Structure Determination for $\mathrm{Cp^*{}_2\overline{Zr{-}OCH{=}C(Zr(I)Cp_2)O}\cdot{}^1/_2C_6H_6}$. Single crystals were mounted in glass capillaries under H_2. Oscillation, Weissenberg, and precession photographs indicated a monoclinic lattice, space group $P2_1/c$($0k0$ absent for k odd, $h0l$ absent for l odd), and twinning by reticular pseudomerohedry across the *ab*-plane with a twin index of 3: the $(h, k, (-l - 2h)/3)$ reflections of the twin lattice were superimposed onto the (h, k, l) reflections of the parent lattice. (The metric relation between a, c, and β is $3c(\cos\beta) = -a$.) The twin fraction varied with each crystal, indicating macroscopic twin domains. One of these crystals was selected for data collection on a locally modified Syntex P2_1 diffractometer. The three check reflections indicated no decomposition and the data were reduced to F_o^2.

The positions of the Zr and I atoms were derived from a Patterson map, and an electron Fourier map phased on these three atoms revealed the remaining non-hydrogen atoms of the Zr complex and a benzene molecule of crystallization. Least-squares refinement of atomic coordinates and U's minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$ gave $R_F = 0.144$;[37] the form factors for all atoms were taken from ref 36. The hydrogen atoms were then located from difference maps and introduced into the model with fixed coordinates and isotropic B's. The refinement of non-hydrogen atoms with anisotropic U's using all the data (4100 reflections) led to $R_F = 0.096$, $R'_F = 0.084$, and $S = 4.44$.

At this stage, the F_o^2 were corrected for twinning in an iterative manner by substracting off an estimate of the twin contribution to the intensity.[38] This led to an improved data set, as evident from the lower goodness-of-fit: $S = 3.04$ ($R_F = 0.074$, $R'_F = 0.059$). After another cycle of least-squares refinement, the F_o^2 data were corrected again, but the correction differed marginally from the first pass: the volume ratio of the twins was 0.19:1; the final results are indicated in Table IV. The remaining errors in the data appear to be normally distributed. To check this, we carried out a parallel refinement in which all affected reflections were deleted. Refinement with this data set led to coordinates and U's that were insignificantly different (within 2σ) from the starting set; the goodness-of-fit (2.93, 2691 reflections total) is essentially the same as from the full data set refinement, and indicates that the twin correction is adequate ($R_F = 0.067$, $R'_F = 0.054$). All results quoted hereafter refer to refinement with the full data set.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 8024869). Use of the Bruker WM500 at the Southern California Regional NMR Facility, supported by National Science Foundation Grant No. CHE 7916324, is acknowledged. B.D.S. acknowledges support from the California Institute of Technology as a Myron A. Bantrell Fellow in Chemistry, 1981–1983.

Registry No. 1, 59487-85-3; **2**, 63637-45-6; **3**, 61396-34-7; **4**, 91202-93-6; **5**, 91202-95-8; **6**, 91208-76-3; **7**, 91202-97-0; **7**·C_6H_6, 91208-77-4; **8**, 91202-99-2; **8**·$^1/_2C_6H_6$, 91203-00-8; **8**-$^{13}C_2$, 91203-02-0; **8**-$^{12}C,^{13}C$, 91203-01-9; **9**, 91203-03-1; **9**-$^{13}C_2$, 91203-04-2; **10**, 91203-05-3; **12**, 91203-08-6; $Cp_2(PMe_3)Zr{=}CDO{-}Zr(D)Cp^*{}_2$, 91202-94-7; $Cp_2(CO)$-$Zr{=}CDO{-}Zr(D)Cp^*{}_2$, 91202-96-9; $Cp_2(PMe_3)Zr{=}CDO{-}Zr(I)Cp^*{}_2$, 91202-98-1; $Cp^*{}_2ZrD_2$, 83708-61-6; $Cp^*{}_2Zr(OCH_3)I$, 91203-06-4; $Cp_2Zr(^{13}CO)_2$, 91203-07-5.

