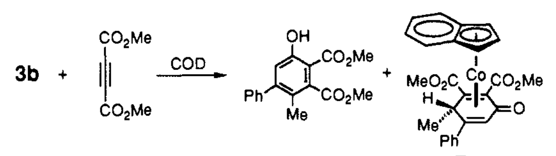
(Table I).[26,27] Compounds **3b** and **3c** were obtained as mixtures of *E* and *Z* isomers, which were identified by ^{1}H NMR shifts[28] and NOE measurements. In both cases the *E* isomer was the major kinetic product, but prolonged heating of the isolated complexes led to mixtures in which the *Z* isomer predominated.[29]

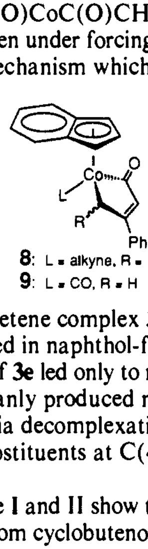
Reaction of the monosubstituted vinylketene complex **3a** with various alkynes produced phenols, unsymmetrical alkynes yielding mixtures of regioisomers (Table II).[27] Such a double C–C bond making cyclization has been suggested to account for cyclohexadienone formation from a two-alkyne reaction with a chromium carbene.[12]

Reaction of the disubstituted vinylketene complex **3b** proceeded well only with the electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD). In addition to phenol **6**, cyclohexadienone complex **7** was obtained (eq 1).[27] The stereochemistry shown for **7** is suggested by the absence of an NOE to any indenyl hydrogens upon irradiation of the methyl doublet. Irradiation of the endo hydrogen quartet produced a small (5%) enhancement of one of the aromatic (indenyl/phenyl) multiplets.



6, 43 % **7**, 16 % (1)

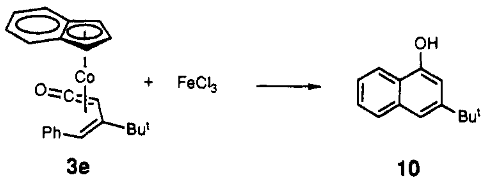
The unreactivity of **3b** with simple alkynes may be due to the methyl group sterically preventing alkyne complexation and formation of an intermediate metallacyclopentenone **8**. Consistent with this idea, CO adds readily to **3a** giving the metallacyclopentenone (η^5-C_9H_7)(CO)CoC(O)CH=C(Ph)CH$_2$ (**9**)[27] while CO will not add to **3b** even under forcing conditions. DMAD may react by an alternate mechanism which bypasses intermediate **8**.



8: L = alkyne, R = Me
9: L = CO, R = H

The (2-phenylvinyl)ketene complex **3e** represents an analogue of intermediates proposed in naphthol-forming reactions of metal carbenes. Thermolysis of **3e** led only to nonspecific decomposition, but FeCl$_3$ oxidation cleanly produced naphthol **10**[31] (eq 2). The cyclization may occur via decomplexation since free vinylketenes bearing unsaturated substituents at C(4) are known to cyclize to phenols.[32]

The reactions in Table I and II show that a convergent synthesis of substituted phenols from cyclobutenones and alkynes is possible via transition-metal insertion chemistry. Continuing efforts are aimed at improving the method through modification of the metal reagent.



3e **10** (2)

Acknowledgment. This investigation was supported by Grant No. CA40157, awarded by the National Cancer Institute, DHHS. M.A.H. acknowledges support via NIH Fellowship No. 1 F32 CA08683-01 from the NCI. We acknowledge the use of a VG 70-S mass spectrometer purchased through funding from the National Institutes of Health, S10-RR-02478, and 300-MHz and 360-MHz NMR instruments purchased through funding from the National Science Foundation, NSF CHE-85-16614 and NSF CHE-8206103, respectively. We thank Professor William Wulff for holding his manuscript to allow joint publication.

Supplementary Material Available: Full synthetic details and spectroscopic and analytical characterization of **1** and **3–9** (10 pages). Ordering information is given on any current masthead page.

