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π-Complexes of Phthalocyanines and Metallophthalocyanines

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Addition of $[Cp^*Ru(MeCN)_3]PF_6$ to M(PcOEt) (PcOEt = octakis(ethoxy)phthalocyanine; M = H_2, Ni (**1**), Cu, VO) in dichloromethane results in the formation of $\{Cp^*Ru[\eta^6\text{-}M(PcOEt)]\}PF_6$. The molecular structure of **1** reveals η^6-coordination of Cp^*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 $[Cp^*Ru(\eta^6\text{-}H_2PcOEt)]PF_6$, 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 M^{-1} 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 Cp^*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-

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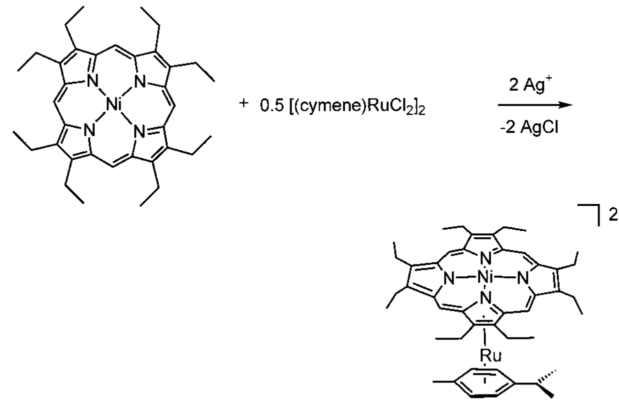
Scheme 1. Synthesis of π-Complexes of Metalloporphyrins



plexes, e.g., {(arene)Ru[η^5-H$_n$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 H$_2$PcOEt, is a modification of that of Cook et al.,[18] but the procedure has been simplified. This preparation begins with the synthesis of dialkoxyphthalonitriles, C$_6$H$_2$-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 transetherification 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 cystalline form. A further advantage to the ethoxy- and isopropoxy-substituted phthalocyanines is that the ^{1}H NMR spectra of their derivatives are quite straightforward.

π-Complexation of Cp*Ru$^+$ to Nickel Phthalocyanines. Addition of [Cp*Ru(MeCN)$_3$]PF$_6$ 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. Donor solvents such as acetone, DMF, and DMSO afforded free Ni(PcOEt) and a solvated ruthenium complex, as established by ^{1}H NMR spectroscopy.

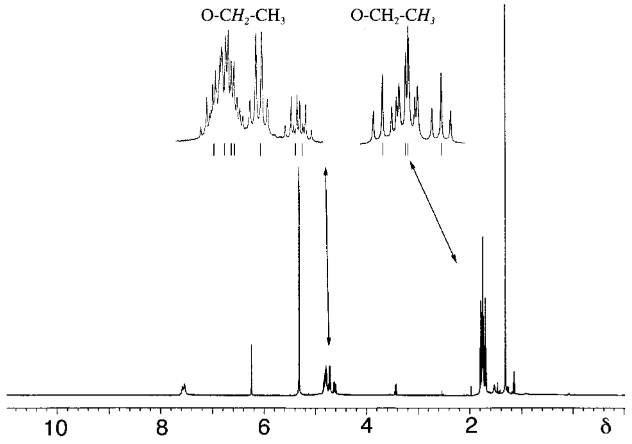
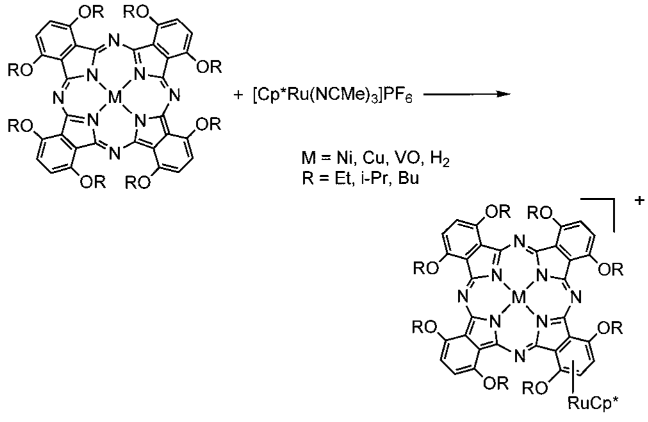


Figure 1. 500 MHz ^{1}H NMR spectrum for a concentrated CD$_2$Cl$_2$ solution of {Cp*Ru[η^6-Ni(PcOEt)]}PF$_6$. The characteristic splitting patterns of the OEt groups are shown in the inset.