Supplementary Material Available: Tables of Gaussian amplitudes, H-atom coordinates, bond lengths and angles, least-squares planes, and listing of structure factor amplitudes for 7 and 8 (75 pages). Ordering information is given on any current masthead page.

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[38] The twin fraction δ is defined by the relation $(kF_o)^2 = F_{cP} + \delta F_{cT}^2$, where k is the scale factor (estimated from the reflections unaffected by the twinning), F_o is the observed structure factor amplitude of the parent reflection, F_{cP} is the F_c of the parent reflection, and F_{cT} is the F_c of the twin reflection. The least-squares solution for δ gives $\delta = [k^2\sum wF_o^2F_{cT}^2 - \sum wF_{cP}^2F_{cT}^2]/\sum wF_{cT}^4$; the weight w is the least-squares weight for the twin reflection. The corrected F'_o is then calculated: $(kF'_o)^2 = (kF_o)^2 - \delta F_{cT}^2$ and used in the next cycle of least-squares refinement of coordinates and U's.

Electronic Structure of Triple-Decker Sandwiches. Photoelectron Spectra and Molecular Orbital Calculations of Bis(η^5-cyclopentadienyl)(μ,η^6-benzene)divanadium and Bis(η^5-cyclopentadienyl)(μ,η^6-mesitylene)divanadium

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received August 2, 1983

Abstract: The first photoelectron spectra of triple-decker sandwich complexes are reported. The complexes $CpV(\mu,\eta^6\text{-}C_6H_6)VCp$ and $CpV(\mu,\eta^6\text{-}C_6H_3Me_3)VCp$ have only 26 valence electrons. Comparison of the experimental results with molecular orbital calculations shows that the ground states have four unpaired electrons. The order of the upper valence electrons differs from that predicted by earlier extended-Hückel calculations.

Molecular orbital calculations on triple-decker sandwich complexes such as [CpMCpMCp] and [$(CO)_3MCpM(CO)_3$] (Cp = η^5-C_5H_5) predicted stable molecules for electron counts of 30 and 34.[1] A number of $M(CO)_3$ and MCp complexes with bridging heteronuclear ligands have been prepared.[2-7] Here, we report the first photoelectron (PE) spectra of triple-decker sandwich complexes. These complexes, $CpV(\mu,\eta^6\text{-}C_6H_6)VCp$ and $CpV(\mu,\eta^6\text{-}C_6H_3Me_3)VCp$,[8] have only 26 valence electrons. Comparison of the experimental results with molecular orbital (MO) calculations provides a definitive determination of the ground state and an assignment of the PE spectra.

Experimental Section

The complexes were kindly provided by Drs. K. Jonas and A. Duff (Max-Planck-Institut für Kohlenforschung, Mülheim, FDR). The spectra were recorded on a Perkin-Elmer PS-18 operating at a resolution of 35 meV for the Fwhm of the Ar $^3P_{3/2}$. Fenske–Hall MO calculations[9] were performed on the Department of Chemistry's VAX 11/780 with standard basis sets[10] and bond distances.[11]

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[1] Lauher, J. W.; Elian, J.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[2] (a) Werner, H.; Salzer, A. *Synth. React. Inorg. Met.-Org. Chem.* **1972**, *2*, 239. (b) Salzer, A.; Werner, H. *Ibid.* **1972**, *2*, 249. (c) Salzer, A.; Werner, H. *Angew. Chem.* **1972**, *84*, 949.

[3] Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046.

[4] Herberich, G. E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 433.

[5] Siebert, W.; Kinberger, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 434.

[6] Edwin, J.; Bochmann, M.; Böhm, M. C.; Brennan, D. E.; Geiger, W. E.; Krüger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, M.; Weiss, J.; Zenneck, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582.

[7] Herberich, G. E.; Hessner, B.; Hultner, g.; Zsolnai, L. *Angew. Chem.* **1982**, *93*, 471.

[8] Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

[9] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

[10] (a) Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. F. *J. Chem. Phys.* **1962**, *44*, 1344. (b) Clementi, E. *Ibid.* **1964**, *40*, 1944. (c) Clementi, E. *IBM J. Res. Dev.* **1965**, *9*, 2.