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[26] Selected data for **3a**: Anal. C, H. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.23 (m, 3 H), 6.96 (m, 2 H), 6.87 (br d, J = 8.3 Hz, 1 H), 6.62 (br d, J = 8.5 Hz, 1 H), 6.56 (m, 1 H), 6.34 (m, 1 H), 6.16 (m, 1 H), 5.87 (m, 2 H), 3.30 (br t, J = 2.3 Hz, 1 H), 3.20 (dd, J = 2.5, 1.1 Hz, 1 H), 1.16 (dd, J = 2.0, 1.1 Hz, 1 H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 224.4 (CO), 136.0, 128.7, 127.9, 127.8, 126.0, 125.4, 121.9, 120.2, 109.8, 108.3, 104.8 (preceding three signals: two quaternary indenyl carbons and CC_6H_5 of vinylketene), 93.4, 74.0, 73.4, 35.3 (CH_2), 27.4 ($CH{=}CO$). IR (CH$_2$Cl$_2$): 1770 (s), 1749 (s), 1384, 1321, 965, 818, 668 cm^{-1}.

[27] All new compounds were spectroscopically characterized and furnished adequate elemental analyses (C, H, ±0.4%) or high-resolution mass spectral data. Details are provided in the supplementary material.

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Redox Properties of Porphycenes and Metalloporphycenes as Compared with Porphyrins

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The porphycenes, structural isomers of porphyrins recently synthesized at the Cologne Laboratory,[1] are attracting considerable attention.[2,3] In light of the paramount importance of redox processes in many photochemical and photobiological reactions of porphyrins, electron-transfer processes of porphycenes are of special interest. Although numerous papers have been published on the electrochemistry of porphyrins,[4] in particular on the effects

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Table I. Half-Wave Potentials for Porphycenes in CH_2Cl_2 + TBAP 0.1 M versus SCE[a]

	ligand oxidation			ligand reduction	
	$E_{1/2}(2)$	$E_{1/2}(1)$	metal $E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$
H_2(TPrPc)	+1.44	+0.97		−0.90	−1.27
Cu(TPrPc)	+1.18	+0.88		−0.97	−1.32
Ni(TPrPc)	+1.34	+0.90		−0.99	−1.36
Co(TPrPc)	+1.22	+0.99	+0.67 (II ↔ III)	−0.99	−1.36
Pt(TPrPc)		+0.91		−0.86	−1.27
Pd(TPrPc)		+0.88		−0.89	−1.28
Fe(TPrPc)$OCOCF_3$	+1.35	+1.13	−0.31 (III → II)	−0.94	−1.30
Fe(TPrPc)Cl	+1.36	+1.13	−0.30 (III ↔ II)	−0.92	−1.29
Al(TPrPc)Cl	+1.21	+1.04		−0.82	−1.10
Mn(TPrPc)Cl	+1.52	+1.23	−0.42 (III ↔ II)	−1.19	−1.55
Sn(TPrPc)Cl_2				−0.45	−0.73
H_2(Pc)		≈+1.0		−0.73	−1.07
H_2(OEPc)	+1.10	+0.87		−0.94	−1.26
Ni(OEPc)	+1.12	+0.81		−1.06	−1.46
Zn(OEPc)	+0.78	+0.64		−1.09	−1.38
Ni(TPrPc-9,10,19,20)	+1.05	+0.81		−0.81	−1.05

[a] For ferrocene in CH_2Cl_2 + TBAP 0.1 M, $E_{1/2}$ = +0.48 V/SCE.

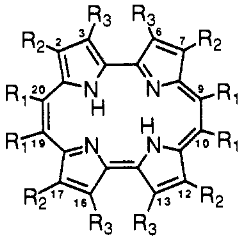

Figure 1. Porphycene ligands: $R_1 = R_2 = R_3$ = H, H_2(Pc); $R_1 = R_3$ = H, $R_2 = C_3H_7$, H_2(TPrPc); $R_1 = C_3H_7$, $R_2 = R_3$ = H, H_2(TPrPc-9,10,19,20); R_1 = H, $R_2 = R_3 = C_2H_5$, H_2(OEPc).

of substitution and/or of metalation on their redox properties,[5-15] information on the corresponding redox behavior of porphycenes is scarce.

