

π -Complexes of Phthalocyanines and Metallophthalocyanines

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Received June 2, 2000

Addition of $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ to $\text{M}(\text{PcOEt})$ (PcOEt = octakis(ethoxy)phthalocyanine; $\text{M} = \text{H}_2, \text{Ni}$ (**1**), Cu , VO) in dichloromethane results in the formation of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-M}(\text{PcOEt})]\}\text{PF}_6$. The molecular structure of **1** reveals η^6 -coordination of $\text{Cp}^*\text{Ru}^{2+}$ to one of the isoindole subunits of the phthalocyanine ligand. The crystal structure reveals the presence of two cofacially stacked Pc units in the asymmetric unit separated by 3.27–3.36 Å. In $[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$, two distinct N–H sites are apparent in the ^1H NMR and IR spectra, but only one is exchangeable. The coordinated macrocycle can be metalated. The UV and electrochemical data indicate that the π -bonded metal center functions as an electron-donating substituent. Luminescence studies indicate that the η^6 -coordination quenches fluorescence to a lesser degree than coordination of metals into the N_4 pocket of the phthalocyanine subunit.

Introduction

Since their discovery in the early 1900s, phthalocyanines and metallophthalocyanines have received much attention. These compounds are especially well known for their intense blue-green color, with extinction coefficients of greater than $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ in the region 650–700 nm. This intense absorption, in combination with the exceptional chemical, thermal, and photochemical stability of these materials, has made phthalocyanines important industrial dyes.¹ Metallophthalocyanines are also useful as catalysts, e.g., for the aerobic oxidation of thiols, which also highlights their considerable stability.^{2–4} Many properties of the phthalocyanines can be varied by changing the metal and the substituents on the heterocycle.⁵ For example, sulfonated phthalocyanines are highly effective sensitizers for the destruction of tumors in photodynamic therapy.^{6–8} Because of their similarity to porphyrins, enzyme mimics and analogues have been prepared with metallophthalocyanines.^{6,7} A large number of octasubstituted phthalocyanines have been synthesized and studied in the context of molecular devices,^{9,10} taking advantage of, for example, their liquid crystalline derivatives^{11,12} and their applications in nonlinear optics.¹³

Our interest in phthalocyanines is based on the possibility that they might function as π -ligands. While there have been thousands of studies on metal phthalocyanines, π -complexation would represent a new coordination mode. Our efforts follow naturally from our previous work on the π -complexation of metalloporphyrins to “arenophilic” metal centers such as (cymene)- Ru^{2+} and $\text{Cp}^*\text{Ir}^{2+}$ (Scheme 1).^{14,15} In the present study, we employ Cp^*Ru^+ , an arenophilic reagent which has found broad use.¹⁶

Because phthalocyanines have two aromatic subunits, the benzene and the pyrrole rings, it is possible for the arenophilic metal to bind to either ring type. Previous studies on π -indole complexes indicate, however, that metals preferentially bind to the benzene rings, not the heterocyclic subunit.¹⁷ In contrast, in the aforementioned π -porphyrin complexes the metals were attached to the pyrroles.¹⁴ Regardless of the bonding mode, an important fundamental issue is the extent to which this π -interaction perturbs the electronic and chemical properties of the macrocyclic complex. The second general goal of this project focused on the possibility that π -complexation would occur with metal-free phthalocyanines; this would give rise to a new family of metallophthalocyanines with a reactive N_4H_2 core. In our previous work on π -porphyrin complexes, we detected but could not isolate the monometallic π -com-

(1) *The Phthalocyanines*; Moser, F., Thomas, A. L., Eds.; CRC Press: Boca Raton, FL, 1983.

(2) Wöhrle, D. In *Phthalocyanines*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989.

(3) *The Phthalocyanines*; Moser, F. H., Thomas, A. L., Eds.; CRC Press: Boca Raton, FL, 1983.

(4) Hanabusa, K.; Shirai, H. In *Phthalocyanines*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989.

(5) Simon, J.; Bassoul, P. In *Phthalocyanines*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989.

(6) Phillips, D. *Pure Appl. Chem.* **1995**, *67*, 117–126.

(7) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19–33.

(8) Brown, S. B.; Truscott, T. G. *Chem. Br.* **1993**, *29*, 955–959.

(9) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. *M. J. Am. Chem. Soc.* **1995**, *117*, 9957–9965.

(10) Pietro, W. J. *Adv. Mater.* **1994**, *6*, 239–242.

(11) Duro, A. J.; de la Torre, G.; Barbera, J.; Serrano, J. L.; Torres, T. *Chem. Mater.* **1996**, *8*, 1061–1066.

(12) Clarkson, G. J.; McKeown, N. B.; Treacher, K. E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1817–1823.

(13) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21–38.

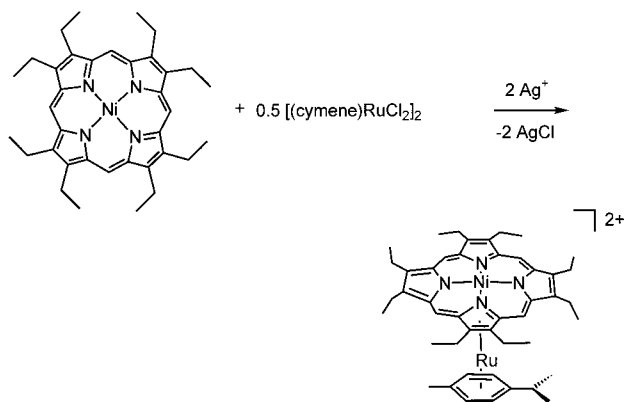
(14) Dailey, K. K.; Rauchfuss, T. B. *Angew. Chem., Intl. Ed. Engl.* **1996**, *35*, 1833–1835.

(15) Dailey, K. K.; Rauchfuss, T. B. *Polyhedron* **1997**, *16*, 3129–3136.

(16) Fagan, P. J.; Ward, M. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719. Koelle, U. *Chem. Rev.* **1998**, *98*, 1313–1334.

(17) Chen, S.; Carperos, V.; Noll, B.; Swope, R. J.; Rakowski DuBois, M. *Organometallics* **1995**, *14*, 1221–1231.

Scheme 1. Synthesis of π -Complexes of Metalloporphyrins



plexes, e.g., $\{(\text{arene})\text{Ru}[\eta^5\text{-H}_n\text{OEP}]\}^{(n+2)+}$, where OEP is octaethylporphyrin.¹⁵

Results

Synthesis of Phthalocyanines. While the chemistry of phthalocyanines is diverse and has a rich history, the preparation of soluble, symmetrical phthalocyanines is not as well developed. For this reason we initially focused on the preparation of the metallomacrocycles themselves. Our synthesis of octaethoxyphthalocyanine, abbreviated H₂PcOEt, is a modification of that of Cook et al.,¹⁸ but the procedure has been simplified. This preparation begins with the synthesis of dialkoxyphthalonitriles, C₆H₂-1,4-(OR)₂-2,3-(CN)₂, by O-alkylation of the corresponding dihydroquinones. Base-catalyzed macrocyclization of these precursors afforded the desired phthalocyanines. In this step we employed NaOEt in ethanol, which, while a slow reaction, yielded a purer product than the corresponding reaction of sodium pentoxide in pentanol. We found that some transesterification occurs to give pentoxy derivatives of PcOEt when the reaction is conducted in pentanol. We also prepared the octaisopropoxyphthalocyanine using a similar procedure in 2-propanol. The isopropoxy and ethoxy-substituted phthalocyanines exhibit good solubility in organic solvents and are easily obtained pure in crystalline form. Derivatives of the octabutoxyphthalocyanines, which are commercially available, are more difficult to obtain in crystalline form. A further advantage to the ethoxy- and isopropoxy-substituted phthalocyanines is that the ¹H NMR spectra of their derivatives are quite straightforward.