[11] Distances used: Cp(centroid)–V = 1.90 Å, Bz(centroid)–V = 1.80 Å, V–C(Cp) = 2.23 Å, V–C(Bz) = 2.28 Å, C–C(Cp) = 1.38 Å, C–C(Bz) = 1.41 Å. These distances are reasonably close to those reported for the crystal structure.[8]

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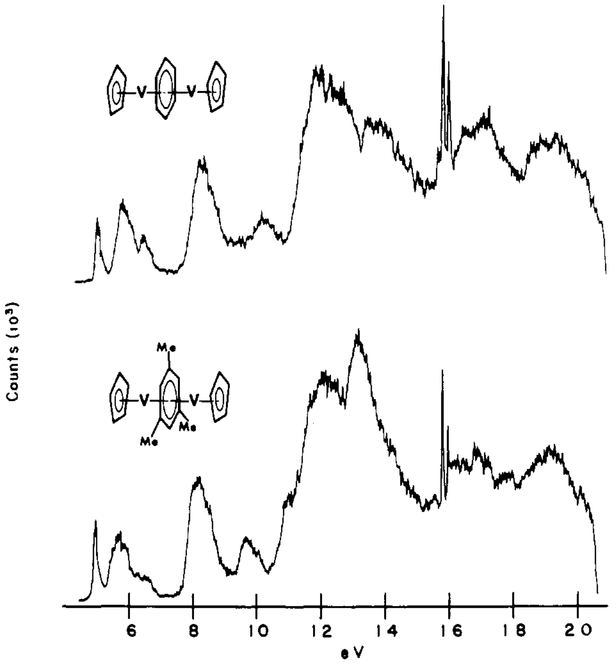

Figure 1. Photoelectron spectra of bis(η^5-cyclopentadienyl)(μ,η^6-benzene)divanadium and bis(η^5-cyclopentadienyl)(μ,η^6-mesitylene)divanadium.

Results and Discussion

The spectra, shown in Figure 1, are characterized by a sharp, low-energy ionization. This peak is followed by two broader bands centered at 6 eV ionization energy (IE). The shape of these bands and the difference between the benzene and mesitylene derivative suggest that more than two ionizations occur in this region. The next band appears at about 8 eV in both spectra; this is followed by a weaker band which shifts to lower IE in the mesitylene derivative. At about 11 eV, a region of intense broad bands begins.

The MO diagram for the upper valence orbitals of the benzene derivative is shown in Figure 2. The left column displays the energy levels of a V atom and the low-energy π-donor orbital of a Cp ring. The V atom interacts with the Cp ring, stabilizing this donor orbital and forming the $3e_1$ MO. Two V 3d orbitals are stabilized by a high-energy π-acceptor orbital on the Cp ring and form the $3e_2$ MO. The $4a_1$ is a nonbonding combination of the V 3d and 4s. We have shown the highest occupied molecular orbital (HOMO) of the CpV fragment as $3e_2^4$. If this fragment were to interact with another Cp ring to form vanadocene, one electron would be lost from the $3e_2$ to the Cp ring and one would be transferred to the $4a_1$ to form the $^3A_1$ ground state ($3e_2^2\ 4a_1^1$). This result has been confirmed by PE spectroscopy.[12]

Figure 2 also shows the formation of the triple-decker sandwich from two CpV fragments and Bz (center column). Although the symmetry of CpVBzVCp is only C_{2v} or C_{2h}, the nearly cylindrical symmetry of the fragments leads to an easy identification of the MO's with the high-symmetry $D_{\infty h}$ point group. Therefore, the final MO's are labeled σ, π, and δ as if this were a linear molecule. The Bz HOMO, stabilized by the VCp $3e_1$ and $4e_1$, forms the $1\pi_g$. The two $3e_1$ orbitals, disturbed somewhat by the Bz, form the $1\pi_u$ and $2\pi_g$. The $3e_2$'s on each CpV form the $1\delta_u$ and $1\delta_g$ MO's of the molecule. The former is strongly stabilized by the lowest unoccupied orbital (LUMO) of the Bz. The two nonbonding $4a_1$ orbitals form the $2\sigma_g$ and $3\sigma_u$. Not shown on the figure are the totally symmetric π combinations of each ring, which would be labeled $1\sigma_g$, $1\sigma_u$, and $2\sigma_u$, nor the MO's corresponding to C–C and C–H σ bonds. Figure 2 predicts that the ground state of this triple-decker sandwich is $1\delta_g^2\ 2\sigma_g^1\ 3\sigma_u^1$ with four unpaired electrons. As we will argue, the alternative closed-shell ground state, $1\delta_g^4$, is ruled out by the PE spectra.