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



The ^{1}H NMR spectrum (Figure 1) of {Cp*Ru[η^6-Ni(PcOEt)]}PF$_6$ 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 CH$_2$ groups, resulting in a total of eight diastereotopic methylene proton positions. Finally, the CH_3 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-

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Table 1. Details of the Crystal Structure Solution and Refinement for $\{Cp^*Ru[\eta^6\text{-}Ni(PcOBu)\}_2(PF_6)_2$

chemical formula	$C_{148}H_{190}F_{12}N_{16}Ni_2O_{16}P_2Ru_2$
cryst size (mm)	0.2 × 0.15 × 0.1
space group	$P\bar{1}$
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 Kα, 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] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1297P)^2 + 53.7830P]$; $P = (F_o^2 + 2F_c^2)$; 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 CH_2Cl_2 by layering with THF.

Dembeck et al.[21,22] have shown that metal π-complexation was useful for the solubilization of polyaramide 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 solvents[3] and can be purified only by sublimation at ~500 °C. Unfortunately, refluxing nitromethane suspensions of Ni(Pc) are unreactive toward $[Cp^*Ru(MeCN)_3]PF_6$.

Structure of $\{Cp^*Ru[\eta^6\text{-}Ni(PcOBu)]\}PF_6$. Tiny crystals (0.2 × 0.15 × 0.1 mm) of this salt were grown from CH_2Cl_2 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 $\{Cp^*Ru[\eta^6\text{-}Ni(PcOBu)]\}^+$ units along with two disordered PF_6^- 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 $\{Cp^*Ru[\eta^6\text{-}Ni(PcOBu)]\}_2^{2+}$ 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 radii[24] (3.40 Å) and the interplanar separation of I_3^--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 $[Cp^*Ru(MeCN)_3]PF_6$ to a dichloromethane solution of **1** resulted in the immediate precipitation of brown solid. ^1H NMR analysis of the solid shows two C_5Me_5 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 $\{[Cp^*Ru]_2(NiPcOEt)\}(PF_6)_2$. 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 $\{Cp^*Ru[\eta^6\text{-}M(PcOEt)]\}PF_6$ (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, CH_2CH_3, and $C_5(CH_3)_5$ 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 $g_{||}$ 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 $\nu_{V=O}$ could not be unambiguously assigned in the IR spectrum of VO(PcOEt), on complexation to give $\{Cp^*Ru[\eta^6\text{-}VO(PcOEt)]\}PF_6$, no change in the VO(PcOEt) portion of the IR spectrum could be discerned.

Interaction of Cp^*Ru^+ with H_2PcOEt. The reaction of Cp^*Ru^+ with H_2PcOEt afforded a stable 1:1 adduct. The structure of this species is of special interest because H_2PcOEt lacks the 4-fold symmetry exhibited by its metalated derivatives. It is known that in H_2PcOR, the N*H*'s are equivalent. The ^1H NMR spectrum of $[Cp^*Ru(\eta^6\text{-}H_2PcOEt)]PF_6$ (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 $[Cp^*Ru(\eta^6\text{-}D_2PcOEt)]PF_6$. The IR spectrum of $[Cp^*Ru(\eta^6\text{-}D_2PcOEt)]PF_6$ shows two ν_{N-D} bands at 2547 and

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for {Cp*Ru[η^6-Ni(PcOBu)]}(PF_6)[a]

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.