π -Complexation of Cp*Ru⁺ to Nickel Phthalocyanines. Addition of [Cp*Ru(MeCN)₃]PF₆ to Ni(PcOEt) (PcOEt = octakis(ethoxy)phthalocyanine) in dichloromethane solutions resulted in a change in color from green to yellow-green over several hours (Scheme 2). The dark green product was easily precipitated with ether. These salts are quite robust; they can be stored in air as solids for months and in methylene chloride solution for many weeks. They can be purified by chromatography on silica gel. The complexes are highly soluble in methylene chloride and chloroform and slightly so in acetonitrile. Solutions of the π -complex are rapidly decomposed by treatment with acids and bases.

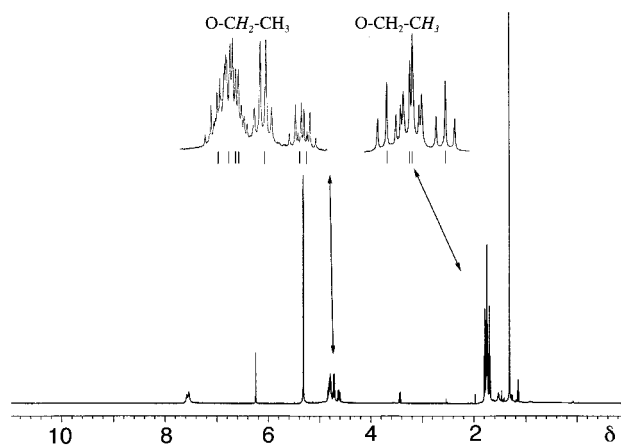
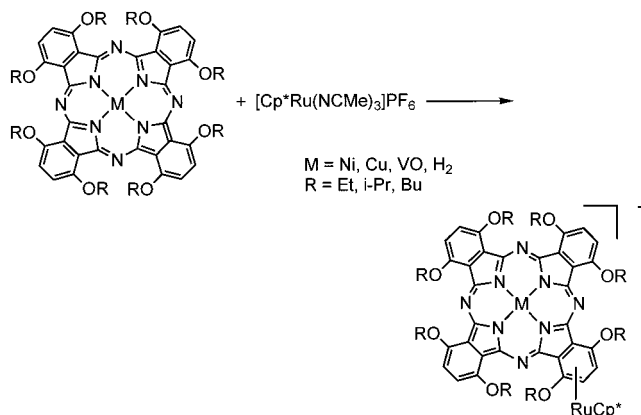


Figure 1. 500 MHz ¹H NMR spectrum for a concentrated CD₂Cl₂ solution of {Cp*Ru[η^6 -Ni(PcOEt)]}PF₆. The characteristic splitting patterns of the OEt groups are shown in the inset.

Scheme 2. Synthesis of [Cp*Ru[η^6 -M(PcOEt)]⁺



Donor solvents such as acetone, DMF, and DMSO afforded free Ni(PcOEt) and a solvated ruthenium complex, as established by ¹H NMR spectroscopy.

The ¹H NMR spectrum (Figure 1) of {Cp*Ru[η^6 -Ni(PcOEt)]}PF₆ establishes the symmetry of the adduct. The resonances for the benzo protons are split into a singlet and broadened multiplet. On the basis of their integrated intensities, these signals are assigned to the π -coordinated and noncoordinated arene units, respectively. As seen in other π -arene complexes,^{19,20} signals for the π -coordinated arene are shifted ca. 1 ppm upfield from the free ligand position. The methylene and methyl group signals are not shifted significantly relative to the free ligand. The methylene region is especially complex due to the presence of four types of CH₂ groups, resulting in a total of eight diastereotopic methylene proton positions. Finally, the CH₃ signals can be assigned to four overlapping triplets. Overall the NMR measurements indicate the lowering of symmetry in the Ni(PcOEt) upon coordination of the Cp*Ru⁺. The positive ion FAB-MS spectrum of **1** exhibits a strong molecular ion peak at *m/z* 1159, corresponding to the monocation fragment **1**⁺. Using procedures for the synthesis of **1**, we prepared Cp*Ru⁺ adducts of both Ni-

(19) Vol'kenau, N. A.; Bolesov, I. N. *J. Organomet. Chem.* **1988**, *288*, 341–348.

(20) Moriaty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157–190.

(18) Cook, M. J.; Dunn, A. J.; Howe, S. D.; Thomson, A. J.; Harrison, K. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2453–2458.

Table 1. Details of the Crystal Structure Solution and Refinement for $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]_2(\text{PF}_6)_2$

chemical formula	$\text{C}_{148}\text{H}_{190}\text{F}_{12}\text{Ni}_{16}\text{Ni}_2\text{O}_{16}\text{P}_2\text{Ru}_2$
cryst size (mm)	$0.2 \times 0.15 \times 0.1$
space group	$P1$
a (Å)	11.143(2)
b (Å)	19.801(4)
c (Å)	34.248(7)
α (deg)	104.92(3)
β (deg)	92.97(3)
γ (deg)	99.56(3)
V (Å ³)	7165(2)
Z	2
D_{calcd} (Mg m ⁻³)	1.418
μ (Mo K α , mm ⁻¹)	0.573
no. of reflns measured	14 758
no. of ind reflns	10 176
goodness-of-fit on F^2	0.946
R_{int}	0.0769
$R1^a$ [$I > 2\sigma$]	0.0832
$wR2^b$ [$I > 2\sigma$]	0.2072

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = \{\sum [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1297P)^2 + 53.7830P]$; $P = (F_o^2 + 2F_c^2)$; n = no. of reflections, and p = no. of parameters.

(PcOBu) and Ni(PcO-*i*-Pr), the butoxy- and isopropoxy-substituted phthalocyanine complexes. These complexes are well behaved, and their spectroscopic properties merit no further discussion. Crystals of the butoxy derivative were obtained from CH₂Cl₂ by layering with THF.

Dembeck et al.^{21,22} have shown that metal π -complexation was useful for the solubilization of polyamide polymers and other insoluble aromatics. Therefore, efforts were made to prepare π -complexes of nickel phthalocyanine itself, i.e., Ni(Pc). As is well known, the compound Ni(Pc) is insoluble in common organic solvents³ and can be purified only by sublimation at ~ 500 °C. Unfortunately, refluxing nitromethane suspensions of Ni(Pc) are unreactive toward [Cp*Ru(MeCN)₃]₂PF₆.