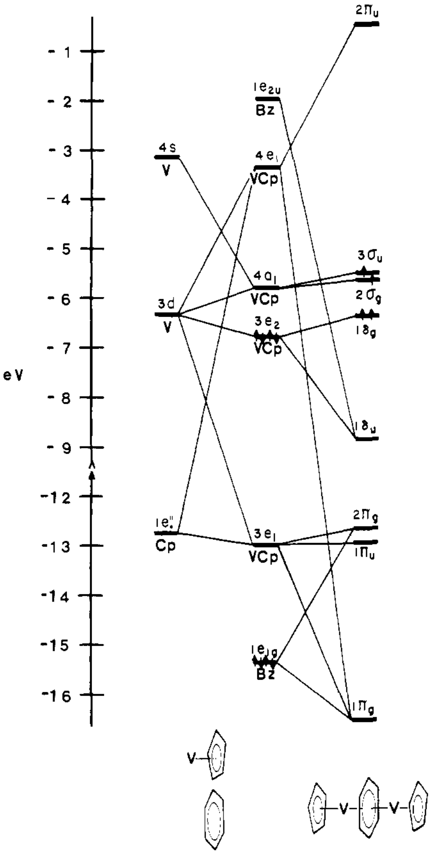

Figure 2. Molecular orbital diagram for the formation of (η^5-C_5H_5)V(μ,η^6-C_6H_6)V(η^5-C_5H_5) from the fragments (η^5-C_5H_5)V and C_6H_6. On the left are shown the important V and Cp orbitals. The center column shows the relative energies of the important orbitals in the fragments (η^5-C_5H_5)V and C_6H_6. On the right are the final levels of the complex CpVBzVCp. The lighter lines connecting the levels indicate the principle components of each orbital.

Table I. Ionization Energies (eV)

exptl mesitylene	exptl benzene	pred benzene	assign MO	% character V	% character Cp	% character Bz
5.05	5.05	4.80	$3\sigma_u$	99		
		4.95	$2\sigma_g$	99		
5.70 5.95	5.85	5.61	$1\delta_g$	92	5	
6.65	6.48	6.68	$1\delta_u$	70	2	27
8.33	8.30	8.27	$2\pi_g$	8	84	7
		8.46	$1\pi_u$	14	84	
9.75	10.10	10.37	$1\pi_g$	15	2	82

The experimental IE's, predicted IE's, assignments, and character of the corresponding MO's are listed in Table I. The predicted values correspond to the negative of the MO energies corrected for any errors by adding an appropriate fraction of the difference between our calculated IE and the experimental IE of free benzene and vanadocene. The predicted values suggest that the first sharp band is due to ionization of an electron from the nonbonding $3\sigma_u$ and $2\sigma_g$ MO's. The second band is due to ionization from the $1\delta_g$ and the high-spin component of the $1\delta_u$. The latter MO, $1\delta_u$, contains four electrons; ionization of one of these can produce either a quartet or a sextet state. The sextet state will have a lower IE than that predicted for the quartet. The third band is then due to the quartet state arising from ionization of the $1\delta_u$. This assignment yields a predicted intensity ratio of the second and third bands of 2:1, very close to that observed. These bands are broader than the first band because the $1\delta_g$ and $1\delta_u$ are V–Cp and V–Bz bonding, respectively, even though they are