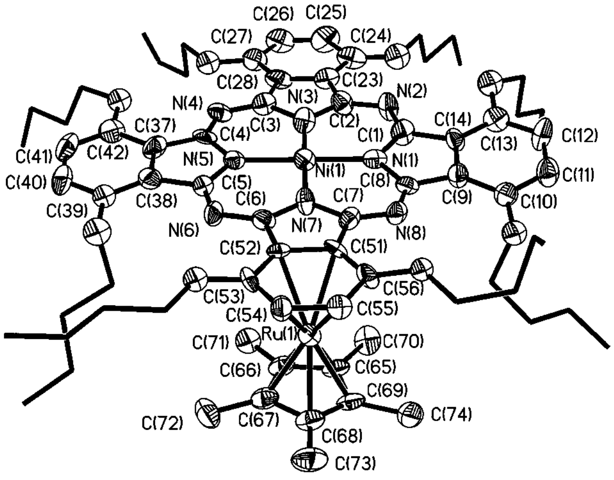


Figure 2. Molecular structure for one of the {Cp*Ru[η^6-Ni(PcOBu)]}$^+$ cations of {Cp*Ru[η^6-Ni(PcOBu)]}PF_6 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% level.

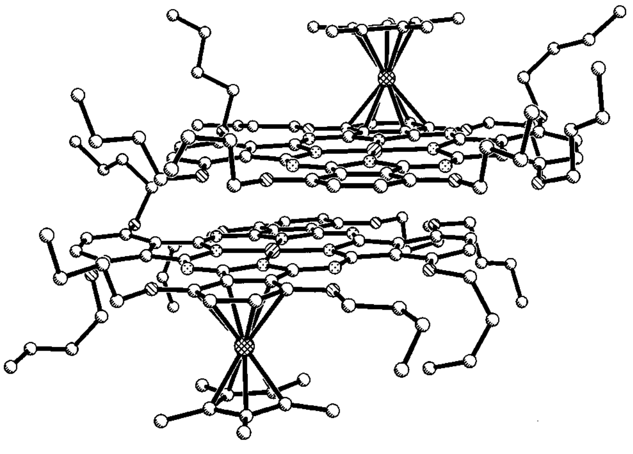


Figure 3. Molecular structure of {Cp*Ru[η^6-Ni(PcOBu)]}-PF_6 showing the two stacked {Cp*Ru[η^6-Ni(PcOBu)]}$^+$ cations in the asymmetric unit.

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

Having confirmed the assignment of the high-field ^{1}H NMR signals for [Cp*Ru(η^6-H_2PcOEt)]PF_6, the next issue is their interpretation. Treatment of solutions of [Cp*Ru(η^6-H_2PcOEt)]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 N*H* proton is on the isoindole subunit bound to Cp*Ru$^+$ and is sterically shielded toward exchange.

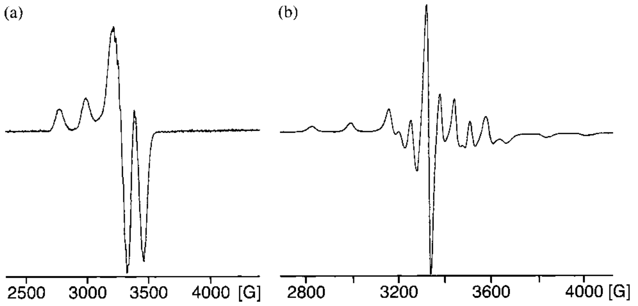
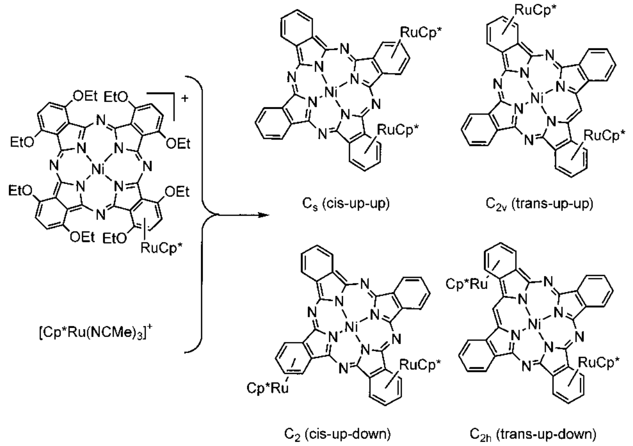