Structure of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]_2\}^+\text{PF}_6^-$. Tiny crystals ($0.2 \times 0.15 \times 0.1$ mm) of this salt were grown from CH₂Cl₂ by layering with THF and examined by X-ray diffraction using an imaging plate detector. Details of the structure refinement are given in Table 1, and selected bond lengths and angles are given in Table 2. As can be seen from Figures 2 and 3, the asymmetric unit consists of two stacked $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]_2\}^+$ units along with two disordered PF₆⁻ anions. This type of structure might have been expected based on the tendency of phthalocyanines to dimerize at concentrations above 10^{-4} – 10^{-6} M.²³ The structure (Figure 2) shows coordination of Cp*Ru⁺ to one of the benzene rings of each Pc subunit. The phthalocyanine ligands are approximately planar except for some slight out-of-plane twisting of the benzene rings of the isoindole subunits adjacent to the complexed isoindole subunit. The stacked $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]_2\}^{2+}$ unit is shown in Figure 3. The two Ni(PcOBu) units are separated by an interplanar distance of 3.28–3.36 Å and are oriented at an angle of 1.0° to one another. The interplanar distance is comparable to both the carbon–carbon van der Waals radii²⁴ (3.40 Å) and the interpla-

nar separation of I₃⁻-doped NiPc (3.22–3.24 Å)^{25–27} and NiPc (3.38 Å).²⁸ The Pc units are not stacked cofacially but rather are aligned such that the Ni atom of one of the rings sits above/below the centroid of the pyrrole ring of the benzenoid subunit trans to the Cp*Ru⁺.

Multiple Addition of Cp*Ru⁺ to Ni(PcOEt). We investigated the possibility of attaching more than one Cp*Ru⁺ center to Ni(PcOR). Addition of 1 equiv of [Cp*Ru(MeCN)₃]₂PF₆ to a dichloromethane solution of **1** resulted in the immediate precipitation of brown solid. ¹H NMR analysis of the solid shows two C₅Me₅ signals (55:45) as well as complex unresolved multiplets in the methylene and methyl regions. These two Cp* signals are less than the four expected for the four possible isomers (Scheme 3) of $\{[\text{Cp}^*\text{Ru}]_2(\text{NiPcOEt})\}(\text{PF}_6)_2$. FAB-MS of this material shows signals for doubly and even triply metalated derivatives.

Cp*Ru⁺ Adducts of Cu(PcOEt) and VO(PcOEt). Qualitative experiments showed that the reaction of Cp*Ru(MeCN)₃⁺ and metallophthalocyanines is fairly general. We pursued this theme for the copper and vanadyl derivatives in order to learn more about the perturbation of the metallophthalocyanine moiety by the organometallic fragment, using EPR spectroscopy.

The salts $\{\text{Cp}^*\text{Ru}[\eta^6\text{-M}(\text{PcOEt})]\}(\text{PF}_6)$ (M = V(O), Cu) were isolated as air stable green solids whose optical characteristics closely resemble those for the aforementioned nickel complexes. The ¹H NMR spectra are quite broad, but four signals can be distinguished for the benzo, CH₂CH₃, and C₅(CH₃)₅ groups. The X-band EPR spectra (Figure 4) of these adducts are typical of those for M(PcOEt) (M = V(O), Cu) both as fluid solution, giving isotropic spectra, and in frozen solution, where axial spectra were obtained and g_{\parallel} and g_{\perp} could be assigned. The spectral parameters are presented in the caption to Figure 4. No evidence was seen for a rhombic spectrum wherein the g_{\perp} would be split due to the presence of the organometallic center.

We were also interested in the possibility that the ruthenium might interact with the oxo group of the vanadyl. Although $\nu_{\text{V=O}}$ could not be unambiguously assigned in the IR spectrum of VO(PcOEt), on complexation to give $\{\text{Cp}^*\text{Ru}[\eta^6\text{-VO}(\text{PcOEt})]\}(\text{PF}_6)$, no change in the VO(PcOEt) portion of the IR spectrum could be discerned.

Interaction of Cp*Ru⁺ with H₂PcOEt. The reaction of Cp*Ru⁺ with H₂PcOEt afforded a stable 1:1 adduct. The structure of this species is of special interest because H₂PcOEt lacks the 4-fold symmetry exhibited by its metalated derivatives. It is known that in H₂PcOR, the NHs are equivalent. The ¹H NMR spectrum of [Cp*Ru(η^6 -H₂PcOEt)]PF₆ (Figure 5), however, shows two signals integrating to one proton each at δ 0.2 and 0.8, which we assign to N–H. These signals are absent in the spectra of the metallophthalocyanines and [Cp*Ru(η^6 -D₂PcOEt)]PF₆. The IR spectrum of [Cp*Ru(η^6 -D₂PcOEt)]PF₆ shows two $\nu_{\text{N-D}}$ bands at 2547 and

(21) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087–2089.

(22) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *Macromol. Symp.* **1994**, *77*, 303–313.

(23) Ledson, D. L.; Twigg, M. V. *Inorg. Chim. Acta* **1975**, *13*, 43–46.

(24) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(25) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6703.

(26) Yakushi, K.; Sakuda, M.; Kuroda, H.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1986**, 1161–1164.

(27) Yakushi, K.; Yamakado, H.; Yoshitake, M.; Kosugi, N.; Kuroda, H.; Sugano, T.; Kinoshita, M.; Kawamoto, A.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 687–696.

(28) Robertson, J. M.; Woodward, I. *J. Chem. Soc.* **1937**, 219–230.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]\}(\text{PF}_6)^4$

Ni(1)–N(1)/N(5)	1.910	C(52)–C(53)/C(51)–C(56)	1.43
Ni(1)–N(3)	1.913(11)	C(53)–C(54)/C(55)–C(56)	1.40
Ni(1)–N(7)	1.916(11)	C(54)–C(55)	1.360(19)
Ru(1)–C(Cp*)	2.16	C(53)–O(7)/C(56)–O(8)	1.35
Ru(1)–C(51)/C(52)	2.262	N(5)–C(5)/C(4)	1.36
Ru(1)–C(53)/C(56)	2.286	C(5)–C(38)/C(4)–C(37)	1.44
Ru(1)–C(54)/C(55)	2.208	C(37)–C(38)	1.46(2)
N(7)–C(6)/C(7)	1.36	C(37)–C(42)/C(38)–C(39)	1.38
C(6)–C(52)/C(7)–C(51)	1.47	C(41)–C(42)/C(39)–C(40)	1.38
C(51)–C(52)	1.46(2)	C(40)–C(41)	1.38(2)
		C(42)–O(5)/C(39)–O(6)	1.35
C(51)–C(52)–C(53)	120.8(10)	C(37)–C(38)–C(39)	122.4(12)
C(52)–C(51)–C(56)	119.6(13)	C(38)–C(37)–C(42)	118.4(17)
C(52)–C(53)–C(54)	116.7(10)	C(37)–C(42)–C(41)	117.6(15)
C(51)–C(56)–C(55)	116.2(12)	C(38)–C(39)–C(40)	117.7(14)
C(53)–C(54)–C(55)	123.9(13)	C(40)–C(41)–C(42)	121.2(13)
C(54)–C(55)–C(56)	122.6(11)	C(39)–C(40)–C(41)	122.7(16)

^a Values for multiple bond lengths are average bond distances.

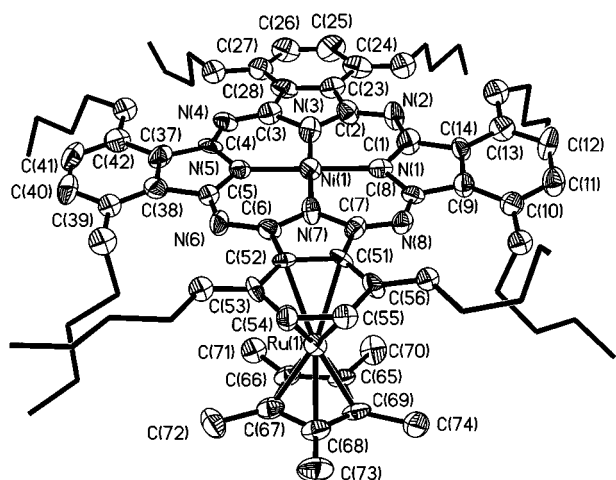


Figure 2. Molecular structure for one of the $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]\}^+$ cations of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]\}(\text{PF}_6)$ showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% level.