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[12] (a) Evans, S.; Green, M. L. H.; Jewitt, B.; King, G. H.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2*, **1974**, *70*, 356. (b) Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; van Tilborg, J.; Robbins, J.; Smart, J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327.

primarily V in character. The appearance of these three bands is incompatible with the alternative closed-shell ground state, $1\delta_g^4$. The strong band at 8.3 eV is assigned to the $2\pi_g$ and $1\pi_u$, primary components of the Cp→V bond. Although these bonds would also have sextet and quartet components, the multiplet splitting is too small to resolve. The fifth band, which shifts IE substantially when benzene is replaced by mesitylene, is assigned to ionizations from the $1\pi_g$ MO which contains substantial arene π character. The ionizations above about 11 eV correspond to ionizations of C–C and C–H σ bonds and the totally symmetric π ligand combinations, the $1\sigma_g$, $1\sigma_u$, and $2\sigma_u$.

The stability of these 26-electron, open-shell, triple-decker sandwiches suggest a rich chemistry for systems with fewer than 30 electrons! These particular vanadium complexes should have both stable anions with 27 and 28 electrons and possibly stable cations with 25 and 24 electrons. It is conceivable that one could prepare a closed-shell triple-decker sandwich with as few as 22 electrons. Although our description of the bonding is similar, the order of our upper valence orbitals differs from that of Lauher et al.,[1] whose order is incompatible with the photoelectron spectra.

Acknowledgment. We thank the Robert A. Welch Foundation, Grant No. A-648, for support of this work, the National Science Foundation for a Departmental instrument grant to purchase the VAX 11/780, and Drs. K. Jonas and A. Duff for the gift of the complexes.

Registry No. $\mathrm{CpV}(\mu,\eta^6\text{-}\mathrm{C_6H_6})\mathrm{VCp}$, 86409-35-0; $\mathrm{CpV}(\mu,\eta^6\text{-}\mathrm{C_6H_3Me_3})\mathrm{VCp}$, 86374-48-3.

Synthesis and Structure of Bis(mercapto)cobalt(III) Porphyrins. Models for the Active Site of Cytochromes P450

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Contribution from the Laboratoire de Cristallochimie et Chimie Structurale (E.R.A. 08), Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France. *Received October 17, 1983*

Abstract: Reaction of 222-cryptated sodium 2,3,5,6-tetrafluoro- and 2,4,5-trichlorobenzenethiolates with chlorocobalt(III) *meso*-tetraphenylporphyrin in chlorobenzene affords the corresponding bis(thiolato)cobalt(III) *meso*-tetraphenylporphyrin complexes. The crystal structure of the 2,3,5,6-tetrafluorobenzenethiolate derivative $[\mathrm{Co(SC_6HF_4)_2(TPP)}][\mathrm{Na}\subset 222]\cdot\mathrm{C_6H_5Cl}$ (**1a**) has been determined. The crystal structure of a similar complex, $[\mathrm{Co(SC_6HF_4)_2(TPP)}][\mathrm{Na}\subset 222]\cdot{}^1/_2\mathrm{C_6H_5Cl}$ (**1b**), obtained by reaction of O_2 in chlorobenzene with the five-coordinate cobalt(II) derivative $[\mathrm{Co(SC_6HF_4)(TPP)}][\mathrm{Na}\subset 222]$ has also been studied: **1a**, triclinic, $a = 13.053$ (5) Å, $b = 25.034$ (9) Å, $c = 12.176$ (5) Å, $\alpha = 103.56$ (2)°, $\beta = 110.57$ (2)°, $\gamma = 82.03$ (2)°, $U = 3614$ Å^3; **1b**, triclinic, $a = 15.963$ (6) Å, $b = 16.007$ (6) Å, $c = 14.806$ (6) Å, $\alpha = 108.10$ (2)°, $\beta = 99.31$ (2)°, $\gamma = 91.41$ (2)°, $U = 3537$ Å^3. The octahedral coordination group has an average equatorial Co–N_p distance of 1.977 (4) Å in **1a** and 1.973 (4) Å in **1b**. The effect of the porphyrin conformation on the Co–N_p distances is discussed, and the orientation and structure of the axial ligands are described. These complexes present in solution and in the solid state d hyperporphyrin type spectra. These spectral properties are similar to those of the species obtained by treatment of the native state of cobalt-substituted cytochrome $\mathrm{P450_{CAM}}$ with dithiothreitol.

Substitution of iron by cobalt in cytochrome $\mathrm{P450_{CAM}}$ has been carried out recently.[1] The EPR spectra of the cobaltous and the oxygenated cobaltous protein indicate an axial ligand other than a nitrogenous base and support sulfur–cysteinate axial ligation. Treatment of the cobalt analogue of $\mathrm{P450_{CAM}}$ in the resting state with dithiothreitol leads to a species presenting a d-type hyperspectrum with a red-shifted Soret band at 464 nm and a near-UV band at 374 nm to which there is no precedent for in cobalt porphyrin systems.

Using weakly reducing alkali metal thiolates, we have recently shown that the spectral characteristics (UV–visible–EPR) of the reduced and reduced oxygenated Co $\mathrm{P450_{CAM}}$ are "mimicked" by five-coordinate (thiolato)- and six-coordinate oxygenated (thiolato)cobalt(II) porphyrins.[2] We show now that the d-type hyperspectrum obtained by treatment of the resting state of Co $\mathrm{P450_{CAM}}$ with a thiol is also mimicked by simple six-coordinate (dithiolato)cobalt(III) porphyrins. We present here the synthesis of two such compounds, their UV–visible spectral characteristics, and two X-ray structures of such a derivative.

Experimental Section

All experiments were done under an inert atmosphere by either Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise stated. Solvents were rigorously purified and dried under argon. The free tetraphenylporphyrin[3] and its cobalt(III) chloro complex[4] were prepared by published methods. 2,4,5-Trichlorobenzenethiol and 2,3,5,6-tetrafluorobenzenethiol were obtained from Aldrich. The sodium salts were prepared by reacting the thiols and NaH in dry doubly distilled THF and precipitated with pentane. The 222 cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained from Merck.

UV–visible spectra were measured on a Cary 210 spectrometer. Solid-state spectra were obtained on samples deposited as thin films on a face of a cell equipped with a gas inlet.

Synthesis and Crystallization of $[\mathrm{Co(SC_6HF_4)_2(TPP)}][\mathrm{Na}\subset 222]$ (1). To a solution of $[\mathrm{Co^{III}(Cl)(TPP)}]$ (50 mg) in 30 mL of chlorobenzene was added after filtration a chlorobenzene solution (20 mL) of sodium 2,3,5,6-tetrafluorobenzenethiolate (101 mg) and cryptand 222 (150 mg). The mixture becomes slowly green. UV $\lambda_{\max}$ (log ϵ_M): 384 (4.28), 465 (4.46), 532 (3.21), 587 (3.31), 634 (3.47) nm.

1 can be precipitated from this green solution by addition of pentane. The bulk sample obtained in this way is, however, always contaminated by free sodium thiolate. Crystals of $[\mathrm{Co(SC_6HF_4)_2(TPP)}][\mathrm{Na}\subset 222]\cdot\mathrm{C_6H_5Cl}$ (**1a**) were obtained by slow diffusion of pentane (75 mL) to this green solution. UV(solid state): 388, 470, 589, 639 nm. **1** can also be prepared by O_2 oxidation of a chlorobenzene solution of the five-coordinate cobalt(II) complex $[\mathrm{Co^{II}(SC_6HF_4)(TPP)}][\mathrm{Na}\subset 222]$.[2,5] Slow

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(1) Wagner, G. G.; Gunsalus, I. C.; Wang, R. M. Y.; Hoffman, B. M. *J. Biol. Chem.* **1981**, *256*, 6266–6273.

(2) Doppelt, P.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 341–344.

(3) Adler, A. O.; Longo, F. R.; Shergalis, J. *J. Am. Chem. Soc.* **1964**, *86*, 3145–3149.

(4) Datta-Gupta, N.; Bardos, T. J. *J. Pharm. Sci.* **1968**, *57*, 300–304.