The present study reports redox information on the porphycene ligands shown in Figure 1 and on metallo derivatives reported in Table I. The syntheses of the ligands were performed as published.[1] Electrochemical measurements were carried out in *N*,*N*-dimethylformamide (DMF) [plus 0.1 M recrystallized tetraethylammonium perchlorate (TEAP)[16]] and in dichloromethane (CH_2Cl_2) [plus purified 0.1 M tetrabutylammonium perchlorate (TBAP)[17]].[18]

The porphycenes studied, i.e., the parent compound [H_2(Pc)], 2,7,12,17-tetrapropylporphycene [H_2(TPrPc)], and 2,3,6,7,12,13,16,17-octaethylporphycene, [H_2(OEPc)], exhibited two reversible[19] one-electron reductions in both DMF and CH_2Cl_2. Unlike the porphyrins, no further reduction was observable on a Hg electrode up to −2.7 V/SCE in DMF. No redox couple was detectable up to +1 V/SCE in DMF, whereas the ligands H_2(TPrPc) and H_2(OEPc) were oxidized in CH_2Cl_2 via two reversible steps. In the latter case, chemical reversibility was observed only at high scan rates, i.e., >2 V/s. The oxidation of H_2(Pc) occurred at about 1 V/SCE, and it was coupled with strong adsorption on the Pt electrode.

As expected from the electron-donating properties of alkyl groups, the reduction potentials increase in the order H_2(Pc), H_2(TPrPc), H_2(OEPc). The change in reduction potential on going from H_2(Pc) to H_2(TPrPc) is greater than from H_2(TPrPc) to H_2(OEPc), indicating that the effect of substitution on the pyrrole rings of porphycenes is not additive. In fact, additivity of the potential shifts with the number of alkyl substituents can hardly be expected since H_2(OEPc)[20] is not planar due to steric interference of the ethyl groups at positions 3 and 6 and positions 13 and 16.

The metalloporphycenes M^{II}(TPrPc) (M = Co, Ni, Cu, Pd, Pt) and M^{II}(OEPc) (M = Ni, Zn) were reducible in both DMF and CH_2Cl_2 in two reversible one-electron steps (Table I). Two reversible one-electron oxidation steps were also observed in CH_2Cl_2, whereas no redox couple was detected in DMF up to +1.1 V/SCE. In addition, oxidation of the coordinated Co^{II} to Co^{III} was observed in Co^{II}(TPrPc) before oxidation of the ligand.

Among the complexes with trivalent ions, that from Al^{III} was not electroactive, whereas those from Fe^{III} and Mn^{III} were reduced to divalent states before reduction of the ring skeleton (Table I). As anticipated, the interconversion potentials M^{II}/M^{III} were dependent on the type of axial ligand X. These reduction potentials were more sensitive to solvent than those of the porphycene ligands.

Comparison of the above results with the redox pattern of the porphyrins leads to the following generalizations:

A. The porphycenes exhibit only two reversible one-electron-reduction steps. This is in striking contrast to the porphyrins, which are reducible via four distinct redox steps of which the last two undergo significant changes with the water content of the solvent.[6,9,21]

B. The difference between the first oxidation and the first reduction potentials of the porphycene ligands is nearly constant throughout the series and equal to $\Delta E_{1/2}$ = 1.85 ± 0.15 V [the same $\Delta E_{1/2}$ was previously measured for H_2(TPrPc), Cu(TPrPc),

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(18) Before use, DMF was purified as previously described;[17] CH_2Cl_2 was dried over molecular sieves (4 Å). Both solvents were stored under argon. Cyclic voltammetry was carried out at rates varying from 10 mV/s to 10 V/s on platinum electrodes (EDI type, Tacussel, France) with a multipurpose computerized device DACFAMOV (Microtec, CNRS, Toulouse, France). All potentials were measured versus a saturated calomel electrode (SCE).