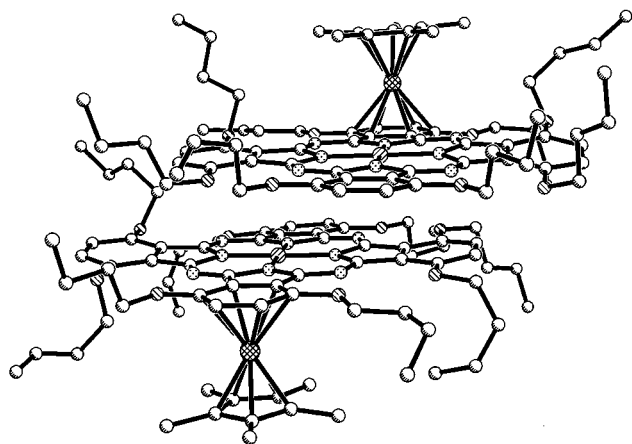


Figure 3. Molecular structure of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]\}(\text{PF}_6)$ showing the two stacked $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Ni}(\text{PcOBu})]\}^+$ cations in the asymmetric unit.

2475 cm^{-1} (vs $\nu_{\text{NH}} = 3304, 3261\text{ cm}^{-1}$), corresponding to $\nu_{\text{NH}}/\nu_{\text{ND}} = 1.37$, close to the value predicted based on the reduced mass effect for N–H.

Having confirmed the assignment of the high-field ^1H NMR signals for $[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$, the next issue is their interpretation. Treatment of solutions of

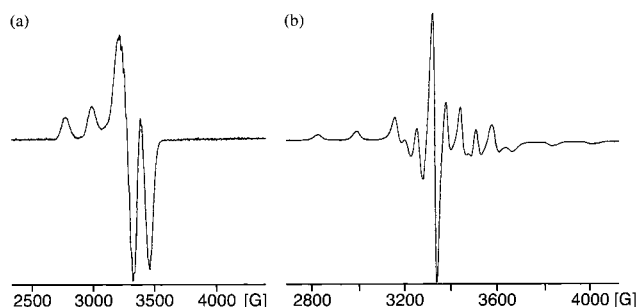
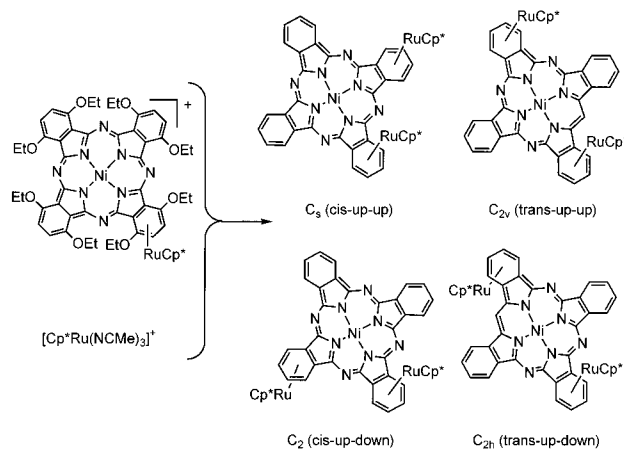


Figure 4. Q-band ESR spectra of frozen CH_2Cl_2 solutions at 77 K for (a) $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Cu}(\text{PcOEt})]\}(\text{PF}_6)$ and (b) $\{\text{Cp}^*\text{Ru}[\eta^6\text{-VO}(\text{PcOBu})]\}(\text{PF}_6)$. ESR parameters (a values in MHz) a: $g_{\parallel} = 2.0949$, $g_{\perp} = 2.0661$, $a_{\text{Cu},\parallel} = 274$, $a_{\text{Co},\perp} = 44$, $a_{\text{N},\parallel} = 44$; b: $g_{\parallel} = 2.139$, $g_{\perp} = 2.0048$, $a_{\text{V},\parallel} = 45$, $a_{\text{V},\perp} = 168$.

Scheme 3. Isomers $[(\text{Cp}^*\text{Ru})_2(\eta^6\text{-}\eta^6\text{-NiPcOEt})]^{2+}$



$[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$ with D_2O results in rapid (<1 min) and selective exchange of the δ 0.2 signal. The signal at δ 0.8 was not exchanged even after 1 day at room temperature. Control experiments using H_2PcOEt result in rapid (<1 min) and complete deuteration to give D_2PcOEt . We therefore conclude that the nonexchanging NH proton is on the isoindole subunit bound to Cp^*Ru^+ and is sterically shielded toward exchange.

The new kind of metallophthalocyanine $[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$ can serve as a ligand for metal ions. To this end, we treated $[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$ with excess copper acetate in refluxing ethanol to give a 40% yield of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-Cu}(\text{PcOEt})]\}(\text{PF}_6)$. ^1H NMR, IR, and FAB-MS spectra confirm that this product is identical

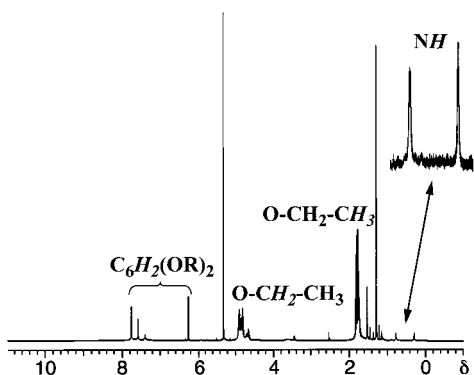


Figure 5. 500 MHz ^1H NMR spectrum of a concentrated CD_2Cl_2 solution of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-H}_2\text{PcOEt}]\}\text{PF}_6$. The two NH signals are shown in the inset.

to that prepared by reaction of $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]\text{PF}_6$ with $\text{Cu}(\text{PcOEt})$.

Electronic Properties of $\text{Cp}^*\text{Ru}[\eta^6\text{-M}(\text{PcOEt})]^+$ ($\text{M} = \text{Ni}, \text{Cu}, \text{VO}, \text{H}_2$). The electronic spectral properties for a series of $\{\text{Cp}^*\text{Ru}[\eta^6\text{-M}(\text{PcOEt})]\}\text{PF}_6$ complexes are summarized in Table 3. A representative spectrum is shown in Figure 6 for the case of $\text{M} = \text{Ni}$. The Soret and Q-bands in the UV-vis spectrum of the adducts in CH_2Cl_2 are bathochromically shifted vs free $\text{M}(\text{PcOEt})$ and H_2PcOEt . This type of behavior has previously been observed for electron-donating substituents and is consistent with a donation of electron density from Cp^*Ru^+ into the Pc.²⁹ In all cases, plots of absorbance vs concentration for both the Soret and Q(0,0)-bands in the 10^{-4} – 10^{-6} M concentration regime show no significant deviations from Beer's Law.