Figure 4. Q-band ESR spectra of frozen CH_2Cl_2 solutions at 77 K for (a) {Cp*Ru[η^6-Cu(PcOEt)]}PF_6 and (b) {Cp*Ru-[η^6-VO(PcOBu)]}PF_6. ESR parameters (a values in MHz) a: $g_{||} = 2.0949$, $g_{\perp} = 2.0661$, $a_{Cu,||} = 274$, $a_{Co,\perp} = 44$, $a_{N,||} = 44$; b: $g_{||} = 2.139$, $g_{\perp} = 2.0048$, $a_{v,||} = 45$, $a_{v,\perp} = 168$.

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



The new kind of metallophthalocyanine [Cp*Ru(η^6-H_2PcOEt)]PF_6 can serve as a ligand for metal ions. To this end, we treated [Cp*Ru(η^6-H_2PcOEt)]PF_6 with excess copper acetate in refluxing ethanol to give a 40% yield of {Cp*Ru[η^6-Cu(PcOEt)]}PF_6. ^{1}H NMR, IR, and FAB-MS spectra confirm that this product is identical

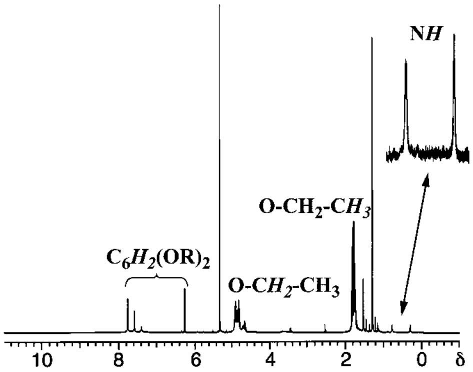


Figure 5. 500 MHz ^{1}H NMR spectrum of a concentrated CD_2Cl_2 solution of {Cp*Ru[η^6-H_2PcOEt)]}PF_6. The two N*H* signals are shown in the inset.

to that prepared by reaction of [Cp*Ru(NCMe)$_3$]PF_6 with Cu(PcOEt).

Electronic Properties of Cp*Ru[η^6-M(PcOEt)]$^+$ (M = Ni, Cu, VO, H_2). The electronic spectral properties for a series of {Cp*Ru[η^6-M(PcOEt)]}PF_6 complexes are summarized in Table 3. A representative spectrum is shown in Figure 6 for the case of M = Ni. The Soret and Q-bands in the UV−vis spectrum of the adducts in CH_2Cl_2 are bathochromically shifted vs free M(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 Ni(PcOEt), VO(PcOEt), Cu(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 [Cp*Ru(H_2PcOEt)]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 [M(PcOEt)] assignable to Pc^{2-}→Pc^{3-} and Pc^{3-}→Pc.$^{4-}$ In contrast, the complexes {Cp*Ru[M(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 Pc$^{2-/3-/4-/5-/6-}$. The results are presented in Table 4, and a representative voltammogram for [Cp*Ru(H_2PcOEt)]PF_6 is given in Figure 7. As can be seen from the data, the $E_{1/2}$ values for the {Cp*Ru[M(PcOEt)]}$_2^{2+/1+}$ and {Cp*Ru[M(PcOEt)]}$_2^{0/1-}$ couples are 110−190 mV more electropositive than those for the corresponding M(PcOEt)$^{0/1-}$ and M(PcOEt)$^{1-/2-}$ couples. The half-wave potentials for the {Cp*Ru-[M(PcOEt)]}$_2^{1+/0}$ and {Cp*Ru[M(PcOEt)]}$_2^{1-/2-}$ couples occur at potentials similar to the M(PcOEt)$^{0/1-}$ and M(PcOEt)$^{1-/2-}$ couples, respectively.

