*C*2/*c*
radiation	Mo Kα (λ = 0.710 73 Å)	
ϱ_{calc}, g/cm^3	1.39	2.05
μ, cm^{-1}	13.53	84.58
transm factor range	n/a	0.2684–0.5441
$R_w(F^2)^b$	0.0995	0.0748
$R(F)^c$	0.0430	0.0384

[a] Data for both samples were collected on a Nicolet P3 diffractometer. Data for **5**·2HCl were collected at −100 °C, while those for [**5**-2H$^+$]·2Ir(CO)$_2$ were collected at −80 °C using a Nicolet LT-2 low-temperature delivery system. Lattice parameters were obtained from the least-squares refinement of 40 reflections with $18.4 < 2\theta < 23.6°$ for **5**·2HCl and 50 reflections with $12.8 < 2\theta < 24.9°$ for [**5**-2H$^+$]·2Ir(CO)$_2$. [b] $R_w = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^4\}^{1/2}$, where the weight, w, is defined as follows: $w = 1/\{\sigma^2(|F_o|^2) + (aP)^2 + bP\}$; $P = [^1/_3(\text{maximum of } (0 \text{ or } |F_o|^2) + {}^2/_3|F_c|^2]$. Here, *a* and *b* are constants suggested during refinement and are 0.0312 and 2.61, respectively, for **5**·2HCl and 0.02 and 0.0, respectively, for [**5**-2H$^+$]·2Ir(CO)$_2$. [c] The conventional *R* index based on *F* where 2901 reflections have $F_o > 4(\sigma(F_o))$.

refined to a final $wR(F^2) = 0.0749$ using all 4121 reflections, with a goodness of fit = 1.171. The conventional *R*(*F*) for 2961 reflections with $F_o > 4\sigma(F_o)$ was equal to 0.0384. A semi-empirical absorption correction was made using SHELXA.[16] The minimum and maximum transmission factors were 0.2684 and 0.5441, respectively. The *R* for averaging 8588 measured reflections into 4121 unique reflections (F^2) was 0.150 before the absorption correction and 0.0504 after the correction was made. Neutral atom scattering factors for the all atoms and the anomalous-dispersion corrections were taken from ref 17. Values used to calculate the linear absorption coefficient are from ref 17. All figures were generated using SHELXTL-*Plus*.[14] Other computer programs used in this work are listed elsewhere.[18]

Synthesis. 2,5-Bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)furan (10). 2,5-Bis(acetoxymethyl)furan[8] (**9**; 3.470 g, 16.35 mmol), ethyl 3-ethyl-4-methylpyrrole-4-carboxylate (**7**; 5.926 g, 32.70 mmol), and 70 mg of *p*-toluenesulfonic acid monohydrate were dissolved in 250 mL of absolute ethanol. The mixture was then heated at reflux under an Ar atmosphere for 20 h. Following this interval, the volume of the solution was reduced on a rotary evaporator to ca. 150 mL. The white precipitate that formed was filtered off, washed with absolute ethanol, and dried in vacuo to yield product **10** (1.385 g, 3.047 mmol) as a white solid. After the filtrate was evaporated to dryness and subjected to column chromatography on silica gel with 99:1 dichloromethane/methanol as eluent, another 0.926 g (2.037 mmol) of product **10** was also obtained (total yield 31%): ^{1}H NMR ($CDCl_3$) δ 1.11 (6H, t, CH_2CH_3), 1.34 (6H, t, $CO_2CH_2CH_3$), 1.97 (6H, s, CH_3), 2.73 (4H, q, CH_2CH_3), 3.86 (4H, s, pyrrole−CH_2−furan), 4.28 (4H, q, $CO_2CH_2CH_3$), 5.92 2H, s, furan-βH), 8.56 (2H br s, N*H*); HRMS *m/e* 454.2469 (calcd for $C_{26}H_{34}O_5N_2$, *m/e* 454.2468).

2,5-Bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)-selenophene (11). 2,5-Bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)furan (**10**; 320 mg, 0.703 mmol) was dissolved in a mixture of 50 mL of absolute ethanol and 30 mL of dichloromethane. Hydrogen selenide was bubbled through the solution for 1 h followed by dry HCl for 2 h. The solution was left to stir under the resulting H_2Se−HCl atmosphere for 6 days. At this point, the solution was filtered and evaporated to dryness. In this way 363 mg (0.701 mmol, 99.7%) of almost pure product **11** was obtained: ^{1}H NMR ($CDCl_3$) δ 1.11 (6H, t, CH_2CH_3), 1.32 (6H, t, $CO_2CH_2CH_3$), 1.97 (6H, s, CH_3), 2.73 (4H, q, CH_2CH_3), 4.05 (4H, s, pyrrole−CH_2−selenophene), 4.27 (4H, q, $CO_2CH_2CH_3$), 6.27 (2H, s, selenophene-βH), 8.52 (2H br s, N*H*); HRMS *m/e* 518.1691 (calcd for $C_{26}H_{34}O_4N_2{}^{80}Se$, *m/e* 518.1684).

3,7,18,22-Tetraethyl-2,8,17,23-tetramethyl-27-selenasapphyrin (5). 2,5-Bis((5-ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)selenophene (**11**; 360 mg, 0.70 mmol) was dissolved in 40 mL of trifluoracetic acid under an Ar atmosphere, and the mixture was stirred at 60 °C for 6 h. The resulting solution was then evaporated to dryness to give 2,5-bis((4-ethyl-3-methylpyrrol-2-yl)methyl)selenophene (**13**) as an oil. This crude product was not characterized in detail but condensed immediately with 218 mg (0.80 mmol) of 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-bipyrrole[2] (**15**) in 1.2 L of absolute ethanol. For this condensation, 700 mg of *p*-toluenesulfonic acid was added and the resulting solution bubbled with oxygen for 24 h with stirring. The solvent was then removed using a rotary evaporator. The resulting residue was then dissolved in a minimal amount of dichloromethane and purified by column chromatography on silica gel using a 4% solution of methanol in dichloromethane as the eluent. The dominant dark green fraction was collected, evaporated to dryness, and resubjected to chromatographic purification using these same conditions. Final purification was effected by recrystallizing from dichloromethane/hexanes. This gave 119 mg (0.175 mmol, 25%) of free base **5**: ^{1}H NMR ($CDCl_3$) δ −2.31 (2H, br s, N*H*), 1.70 (6H, t, bipyrrole−CH_2CH_3), 1.85 (6H, t, tripyrrane−CH_2CH_3), 3.47 (6H, s, bipyrrole−CH_3), 3.50 (6H, s, tripyrrane−CH_3), 3.98 (4H, m, bipyrrole−CH_2CH_3), 3.99 (4H, m, tripyrrane−CH_2CH_3), 10.17 (2H, s, selenophene-βH), 10.22 (2H, s, pyrrole−*meso*-*H*-pyrrole), 10.96 (2H, s, selenophene−*meso*-*H*-pyrrole); ^{13}C NMR ($CDCl_3$) δ 11.6, 14.9, 17.1, 17.9, 20.0, 53.4, 105.1, 112.6, 125.1, 131.6, 132.9, 134.9, 136.9, 137.9, 142.5, 144.7, 145.2, 151.1; HRMS *m/e* 609.2509 (calcd for $C_{36}H_{41}N_4{}^{80}Se$, *m/e* 609.2496); UV−vis (CH_2Cl_2) (nm (log ϵ)) 464 (5.19) (Soret), 587 (3.98), 631 (3.87), 674 (3.74), 741 (3.66) (Q-bands). Anal. Calcd for $C_{36}H_{40}N_4Se$: C, 71.15; H, 6.63; N, 9.22. Found: C, 70.88; H, 6.73; N, 9.02.