The luminescent properties of the phthalocyanines are well known.³⁰ We obtained emission spectra for 10^{-6} M solutions of $\text{Ni}(\text{PcOEt})$, $\text{VO}(\text{PcOEt})$, $\text{Cu}(\text{PcOEt})$, H_2PcOEt , and the corresponding Cp^*Ru^+ adducts in CH_2Cl_2 . In each case, excitation of the Soret band at 320 nm produces emission at the Q-band in the region 650–850 nm. This emission is drastically reduced at the Q(1,0) and especially the Q(0,0) bands on insertion of a metal ion into the central N_4 core. In contrast, the corresponding luminescent properties of $[\text{Cp}^*\text{Ru}(\text{H}_2\text{PcOEt})]\text{-PF}_6$ show only a moderate decrease in emission in the Q-band region. This indicates that π -coordination of the Cp^*Ru^+ cation to a benzene ring exerts less of a perturbation than insertion of a metal into the N_4 core.

Electrochemical Measurements. In view of the rich electrochemical properties of metallophthalocyanines,³¹ we examined the redox properties of the corresponding Cp^*Ru^+ derivatives. Our studies focused on the reversible reduction processes that occur in CH_2Cl_2 solutions between –800 and –1500 mV vs Ag/AgCl . Two reversible reductions are observed for free $[\text{M}(\text{PcOEt})]$ assignable to $\text{Pc}^{2-} \rightarrow \text{Pc}^{3-}$ and $\text{Pc}^{3-} \rightarrow \text{Pc}^{4-}$. In contrast, the complexes $\{\text{Cp}^*\text{Ru}[\text{M}(\text{PcOEt})]\}^+$ exhibit four reduction waves in this region. Since Ru^{II} complexes are known not to undergo reduction at these potentials,³² we assign these waves to the four one-electron couples between the species $\text{Pc}^{2-/-3-/-4-/-5-/-6-}$. The results are

presented in Table 4, and a representative voltammogram for $[\text{Cp}^*\text{Ru}(\text{H}_2\text{PcOEt})]\text{PF}_6$ is given in Figure 7. As can be seen from the data, the $E_{1/2}$ values for the $\{\text{Cp}^*\text{Ru}[\text{M}(\text{PcOEt})]\}_2^{2+/1+}$ and $\{\text{Cp}^*\text{Ru}[\text{M}(\text{PcOEt})]\}_2^{0/1-}$ couples are 110–190 mV more electropositive than those for the corresponding $\text{M}(\text{PcOEt})^{0/1-}$ and $\text{M}(\text{PcOEt})^{1-/2-}$ couples. The half-wave potentials for the $\{\text{Cp}^*\text{Ru}[\text{M}(\text{PcOEt})]\}_2^{1+/0}$ and $\{\text{Cp}^*\text{Ru}[\text{M}(\text{PcOEt})]\}_2^{1-/2-}$ couples occur at potentials similar to the $\text{M}(\text{PcOEt})^{0/1-}$ and $\text{M}(\text{PcOEt})^{1-/2-}$ couples, respectively.

Conclusions

The first π -complexes of phthalocyanines were prepared as air- and moisture-stable solids by the reaction of $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ with metalated and metal-free octakis(alkoxy)phthalocyanines (PcOR). The molecular structure of these complexes shows a cofacially stacked dimeric structure in which the Cp^*Ru^+ group is η^6 bound to a benzene group of one of the isoindole subunits. The complex $[\text{Cp}^*\text{Ru}(\eta^6\text{-H}_2\text{PcOEt})]\text{PF}_6$ represents a new class of metallophthalocyanines which lack a metal in the N_4 core. In this complex, the NH groups are chemically inequivalent, and the coordinated macrocycle undergoes metalation. Complexation with Cp^*Ru^+ alters the electronic properties of the phthalocyanine ligand in a manner similar to electron-donating substituents.

Experimental Section

Starting reagents were either purchased from Aldrich or, unless noted otherwise, prepared in the manner described in previous papers. We prepared $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ using literature procedures.³³ All reactions were performed under a dinitrogen atmosphere using standard Schlenk techniques. Dichloromethane was distilled from CaH_2 under N_2 . *n*-Hexane was distilled from Na/K under N_2 . Ethyl ether was distilled from Na under N_2 .

Optical spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. Infrared spectra were obtained with a Mattson Galaxy Series FT-IR 3000 as KBr pellets. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a U500 of Keck 750 Varian FT-NMR spectrometer. Constants are quoted in hertz. Mass spectra were obtained by the University of Illinois Mass Spectroscopy Laboratory. Microanalyses were obtained in the School of Chemical Sciences Microanalytical Laboratory.

CV data were recorded on a Bioanalytical System BAS-CV 50 W electrochemical analyzer with a Pt working electrode. All CV measurements were performed at ambient temperature under a nitrogen atmosphere in 0.1 mM CH_2Cl_2 solutions of $(n\text{-Bu})_4\text{NPF}_6$ vs Ag/AgCl as the reference electrode. Analyte concentrations were 1.0 mM. The ohmic resistance of the cell was compensated for each measurement. $E_{1/2}$ values are reported vs Ag/AgCl ; the couples are described as reversible provided $i_a/i_c = 1 \pm 0.1$.

3,6-Diethoxyphthalonitrile. A degassed solution of 5.20 g (32.5 mmol) of 2,3-dicyanohydroquinone in 125 mL of acetone was treated with 5.00 g (63.2 mmol) of K_2CO_3 and 13.0 mL (163 mmol) of ethyl iodide. The light yellow slurry was stirred under reflux for 60 h. After cooling, the orange solid was filtered off and washed with 100 mL of water and 100 mL of Et_2O and then dried under vacuum to afford 6.18 g of white crystals. An additional 0.33 g could be recovered from the

(29) Schmid, G.; Witke, E.; Schlick, U.; Knecht, S.; Hanack, M. *J. Mater. Chem.* **1995**, *5*, 855.

(30) Vincett, P. S.; Voight, E. M.; Rieckhoff, K. E. *J. Chem. Phys.* **1971**, *55*, 4131–4140.

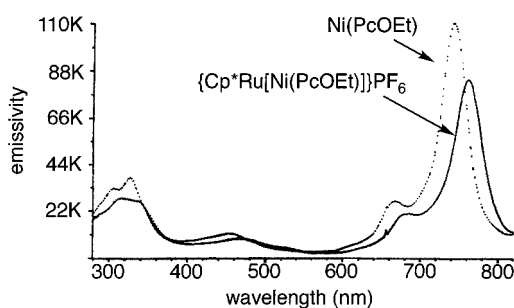
(31) Lever, A. B. P. *J. Porphyrins Phthalocyanines* **1999**, *3*, 488.

(32) Robertson, J. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1982**, *228*, 171–177.

(33) Steinmetz, B.; Schenk, W. A. *Organometallics* **1999**, *18*, 943.