Conclusions

The first π-complexes of phthalocyanines were prepared as air- and moisture-stable solids by the reaction of [Cp*Ru(MeCN)$_3$]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 [Cp*Ru(η^6-H_2PcOEt)]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 [Cp*Ru(MeCN)$_3$]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. Infared spectra were obtained with a Mattson Galaxy Series FT-IR 3000 as KBr pellets. ^{1}H and ^{13}C{^{1}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-Bu)$_4$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

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Table 3. Electronic Spectral Properties of Several {Cp*Ru[η^6-M(PcOEt)}PF$_6$ 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		750	209 000
[Cp*Ru(NiPcOEt)]PF$_6$			NiPcOEt	304	23 600
	324	23 800		326	28 100
	460	7100		452	7300
	678	17 500		664	20 400
	756	61 700		740	92 300

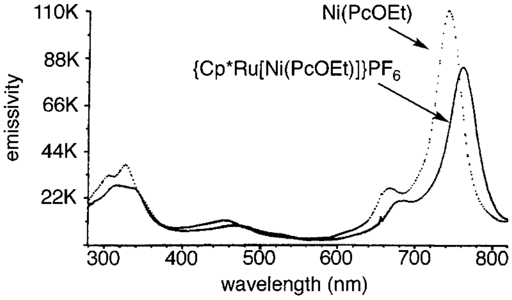

Figure 6. Electronic spectra of {Cp*Ru[η^6-Ni(PcOEt)]}-PF$_6$ and Ni(PcOEt). The emissivity values were calculated from absorption data for 10^{-5} M solutions.

Table 4. Summary of Electrochemical Results for Several {Cp*Ru[η^6-M(PcOEt)}PF$_6$ 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		

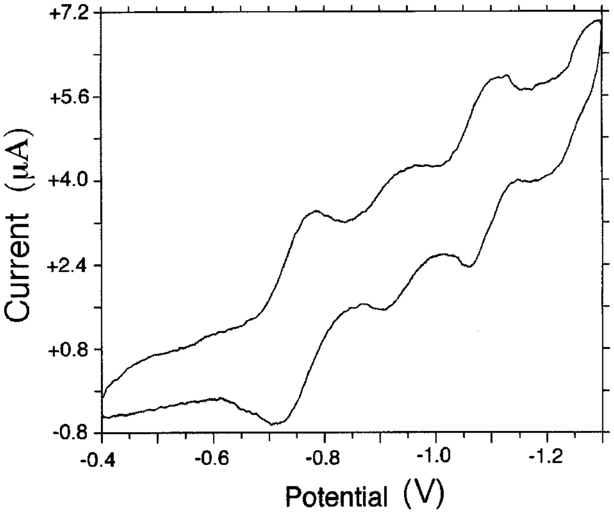

Figure 7. Cyclic voltamogram of a solution of 10^{-3} M {Cp*Ru[η^6-H$_2$PcOEt)]}PF$_6$ in CH$_2$Cl$_2$. The data were obtained using a Pt working electrode and Ag/AgCl reference electrode at a scan rate of 100 mV/s. Potentials are reported vs Ag/AgCl.

filtrate. Yield: 6.51 g (93%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.19 (s, 1H, C$_6$*H*$_2$), 4.14 (q, 2H, OC*H*$_2$CH$_3$), 1.46 (t, 3H, OCH$_2$C*H*$_3$).

1,4,8,11,15,18,22,25-Octaethoxy-29*H*,31*H*-phthalocyanine, H$_2$PcOEt. 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 washed successively with three 25 mL portions of H$_2$O, six 25 mL portions of EtOH, and two 25 mL portions of Et$_2$O. The product was extracted using four 25 mL portions of CHCl$_3$. The CHCl$_3$ 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 CHCl$_3$ using 250 mL of EtOH followed by drying under vacuum for 16 h gave pure product. Yield: 0.325 g (65%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.64 (s, 1H, Ar C−H), 4.89 (q, 2H, OC*H*$_2$-CH$_3$), and 1.80 (t, 3H, OCH$_2$C*H*$_3$), 0.21 (s, 2H, N*H*). IR: ν_{NH} 3293 cm^{-1}. FAB-MS: 868 (M$^+$). UV−vis (CH$_2$Cl$_2$): λ [nm] (ϵ[M^{-1}cm^{-1}]) 330 (33000), 410 (8600), 450 (7400), 676 (19400), 768 (79800).

Ni(PcOEt). A solution of 0.500 g (0.577 mmol) of H$_2$PcOEt and 1.44 g of Ni(OAc)$_2$·4H$_2$O 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 H$_2$O to precipitate dark green microcrystals. The product was collected by filtration, washed with two 10 mL portions each of H$_2$O, EtOH, and Et$_2$O, and then dried under vacuum for 6 h. Yield: 0.417 g (78%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.54 (s, 1H, Ar C−H), 4.83 (q, 2H, $\mathrm{O}CH_2\mathrm{CH_3}$), and 1.75 (t, 3H, $\mathrm{OCH_2}CH_3$). FAB-MS: 923 (M^+). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 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. $Cu(OAc)_2 \cdot H_2O$ was used as the Cu^{2+} source to give Cu(PcOEt) in 61% yield. An equimolar mixture of $VOSO_4 \cdot 3H_2O$ and $NaHCO_3$ was used as the VO^{2+} source to give VO(PcOEt) in 35% yield.

Cu(PcOEt): ^1H NMR (500 MHz, CD_2Cl_2): δ 1.57 (bs, 24H), 4.51 (bs, 16 H). FAB-MS: 928 (M^+). UV−vis λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 328 (37200), 452 (7900), 670 (24100), 750 (145000). ESR (298 K, 9.46 GHz): $g_{||} = 2.0949$, $g_{\perp} = 2.0661$, $a_{||} = 274$ MHz, $a_{\perp} = 44$ MHz.

VO(PcOEt): ^1H NMR (500 MHz, CD_2Cl_2): δ 1.851 (bs, 24H), 5.02 (bs, 16H), 8.5 (bs, 10H). FAB-MS: 932 (M^+). UV−vis (CH_2Cl_2) λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 338 (32900), 478 (6500), 702 (20000), 788 (86600). ESR (298 K, 9.46 GHz): $g_{\mathrm{peff}} = 1.990$, $a_{\mathrm{eff}} = 243$ MHz; (102 K, 9.46 GHz): $g_{||} = 2.139$, $g_{\perp} = 2.0048$, $a_{||} = 45$ 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 K_2CO_3, 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 H_2O. Yield: 9.32 g (78%). ^1H NMR (400 MHz, CD_2Cl_2): 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-29*H*,31*H*-phthalocyanine, H_2Pc-*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 (H_2). 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 CH_2Cl_2. The CH_2Cl_2 extract, in 200 mL portions, was shaken with 100 mL of H_2O containing a few drops of acetic acid. After vigorous shaking, 1 M aqueous NaOH was added dropwise until the pH was neutral. The CH_2Cl_2 layer was then isolated, and the solvent was removed under vacuum. Yield: 3.58 g (36%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 8H), 4.96 (septet, 8H), 1.580 (d, 48H). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 328 (58000), 402 (30000), 772 (142000).

Ni(PcO-*i*-Pr). A 250 mL flask was charged with 1.00 g (1.02 mmol) of H_2Pc-*i*-OPr, 2.54 g (10.2 mmol) of $Ni(OAc)_2 \cdot 4H_2O$, and 150 mL of DMF. The reaction mixture was heated to reflux for 2 h. The cooled solution was treated with 100 mL of H_2O to precipitate the product, which was collected by filtration, washed with 50 mL of H_2O, and dried in air for 2 h. The product was reprecipitated from a minimum volume of CH_2Cl_2 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, CD_2Cl_2): δ 7.46 (s, 8H), 4.89 (septet, 8H), 1.56, 1.55 (d, 48H). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 304 (54000), 436 (17000), 670 (39000), 740 (94000).

{Cp*Ru[η^6-M(PcOEt)]}PF_6. A solution of 0.108 mmol of M(PcOEt) in 10 mL of CH_2Cl_2 was added dropwise to a suspension of 55 mg (0.108 mmol) of $[(C_5Me_5)Ru(MeCN)_3]PF_6$ in 15 mL of CH_2Cl_2. 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 Et_2O 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 Et_2O, and dried under vacuum for 1 h.

{Cp*Ru[η^6-Ni(PcOEt)]}PF_6. Yield: 90%. ^1H NMR (500 MHz, CD_2Cl_2): 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 ($M^+ - PF_6$), 923.2 ($NiOEtPc^+$). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 324 (23800), 460 (7100), 678 (17500), 756 (61700). Anal. Calcd for $C_{58}H_{63}F_6N_8NiO_8PRu$ (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)]}PF_6. Yield: 75%. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.33 (bs), 1.60 (bs), 4.50 (bs), 8.7 (bs). FAB-MS: 1164.4 ($M^+ - PF_6$), 1075.3 ($M^+ - PF_6 - C_2H4$). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 332 (57100), 464 (13600), 680 (37800), 686 (42100), 768 (158000). Anal. Calcd for $C_{58}H_{63}CuF_6N_8O_8PRu$ (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)]}PF_6. Yield: 94%. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.52 (bs), 1.82 (bs), 4.96 (bs), 8.4 (bs). FAB-MS: 1168.3 ($M^+ - PF_6$), 1140.3 ($M^+ - PF_6 - C_2H_4$). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 340 (42500), 492 (11700), 714 (23200), 806 (87000). Anal. Calcd for $C_{58}H_{63}F_6N_8O_9PRuV$ (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-H_2PcOEt)]PF_6. Yield: 89%. ^{1}NMR (500 MHz, CD_2Cl_2): 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 ($M^+ - PF_6$). UV−vis (CH_2Cl_2), λ [nm] ($\epsilon[M^{-1}\ cm^{-1}]$): 332 (36200), 466 (9900), 700 (30300), 780 (11300). Anal. Calcd for $C_{58}H_{65}F_6N_8O_8PRu$ (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 H_2PcOEt. H−D Exchange in [Cp*Ru(η^6-H_2PcOEt)]PF_6. A solution of 2 mg of [Cp*Ru(η^6-H_2PcOEt)]PF_6 in 1 mL of CD_2Cl_2 was treated with 0.2 mL of 99.9% D_2O, and this solution was shaken vigorously for 1 min. ^1H NMR (500 MHz, CD_2Cl_2): 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 H_2PcOEt. A solution of 100 mg of H_2PcOEt in 15 mL of CH_2Cl_2 was treated with 10 mL of 99.9% D_2O. The resulting emulsion was stirred vigorously for 30 min, and then the methylene chloride layer was dried over $MgSO_4$, filtered, and evaporated under vacuum. The resulting solid was dried under vacuum for 10 h. ^1H NMR (500 MHz, CD_2Cl_2): 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-D_2PcOEt)]PF_6. A solution of 0.038 g (0.044 mmol) of D_2PcOEt in 5 mL of CH_2Cl_2 was treated with 0.022 g (0.044 mmol) of $[Cp^*Ru(MeCN)_3]PF_6$ in 5 mL of CH_2Cl_2. 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 Et_2O 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 Et_2O, and dried under vacuum for 6 h. Yield: 33 mg (60%). ^1H NMR (500 MHz, CD_2Cl_2): 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}.

Prepartation of [Cp*Ru(η^6-CuPcOEt)]PF_6 from [Cp*Ru(η^6-H_2PcOEt). A suspension of 120 mg (0.601 mmol) of Cu$(OAc)_2\cdot H_2O$ and 60 mg of [Cp*Ru(η^6-H_2PcOEt) 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 Et_2O was added to precipitate green product, which was collected by filtration, washed twice with 5 mL portions of Et_2O, and dried under vacuum for 8 h. Yield: 26 mg (41%).

Reaction of {Cp*Ru[η^6-Ni(PcOEt)]}PF_6 with [Cp*Ru$(NCMe)_3$]PF_6. A solution of 10.0 mg (0.0200) of [Cp*Ru$(NCMe)_3$]PF_6 was added dropwise to a solution of 26.0 mg (0.0200 mmol) of {Cp*Ru[η^6-Ni(PcOEt)]}PF_6 in 2 mL of CH_2Cl_2 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 Et_2O, and dried under vacuum for 30 min. