and Ni(TPrPc)^3]. This difference is smaller than the same parameter in porphyrins ($\Delta E_{1/2}$ = 2.25 ± 0.15 V).[10] Assuming that $\Delta E_{1/2}$ is equal to the energy difference between the HOMO and the LUMO, this result is consistent with the observed lower energies of the first absorption maxima of the porphycenes,[3] as compared with the porphyrins (see supplementary material). A further characteristic of the porphycenes is the constant difference (0.35 ± 0.07 V) between the first and second reduction potentials of the ligand. This difference is independent of the nature of the coordinated metal.

C. Substituent effects are observed, which qualitatively relate to inductive interactions with the π-electron system of the porphycenes (Table I). However, it is remarkable that the four propyl groups exert a more attenuated effect on the energy of the electron transfer when they are on the CHCH bridge [Ni(TPrPc-9,10,19,20)] rather than on the 2,7,12,17-positions of the pyrroles [Ni(TPrPc)]. This is consistent with recent spectroscopic results.[2a] Comparison of the reduction potentials of the Ni complexes of TPrPc, TPrPc-9,10,19,20 and OEPc clearly reveal that the effect of alkyl groups is not additive. Again, this difference is due to the distortion of the ring observed by substitutions on positions 9, 10, 19, and 20.[1c] Such a distortion will weaken the inductive substituent effects on the redox and other characteristics of the molecule.

D. In striking contrast with the Co^{II}–porphyrins, the Co^{II}–porphycene was not reducible to the Co^{I} derivative.

From these results it is clear that the decrease in symmetry in the porphycenes as compared to the porphyrins and the distortion of the porphycene ring caused by steric interference of the substituents[20] have a profound effect on the electrochemical properties of these systems. Further studies are under way to elucidate electrochemical reaction mechanisms and to characterize the electrogenerated species.

Supplementary Material Available: Table of half-wave potentials of porphycenes in DMF and syntheses and spectral data of metalloporphycenes (9 pages). Ordering information is given on any current masthead page.

Novel Synthetic Route to Scandium Porphyrin Derivatives and the First Structurally Characterized Metalloporphyrin–η⁵-Cyclopentadienyl Sandwich Compound

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The ability of metalloporphyrin moieties to support a host of coordination geometries with a wide variety of co-ligands is well documented.[1,2] Metalloporphyrin π-complexes are rare, however, and to the best of our knowledge, derivatives with many-electron π-ligands such as η^6-arenes and η^5-cyclopentadienyls have never been isolated.[2,3] We are studying porphyrin complexes of the larger early transition metals with a view to exploiting their

electron-deficient, out-of-plane nature to prepare novel derivatives with unusual structures and reactivities. Relatively few of these are known, due, we believe, to the dearth of useful synthetic routes to out-of-plane early metal porphyrin starting materials.[1,3,4] Here we describe use of the recently reported dilithium salt [Li-(THF)₄][LiOEP][5] (OEP = dianion of octaethylporphyrin) to effect a remarkably facile synthesis of (OEP)ScCl (1) and the first definitive examples of η^5-cyclopentadienylporphyrin derivatives, the sandwich compounds (OEP)Sc(η^5-C₅R₅).

The metathesis reaction shown in eq 1 (100 °C, toluene, 2 h) provides a simple, high-yield route to gram quantities of the chloride **1**. After filtration, **1** was obtained as red crystals by

$$[Li(THF)_4][LiOEP] + ScCl_3(THF)_3 \rightarrow (OEP)ScCl + 2LiCl$$
$$\mathbf{1}$$

<div align="right">(1)</div>

addition of pentane and cooling to −40 °C overnight; isolated yields are typically >90%.[6] This synthetic route offers several advantages over previously reported syntheses of scandium porphyrins.[1b,3,7] For instance, it avoids high-boiling solvents that are often difficult to remove without resorting to chromatography (a procedure that frequently results in the formation of oxo species) and is simple to perform on a large scale. We are aware of only one other report of a metalloporphyrin synthesis using this approach. Buchler et al. have reported the reaction of Li₂OEP with Y(OEP)acac to give low yields of Y(OEP)₂.[8] In this case, however, the dilithium salt was prepared in situ and was found to be unstable under the reaction conditions employed.

Although **1** is somewhat moisture-sensitive in solution, it is air-stable as a solid. As shown in eqs 2 and 3, it is a useful precursor to a wide range of (OEP)ScR derivatives. For example, five-coordinate alkyl, amide, and alkoxide complexes were prepared in toluene via reactions such as[9]

$$1 + MR \rightarrow (OEP)ScR + MCl$$

<div align="right">(2)</div>

(M = Li, R = CH(SiMe₃)₂, N(SiMe₃)₂; M = K, R = OSiMe₃)
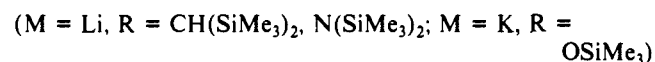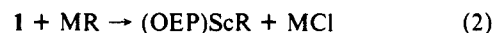
More noteworthy, however, are the novel η^5-cyclopentadienyl derivatives prepared by straightforward metathesis reactions in THF at room temperature (eq 3). A simple workup (removal

$$1 + LiC_5H_5 \rightarrow (OEP)Sc(\eta^5\text{-}C_5H_5) + LiCl$$
$$\mathbf{2a}$$