(19) The peak potential difference is constant and close to 60 mV up to 5 V/s in DMF and up to 1 V/s in CH_2Cl_2. The plot of the peak currents I_{pc} and I_{pa} versus the square root of the scan rate was a line crossing the origin, and the ratio I_{pa}/I_{pc} was equal to 1 at all scan rates.

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and Ni(TPrPc)[3]. This difference is smaller than the same parameter in porphyrins ($\Delta E_{1/2} = 2.25 \pm 0.15$ 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 $\mathrm{Co^{II}}$–porphyrins, the $\mathrm{Co^{II}}$–porphycene was not reducible to the $\mathrm{Co^{I}}$ 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.

Acknowledgment. We thank Dr. J. Fajer for kind communication of results now published,[3] while this paper was in preparation.

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–η^5-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-C$_5$R$_5$).

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 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 Li$_2$OEP 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.

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

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]

$$\mathbf{1} + \mathrm{MR} \rightarrow \mathrm{(OEP)ScR} + \mathrm{MCl} \qquad (2)$$

$$(\mathrm{M = Li,\ R = CH(SiMe_3)_2,\ N(SiMe_3)_2;\ M = K,\ R = OSiMe_3})$$

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 of solvent and crystallization from toluene/pentane) gave dark red (OEP)Sc(η^5-C$_5$H$_5$) (**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.

$$\mathbf{1} + \mathrm{LiC_5H_5} \rightarrow \underset{\mathbf{2a}}{\mathrm{(OEP)Sc(\eta^5\text{-}C_5H_5)}} + \mathrm{LiCl} \qquad (3)$$

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[6] All reported compounds were analytically pure; see supplementary material for full characterization data. Selected data for **1**: ^{1}H NMR (300 MHz, 10^{-3} M CDCl$_3$, 20 °C) δ 10.48 (s, 4 H, CH), 4.19 (m, 16 H, CH_2CH$_3$), 1.97 (t, J = 7 Hz, 24 H, CH$_2$CH_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**: ^{1}H NMR (benzene-d_6) δ 1.68 (s, 5 H, C$_5$H$_5$); UV/vis λ (log ϵ) 568 (4.4), 532 (4.1), 390 (5.4). **2b**: ^{1}H NMR (benzene-d_6) δ −0.61 (s, 15 H, C$_5$Me$_5$); UV/vis λ (log ϵ) 572 (4.4), 534 (4.1), 394 (5.3). **2c**: ^{1}H NMR (benzene-d_6) δ 1.57 (t, J = 2 Hz, 2 H, C$_5$$H_4$Me), 1.49 (t, J = 2 Hz, 2 H, C$_5$$H_4$Me), −0.62 (s, 3 H, C$_5H_4$$Me$); UV/vis λ (log ϵ) 568 (4.6), 532 (4.3), 402 (5.5).

[7] (a) Gouterman, M.; Holten, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139. (b) Buchler, J. W.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Liebigs Ann. Chem.* **1971**, *745*, 135. (c) Buchler, J. W.; Schneehage, H. H. *Tetrahedron Lett.* **1972**, 3803.

[8] Buchler, J. W.; Hütterman, J.; Löffler, J. *Bull. Soc. Chem. Jpn.* **1988**, *61*, 71. In this case "Li$_2$OEP" was prepared by deprotonation of H$_2$OEP with an excess of ^{n}BuLi in trichlorobenzene.

[9] Selected ^{1}H NMR data for (OEP)ScCH(SiMe$_3$)$_2$ (C$_6$D$_6$): δ −1.84 (s, 18 H, SiMe$_3$), −5.78 (br s, 1 H, CH). (OEP)ScN(SiMe$_3$)$_2$ (C$_6$D$_6$): δ −1.81 (s, 18 H, SiMe$_3$). (OEP)ScOSiMe$_3$ (C$_6$D$_6$): δ −0.79 (s, 9 H, SiMe$_3$). Full details regarding synthesis and characterization of these compounds [including the X-ray crystal structure of (OEP)ScCH(SiMe$_3$)$_2$] will be given in a full paper.

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