Bis(hydrochloride) Salt of 3,7,18,22-Tetraethyl-2,8,17,23-tetramethyl-27-selenasapphyrin Dichloride Salt (5·2HCl). Selenasapphyrin **5** (24.9 mg, 0.041 mmol) was dissolved in 10 mL of chloroform. The solution was then stirred under an HCl atmosphere for 30 min before the resulting green crystalline precipitate was filtered off, washed with chloroform, and air-dried. This gave 26.5 mg of **5**·2HCl (0.039 mmol, 95%). Data for this bis(hydrochloride): ^{1}H NMR (CD_3OD) δ 1.88 (6H, t, bipyrrole−CH_2CH_3), 1.96 (6H, t, tripyrrane−CH_2CH_3), 3.99 (6H, s, bipyrrole−CH_3), 4.11 (6H, s, tripyrrane−CH_3), 4.55 (4H, q, bipyrrole−CH_2CH_3), 4.70 (4H, q, tripyrrane−CH_2CH_3), 11.63 (2H, s, selenophene-βH), 11.92 (2H, s, pyrrole−*meso*-*H*-pyrrole), 12.78 (2H, s, selenophene−*meso*-*H*-pyrrole); ^{13}C NMR (CD_3OD) δ 12.0, 15.1, 17.1, 17.5, 21.1, 105.2, 114.2, 131.0, 134.9, 136.1, 137.6, 142.6, 142.9, 144.7, 147.8, 148.5; UV−vis (CH_2Cl_2) (nm) 474 (Soret), 651, 700 (Q-bands).

(3,7,1 8,22-Tetraethyl-2,8,17,23-tetramethyl-27-selenasapphyrin-ato)tetracarbonyldiiridium(I) ([5-2H$^+$]·2Ir(CO)$_2$). Selenasapphyrin **5** (25 mg, 0.041 mmol) and 50 mg (0.16 mmol) of $[IrCl(CO)_3]_n$ were stirred in 5 mL of benzonitrile at 95 °C under an argon atmosphere. After several hours, the green solution turned deep red. Stirring was then continued for 3 days. At this juncture, the solvent was evaporated off using a vacuum line. The residue was taken up in a minimal amount of dichloromethane and chromatographed on silica gel using dichloromethane as the eluent. The first bright red band was collected, evaporated to dryness, and recrystallized from dichloromethane/methanol to give 22 mg of [**5**-2H$^+$]·2Ir(CO)$_2$ as a dark red product (0.020 mmol, 48.5%): ^{1}H NMR ($CDCl_3$) δ 1.29 (6H, t, bipyrrole−CH_2CH_3), 1.86 (6H, t, tripyrrane−CH_2CH_3), 3.29 (6H, s, bipyrrole−CH_3), 3.68 (4H, m, bipyrrole−CH_2CH_3), 3.72 (6H, s, tripyrrane−CH_3), 3.96 (4H, m, tripyrrane−CH_2CH_3), 10.12 (2H, s, selenophene-βH), 10.47 (2H, s, pyrrole−*meso*-*H*-pyrrole), 11.16 (2H, s, selenophene−

(16) Sheldrick, G. M. SHELXA. Program used to apply an absorption correction to X-ray diffraction data based on differences between F_o^2 and F_c^2.
(17) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
(18) Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607.

meso-H-pyrrole); HRMS *m/e* 1103.1397 (calcd for $C_{40}H_{39}N_4O_4{}^{80}Se^{193}Ir_2$, *m/e* 1103.1372); UV−vis ($CHCl_3$) (nm) 525 (Soret), 627, 689, 756 (Q-bands).

5,32-Bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)thiophene (12). 2,5-Bis((5-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-2-yl)methyl)furan (**10**) (1.144 g, 2.51 mmol) was dissolved in 500 mL of absolute ethanol. H_2S was passed through the solution for 0.5 h, which was then further bubbled with gaseous HCl for an additional 0.5 h. The solution was then left to stir under the resulting H_2S−HCl atmosphere for 1 month. Subsequently, the mixture was evaporated to dryness in vacuo. At this juncture, ^1H NMR indicated 80% conversion of the starting furane-containing material to corresponding thiophene derivative. However, practically no other byproducts were detected at this point. The reaction was thus worked up by recrystallizing the crude product from dichloromethane/ethanol. This gave 377 mg of product **12** (0.801 mmol, 32%). This latter compound was then converted to 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin (**6**) via 2,5-bis((4-ethyl-3-methylpyrrol-2-yl)methyl)thiophene (**14**) as previously described.[2b]

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Supporting Information Available: Tables listing detailed experimental data for X-ray diffraction, fractional atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles and atom-labeling schemes for **5**·2HCl and [**5**-$2H^+$]·$2Ir(CO)_2$ (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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