Table 3. Electronic Spectral Properties of Several {Cp*Ru[η⁶-M(PcOEt)]PF₆ Complexes Compared with That for M(PcOEt) Complexes

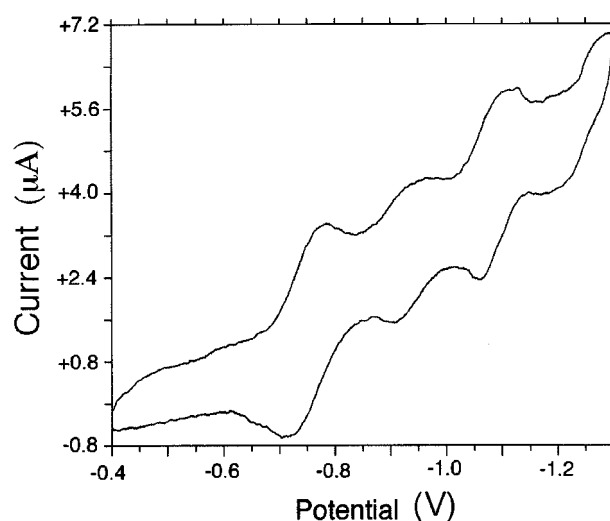
complex	λ (nm)	ε (L/mol·cm)	complex	λ (nm)	ε (L/mol·cm)
[Cp*Ru(VOPcOEt)]PF ₆	340	42 500	VOPcOEt	338	32 900
	492	11 700		478	6500
	714	23 200		702	20 000
	806	87 000		788	86 600
[Cp*Ru(H ₂ PcOEt)]PF ₆	332	36 200	H ₂ PcOEt	330	33 000
				410	8600
	466	9900		450	7400
	700	30 300		676	19 400
	780	113 000		768	79 800
[Cp*Ru(CuPcOEt)]PF ₆	332	57 100	CuPcOEt	328	37 200
	464	13 600		452	7900
	680	37 800		670	24 100
	686	42 100			
	768	158 000			
[Cp*Ru(NiPcOEt)]PF ₆			NiPcOEt	750	209 000
	324	23 800		304	23 600
	460	7100		326	28 100
	678	17 500		452	7300
	756	61 700		664	20 400
		740	92 300		

**Figure 6.** Electronic spectra of {Cp*Ru[η⁶-Ni(PcOEt)]}-PF₆ and Ni(PcOEt). The emissivity values were calculated from absorption data for 10⁻⁵ M solutions.**Table 4. Summary of Electrochemical Results for Several {Cp*Ru[η⁶-M(PcOEt)]PF₆ Complexes Compared with That for M(PcOEt) Complexes (All Waves Are Reversible)**

complex	E _{1/2} (mV, vs Ag/AgCl)	complex	E _{1/2} (mV, vs Ag/AgCl)
{Cp*Ru[η ⁶ -VO(PcOEt)]PF ₆	-680	VOPcOEt	-860
	-840		-1200
	-1050		
	-1210		
{Cp*Ru[η ⁶ -H ₂ PcOEt]PF ₆	-770	H ₂ PcOEt	-880
	-920		-1240
	-1100		
	-1290		
{Cp*Ru[η ⁶ -Cu(PcOEt)]PF ₆	-810	CuPcOEt	-1000
	-1010		-1360
	-1200		
	-1380		
{Cp*Ru[η ⁶ -Ni(PcOEt)]PF ₆	-870	NiPcOEt	-1030
	-1040		-1420
	-1260		
	-1440		

filtrate. Yield: 6.51 g (93%). ¹H NMR (CD₂Cl₂): δ 7.19 (s, 1H, C₆H₂), 4.14 (q, 2H, OCH₂CH₃), 1.46 (t, 3H, OCH₂CH₃).

1,4,8,11,15,18,22,25-Octaethoxy-29H,31H-phthalocyanine, H₂PcOEt. A refluxing suspension of 0.500 g (2.3 mmol) of 3,6-diethoxyphthalonitrile in 25 mL of ethanol was treated with 0.600 g (86.5 mmol) Li in 0.050 g pieces at 1 min intervals. As the Li was added, a large quantity of gas was evolved and the reaction mixture turned dark green. The mixture was heated at reflux under nitrogen for 8 days. On cooling, 50 mL of EtOH was added, and the resulting suspension was filtered through a 2.0 cm Celite 545 plug and medium sintered glass Schlenk frit. The product, which remains on the Celite, was

**Figure 7.** Cyclic voltammogram of a solution of 10⁻³ M {Cp*Ru[η⁶-H₂PcOEt)]PF₆ in CH₂Cl₂. The data were obtained using a Pt working electrode and Ag/AgCl reference electrode at a scan rate of 100 mV/s. Potentials are reported vs Ag/AgCl.

washed successively with three 25 mL portions of H₂O, six 25 mL portions of EtOH, and two 25 mL portions of Et₂O. The product was extracted using four 25 mL portions of CHCl₃. The CHCl₃ extracts were then combined, and the total volume was reduced to ca. 5 mL using a rotary evaporator. During this procedure the product began to precipitate. Finally, 100 mL of EtOH was added to complete precipitation of the product. The product was collected by filtration using a medium sintered glass Schlenk frit. Reprecipitation from 50 mL of CHCl₃ using 250 mL of EtOH followed by drying under vacuum for 16 h gave pure product. Yield: 0.325 g (65%). ¹H NMR (CD₂Cl₂): δ 7.64 (s, 1H, Ar C-H), 4.89 (q, 2H, OCH₂-CH₃), and 1.80 (t, 3H, OCH₂CH₃), 0.21 (s, 2H, NH). IR: ν_{NH} 3293 cm⁻¹. FAB-MS: 868 (M⁺). UV-vis (CH₂Cl₂): λ [nm] (ε [M⁻¹cm⁻¹]) 330 (33000), 410 (8600), 450 (7400), 676 (19400), 768 (79800).

Ni(PcOEt). A solution of 0.500 g (0.577 mmol) of H₂PcOEt and 1.44 g of Ni(OAc)₂·4H₂O in 75 mL of DMF was heated under reflux with stirring for 4 h. After cooling to room temperature, the reaction mixture was treated with 200 mL of H₂O to precipitate dark green microcrystals. The product was collected by filtration, washed with two 10 mL portions each of H₂O, EtOH, and Et₂O, and then dried under vacuum for 6 h. Yield: 0.417 g (78%). ¹H NMR (CD₂Cl₂): δ 7.54 (s,

1H, Ar C-H), 4.83 (q, 2H, OCH₂CH₃), and 1.75 (t, 3H, OCH₂CH₃). FAB-MS: 923 (M⁺). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 304 (23600), 326 (28100), 452 (7300), 664 (20400), 740 (92300).

Cu(PcOEt) and VO(PcOEt). The syntheses for these compounds were accomplished in a manner precisely analogous with that for Ni(PcOEt) above. Cu(OAc)₂·H₂O was used as the Cu²⁺ source to give Cu(PcOEt) in 61% yield. An equimolar mixture of VOSO₄·3H₂O and NaHCO₃ was used as the VO²⁺ source to give VO(PcOEt) in 35% yield.

Cu(PcOEt): ¹H NMR (500 MHz, CD₂Cl₂): δ 1.57 (bs, 24H), 4.51 (bs, 16 H). FAB-MS: 928 (M⁺). UV-vis λ [nm] (ϵ [M⁻¹ cm⁻¹]): 328 (37200), 452 (7900), 670 (24100), 750 (145000). ESR (298 K, 9.46 GHz): $g_{\parallel} = 2.0949$, $g_{\perp} = 2.0661$, $a_{\parallel} = 274$ MHz, $a_{\perp} = 44$ MHz.

VO(PcOEt): ¹H NMR (500 MHz, CD₂Cl₂): δ 1.851 (bs, 24H), 5.02 (bs, 16H), 8.5 (bs, 10H). FAB-MS: 932 (M⁺). UV-vis (CH₂-Cl₂) λ [nm] (ϵ [M⁻¹ cm⁻¹]): 338 (32900), 478 (6500), 702 (20000), 788 (86600). ESR (298 K, 9.46 GHz): $g_{\text{eff}} = 1.990$, $a_{\text{eff}} = 243$ MHz; (102 K, 9.46 GHz): $g_{\parallel} = 2.139$, $g_{\perp} = 2.0048$, $a_{\parallel} = 45$ MHz, $a_{\perp} = 168$ MHz.

3,6-Diisopropoxyphthalonitrile. A 500 mL round-bottom flask was charged with 9.65 g (60.2 mmol) of 2,3-dicyanohydroquinone, 24.98 g (180.7 mmol) of K₂CO₃, and 51.22 g (301 mmol) of 2-iodopropane followed by 250 mL of acetone. The reaction mixture was heated at reflux with vigorous stirring for 7 days. Upon cooling, the reaction mixture was filtered through a medium porosity frit and the insoluble side products were washed with 50 mL of acetone. The combined filtrate and washings were then evaporated to leave a light yellow powder. This powder was dissolved in a minimum of acetone, and colorless microcrystals precipitated by the addition of an excess of H₂O. Yield: 9.32 g (78%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.20 (s, 2H), 4.60 (septet, 2H), and 1.37, 1.38 (d, 12H).

1,4,8,11,15,18,22,25-Octaisopropoxy-29H,31H-phthalocyanine, H₂Pc-*i*-OPr. A suspension of 10 g (40.9 mmol) of 3,6-diisopropoxyphthalonitrile in 350 mL of 2-propanol was heated to reflux. This solution was treated with 8.27 g (1.191 mmol) of Li wire, which was added in small portions through the reflux condenser over the course of 1 h. During the addition, the color of the mixture turned from colorless to blue to dark green with concomitant evolution of gas (H₂). After the Li had been added, the reaction mixture was heated at reflux for 7 days. The cooled reaction mixture was transferred to a 1 L Erlenmeyer flask and diluted with ~300 mL of 2-propanol followed by 60 mL of acetic acid. The pH of the reaction mixture was then adjusted to ~7 by addition of NaOH, and the reaction mixture was evaporated to dryness. The residue was subjected to Soxhlet extraction with 2-propanol to remove brown-colored byproducts. These extracts were discarded, and the solids were extracted with 1 L of CH₂Cl₂. The CH₂Cl₂ extract, in 200 mL portions, was shaken with 100 mL of H₂O containing a few drops of acetic acid. After vigorous shaking, 1 M aqueous NaOH was added dropwise until the pH was neutral. The CH₂Cl₂ layer was then isolated, and the solvent was removed under vacuum. Yield: 3.58 g (36%). ¹H NMR (400 MHz, CDCl₃): δ 7.53 (s, 8H), 4.96 (septet, 8H), 1.580 (d, 48H). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 328 (58000), 402 (30000), 772 (142000).

Ni(PcO-*i*-Pr). A 250 mL flask was charged with 1.00 g (1.02 mmol) of H₂Pc-*i*-OPr, 2.54 g (10.2 mmol) of Ni(OAc)₂·4H₂O, and 150 mL of DMF. The reaction mixture was heated to reflux for 2 h. The cooled solution was treated with 100 mL of H₂O to precipitate the product, which was collected by filtration, washed with 50 mL of H₂O, and dried in air for 2 h. The product was reprecipitated from a minimum volume of CH₂-Cl₂ by addition of 120 mL of hexane followed by reducing the solvent volume to ca. 100 mL under vacuum. The product was collected by filtration and dried in air (~1 h). Yield: 0.86 g (81%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.46 (s, 8H), 4.89 (septet,

8H), 1.56, 1.55 (d, 48H). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 304 (54000), 436 (17000), 670 (39000), 740 (94000).

{Cp*Ru(η^6 -M(PcOEt))}PF₆. A solution of 0.108 mmol of M(PcOEt) in 10 mL of CH₂Cl₂ was added dropwise to a suspension of 55 mg (0.108 mmol) of [(C₅Me₅)Ru(MeCN)₃]PF₆ in 15 mL of CH₂Cl₂. After stirring the reaction mixture at room temperature for 10 h, the solvent volume was reduced to ca. 5 mL under vacuum. This solution was slowly diluted with 25 mL of Et₂O to give a suspension of a dark green powder in a pale green solution. After 0.5 h, the product was collected by filtration, washed twice with 5 mL portions of Et₂O, and dried under vacuum for 1 h.

{Cp*Ru(η^6 -Ni(PcOEt))}PF₆. Yield: 90%. ¹H NMR (500 MHz, CD₂Cl₂): δ 1.34 (s), 1.71 (t, $J = 7$ Hz), 1.75 (t, $J = 7$ Hz), 1.76 (t, $J = 7$ Hz), 1.780 (t, $J = 7$ Hz), 4.6–4.9 (m), 6.14 (s), 7.56 (s), 7.60 (s). FAB-MS: 1159 (M⁺ - PF₆), 923.2 (NiOEtPc⁺). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 324 (23800), 460 (7100), 678 (17500), 756 (61700). Anal. Calcd for C₅₈H₆₃F₆N₈-NiO₈PRu (1304): C, 53.39; H, 4.87; F, 8.74; N, 8.59; Ni, 4.50; P, 2.37; Ru, 7.75. Found: C, 52.84; H, 5.18; F, 8.47; N 8.25; Ni, 4.32; P, 2.32; Ru, 8.12.

{Cp*Ru(η^6 -Cu(PcOEt))}PF₆. Yield: 75%. ¹H NMR (500 MHz, CD₂Cl₂): δ 1.33 (bs), 1.60 (bs), 4.50 (bs), 8.7 (bs). FAB-MS: 1164.4 (M⁺ - PF₆), 1075.3 (M⁺ - PF₆ - C₂H₄). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 332 (57100), 464 (13600), 680 (37800), 686 (42100), 768 (158000). Anal. Calcd for C₅₈H₆₃-CuF₆N₈O₈PRu (1310): C, 53.19; H, 4.85; Cu, 4.85; F, 8.70; N, 8.56; P, 2.36; Ru, 7.72. Found: C, 54.52; H, 5.51; Cu, 4.42; F, 9.05; N 8.99; P, 1.84; Ru, 8.27.

{Cp*Ru(η^6 -VO(PcOEt))}PF₆. Yield: 94%. ¹H NMR (500 MHz, CD₂Cl₂): δ 1.52 (bs), 1.82 (bs), 4.96 (bs), 8.4 (bs). FAB-MS: 1168.3 (M⁺ - PF₆), 1140.3 (M⁺ - PF₆ - C₂H₄). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 340 (42500), 492 (11700), 714 (23200), 806 (87000). Anal. Calcd for C₅₈H₆₃F₆N₈O₉PRuV (1313): C, 53.05; H, 4.84; F, 8.68; N, 8.53; P, 2.36; Ru, 7.70; V, 3.88. Found: C, 52.50; H, 4.87; F, 8.17; N 8.55; P, 2.22; Ru, 6.17; V, 3.80.

[Cp*Ru(η^6 -H₂PcOEt)]PF₆. Yield: 89%. ¹NMR (500 MHz, CD₂Cl₂): δ 1.29 (s), 1.72–83 (m), 4.60–4.95 (m), 6.24 (s), 7.43 (bs), 7.58 (s), 7.76 (s). FAB-MS: 1103.4 (M⁺ - PF₆). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 332 (36200), 466 (9900), 700 (30300), 780 (11300). Anal. Calcd for C₅₈H₆₅F₆N₈O₈PRu (1248): C, 55.81; H, 5.25; F, 9.13; N, 8.98; P, 2.48; Ru, 8.10. Found: C, 55.61; H, 5.19; F, 9.07; N 9.12; P, 2.10; Ru, 6.86.