<div align="right">(3)</div>
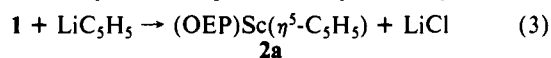
of solvent and crystallization from toluene/pentane) gave dark red (OEP)Sc(η^5-C₅H₅) (2a) in 95% yield.[6] Pentamethylcyclopentadienyl (Cp*, 2b) and methylcyclopentadienyl (Cp′, 2c) derivatives were prepared similarly, via the corresponding sodium salts, in 96% and 81% yields, respectively.

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(6) All reported compounds were analytically pure; see supplementary material for full characterization data. Selected data for **1**: ¹H NMR (300 MHz, 10⁻³ M CDCl₃, 20 °C) δ 10.48 (s, 4 H, CH), 4.19 (m, 16 H, C*H*₂CH₃), 1.97 (t, *J* = 7 Hz, 24 H, CH₂C*H*₃); UV/vis (10⁻⁵ M, THF) λ (log ε) 572 (4.5), 534 (4.2), 398 (5.4); EI/MS, 612 (M⁺, 100), 597 (M⁺ − 15, 25). **2a**: ¹H NMR (benzene-*d₆*) δ 1.68 (s, 5 H, C₅H₅); UV/vis λ (log ε) 568 (4.4), 532 (4.1), 390 (5.4). **2b**: ¹H NMR (benzene-*d₆*) δ −0.61 (s, 15 H, C₅Me₅); UV/vis λ (log ε) 572 (4.4), 534 (4.1), 394 (5.3). **2c**: ¹H NMR (benzene-*d₆*) δ 1.57 (t, *J* = 2 Hz, 2 H, C₅*H*₄Me), 1.49 (t, *J* = 2 Hz, 2 H, C₅*H*₄Me), −0.62 (s, 3 H, C₅H₄*Me*); UV/vis λ (log ε) 568 (4.6), 532 (4.3), 402 (5.5).

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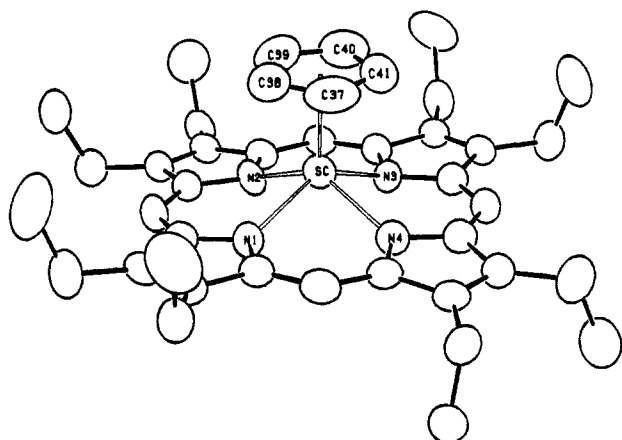
(8) Buchler, J. W.; Hütterman, J.; Löffler, J. *Bull. Soc. Chem. Jpn.* **1988**, *61*, 71. In this case "Li₂OEP" was prepared by deprotonation of H₂OEP with an excess of ⁿBuLi in trichlorobenzene.

(9) Selected ¹H NMR data for (OEP)ScCH(SiMe₃)₂ (C₆D₆): δ −1.84 (s, 18 H, SiMe₃), −5.78 (br s, 1 H, CH). (OEP)ScN(SiMe₃)₂ (C₆D₆): δ −1.81 (s, 18 H, SiMe₃). (OEP)ScOSiMe₃ (C₆D₆): δ −0.79 (s, 9 H, SiMe₃). Full details regarding synthesis and characterization of these compounds [including the X-ray crystal structure of (OEP)ScCH(SiMe₃)₂] will be given in a full paper.

Figure 1. Crystal and molecular structure of $Sc(OEP)(\eta^5\text{-}C_5H_5)$. Thermal ellipsoids are depicted at the 75% probability level. Selected distances (Å): Sc-N(av) 2.190 (3), Sc-C(Cp)(av) 2.494 (4), Sc-Cp centroid 2.196. Selected bond angles (deg): Cp-Sc-N(av) 111.28, N(1)-Sc-N(2) 82.1 (1), N(1)-Sc-N(4) 82.7 (1), N(2)-Sc-N(3) 82.4 (1), N(3)-Sc-N(4) 82.4 (1).

Compounds **2a-c** are air-stable, sublimable solids that can be dissolved in a variety of aerated polar and nonpolar solvents without decomposition. In the EI mass spectrum, intense peaks were observed for the molecular ions $(OEP)Sc(\eta^5\text{-}Cp)^+$ (*m/e* 642, 57% in **2a**, 712, 37% in **2b**) and signals due to $(OEP)Sc^+$ (100%) formed by loss of the Cp ligand. As expected, the OEP ethyl groups are diastereotopic showing complex multiplets for the methylene hydrogens by ^1H NMR spectroscopy. More surprising are the pronounced upfield shifts in ^1H NMR signals of the cyclopentadienyl substituents resulting from strong ring currents in the porphyrin core. In **2a** for example, the $\eta^5\text{-}C_5H_5$ protons resonate at δ 1.68, far outside the usual range of δ 4-6. Methyl substituents on cyclopentadienyls experience shielding of a similar magnitude; for instance, the Cp* methyls in **2b** are seen at δ -0.61. The latter value is similar to that observed by Sewchok et al. during their attempted preparation of (TTP)ScCp* (δ -0.42), a tetra-arylporphyrin analogue to **2a-c**; this material was reportedly hydrolytically sensitive and could not be isolated.[3] UV-vis spectra of **2a-c** closely resemble the starting chloride **1**.

The unusual nature of these compounds called for complete structural characterization by X-ray crystallography; the results for the Cp derivative **2a** are displayed in Figure 1.[10] The scandium is regularly coordinated by the four porphyrin nitrogens and the $\eta^5\text{-}Cp$ ligand; bond distances to the individual atoms in each ligand are identical within experimental error with Sc-N(av) = 2.190 (3) Å and Sc-C(av) = 2.494 (4) Å. In the related derivatives (TTP)ScCl[3] and Cp*2ScMe,[11] the corresponding values are Sc-N(av) = 2.17 (3) Å and Sc-C(av) = 2.46 (1) Å, respectively. In **2a** the scandium is 0.80 Å from the mean plane of the nitrogens and 2.196 Å from that of the Cp; the latter is planar to within less than 1 esd. The porphyrin core is only slightly ruffled, with rings 1 and 3 tilted "down" from the scandium and rings 2 and 4 twisted "up"; angles between the pyrrole planes and the mean plane of the porphyrin are -1.7°, 5.6°, -1.7°, and 5.6° for pyrroles 1-4, respectively. Parameters associated with the Cp ligand are unexceptional, and there are no particularly close interactions between adjacent molecules.

Supplementary Material Available: Full characterization data for compounds **1** and **2a-c** and details of the structure determination of **2a** including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (15 pages); listing of observed and calculated structure factors for **2a** (27 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Cp2Ta(CH2)2Ir(CO)2: An Early-Late Heterobimetallic Complex That Catalytically Hydrogenates, Isomerizes, and Hydrosilates Alkenes

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Despite the plethora of soluble early-late heterobimetallic complexes that have been prepared,[1] few are known that exhibit catalytic activity as intact binuclear species.[2] As an extension of our earlier studies of tantalum-platinum and -cobalt complexes,[3] we have carried out the synthesis and chemistry of the new complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (**1a**). We report here our preliminary finding that complex **1a**, which is surprisingly air and water stable, catalytically hydrogenates, isomerizes, and hydrosilates olefins under mild conditions. We have also obtained direct NMR evidence under catalytic operating conditions that **1a** remains intact during the reaction. Despite the similarity of the hydrogenation and hydrosilation processes, a kinetic study of the reactions of **1a** shows that they proceed by different mechanisms.

As illustrated in Scheme I, treatment of $Cp_2Ta(CH_2)(CH_3)$[4] with $(\eta^5\text{-indenyl})Ir(CO)_2$[5] leads to the extrusion of 1 equiv of indene and the formation of bis-bridging methylene complex **1a** in 88% isolated yield. The related complex **1b** can be prepared by using the analogous starting material $Cp(\eta^5\text{-}C_9H_7)Ta(CH_2)(CH_3)$. Although we have not been able to obtain X-ray quality crystals of **1a**, it is quite similar in spectroscopic properties to **1b**, and a crystal structure of the latter complex has been completed. In this material, the tantalum center is pseudotetrahedral (like its mononuclear alkylidene precursor) and the iridium center is square planar. The Ta-CH2 distance in **1b** (2.132 (8) Å) (Figure 1) is intermediate between average Ta—CH2R (2.26 Å) and Ta=CHR (2.02 Å) bond lengths.[6] The Ta-Ir bond length of 2.858 (1) Å is consistent with the presence of a metal-metal single bond. We assume that the mechanism of formation of these materials is related to that proposed earlier for the formation of $Cp_2Ta(CH_2)_2Pt(H)PMe_3$.[3a]

In the presence of H2, compound **1a** catalyzes the hydrogenation of ethylene and the isomerization of higher olefins.[7] Isomerization does not occur in the absence of H2. However, chemoselectivity depends on the solvent used. Thus, in benzene at 45 °C, ethylene is the only alkene hydrogenated (1 turnover/3 h); mono- and disubstituted alkenes isomerize at a similar velocity to an equilibrium mixture of *E* and *Z* internal alkenes. In THF at 45 °C,

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