Experiments Involving Deuterated H₂PcOEt. H-D Exchange in [Cp*Ru(η^6 -H₂PcOEt)]PF₆. A solution of 2 mg of [Cp*Ru(η^6 -H₂PcOEt)]PF₆ in 1 mL of CD₂Cl₂ was treated with 0.2 mL of 99.9% D₂O, and this solution was shaken vigorously for 1 min. ¹H NMR (500 MHz, CD₂Cl₂): δ 0.2 (s, 0.1H), 0.8 (s, 1H), 1.29 (s), 1.72–83 (m), 4.60–4.95 (m), 6.24 (s), 7.43 (bs), 7.58 (s), 7.76 (s).

H-D Exchange in H₂PcOEt. A solution of 100 mg of H₂PcOEt in 15 mL of CH₂Cl₂ was treated with 10 mL of 99.9% D₂O. The resulting emulsion was stirred vigorously for 30 min, and then the methylene chloride layer was dried over MgSO₄, filtered, and evaporated under vacuum. The resulting solid was dried under vacuum for 10 h. ¹H NMR (500 MHz, CD₂Cl₂): δ 0.2 (s), 0.8 (s), 1.29 (s), 1.72–83 (m), 4.60–4.95 (m), 6.24 (s), 7.43 (bs), 7.58 (s), 7.76 (s). IR: ν_{ND} 2547, 2475 cm⁻¹.

Synthesis of [Cp*Ru(η^6 -D₂PcOEt)]PF₆. A solution of 0.038 g (0.044 mmol) of D₂PcOEt in 5 mL of CH₂Cl₂ was treated with 0.022 g (0.044 mmol) of [Cp*Ru(MeCN)₃]PF₆ in 5 mL of CH₂Cl₂. The reaction mixture was stirred at room temperature for 10 h, and the solvent volume was reduced to ca. 5 mL under vacuum. This solution was slowly diluted with 25 mL of Et₂O to give a suspension of dark green solid in faint green solution. After 0.5 h, the product was collected by filtration, washed twice with 5 mL portions of Et₂O, and dried under vacuum for 6 h. Yield: 33 mg (60%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.2 (s, 0.3H), 0.8 (s, 0.3H), 1.29 (s), 1.72–83 (m),

4.60–4.95 (m), 6.24 (s), 7.43 (bs), 7.58 (s), 7.76 (s). IR: ν_{ND} 2542, 2488 cm^{-1} .

Preparation of [Cp*Ru(η^6 -CuPcOEt)]PF₆ from [Cp*Ru(η^6 -H₂PcOEt)]. A suspension of 120 mg (0.601 mmol) of Cu(OAc)₂·H₂O and 60 mg of [Cp*Ru(η^6 -H₂PcOEt)] in 50 mL of EtOH was heated at reflux under nitrogen for 3 h. Solvent volume was reduced to ca. 10 mL, and 25 mL of Et₂O was added to precipitate green product, which was collected by filtration, washed twice with 5 mL portions of Et₂O, and dried under vacuum for 8 h. Yield: 26 mg (41%).

Reaction of {Cp*Ru(η^6 -Ni(PcOEt))}PF₆ with [Cp*Ru(NCMe)₃]PF₆. A solution of 10.0 mg (0.0200) of [Cp*Ru(NCMe)₃]PF₆ was added dropwise to a solution of 26.0 mg (0.0200 mmol) of {Cp*Ru(η^6 -Ni(PcOEt))}PF₆ in 2 mL of CH₂Cl₂ with stirring to precipitate brown solid product. Solvent volume was reduced to ca. 3 mL under vacuum to precipitate additional product, which was collected by filtration, washed with two 5 mL portions of Et₂O, and dried under vacuum for 30 min. Yield: 25 mg (75%). ¹H NMR (500 MHz, CD₂Cl₂): δ 1.3 (bs), 1.47 (bs), 1.68–1.86 (br mult), 4.55–4.83 (br mult), 6.36–6.50 (mult), 7.60 (br mult). FAB-MS: 1394 {[Cp*Ru]₂(NiPcOEt) – H}⁺; 1159 [Cp*Ru(NiPcOEt)]⁺; 1541 [Cp*Ru]₂(NiPcOEt)(PF₆)⁺; 1631 {[Cp*Ru]₃(NiPcOEt) – 2H}⁺.

{Cp*Ru(η^6 -Ni(PcO-*i*-Pr))}PF₆. A solution of 48 mg (0.096 mmol) of [Cp*Ru(CH₃CN)₃]PF₆ in 20 mL of CH₂Cl₂ was added dropwise to a solution of 0.100 g (0.096 mmol) of Ni(PcO-*i*-Pr) in 20 mL of CH₂Cl₂. The resulting solution was stirred at room temperature for 3 h, and the solvent was removed under vacuum. The resulting green powder was dissolved in a minimum volume (~4 mL) of CH₂Cl₂ and loaded onto a 22 × 2.5 cm silica gel column. Unreacted **3** was removed by eluting with Et₂O. The product, **4**, eluted from the column as a dark green band with THF (further elution with THF produced a dark brown band). The product was obtained by removing the THF solvent under vacuum and reprecipitated from a minimum volume of CH₂Cl₂ by addition of THF. Yield: 0.052 g

(38%). ¹H NMR (500 MHz, CD₂Cl₂): δ 7.50 (br, m, 6H), 6.43 (s, 2H), 5.04–4.83 (br, m, 8H), 1.73 (d, 6H), 1.667 (d, 6H), 1.658 (d, 6H), 1.623 (d, 6H), 1.616 (d, 6H), 1.592 (d, 6H), 1.545 (d, 6H), 1.493 (d, 6H), 1.486 (s, 15H). FAB-MS: 1271.4 (M⁺). UV-vis (CH₂Cl₂), λ [nm] (ϵ [M⁻¹ cm⁻¹]): 314 (65000), 338 (55000), 460 (19000), 686 (47000), 764 (147000).

X-ray Crystallography. Tiny crystals (0.2 × 0.15 × 0.1 mm) of {Cp*Ru(η^6 -Ni(PcOBu))}PF₆ were grown from CH₂Cl₂ by layering with THF. Single-crystal structural analysis was performed at 190 K using a Stoe-IPDS diffractometer (Mo K α radiation) equipped with an imaging plate detector and a rotating anode (Siemens). Structure solution and refinement were carried out using SHELXS 86³⁴ and SHELXTL 97³⁵ software and direct methods techniques. The structure was refined on F^2 . All Ni, Ru, P, C, and N atoms were refined anisotropically except the C atoms of the octabutoxy groups, which were refined isotropically. All other non-hydrogen atoms were refined isotropically. Positions for all H atoms were calculated to yield $R = 0.0832$ and $R_w = 0.2072$. Further details of the structure refinement are given in Table 1.

Acknowledgment. This research was supported by United States Department of Energy under DEFG02-90ER14146 and DEFG02-96ER45439. S.M.C. would like to thank the National Science Foundation for a graduate fellowship. We thank Kevin Klausmeyer for assistance in the early stages of this work.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and structure factors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000467I

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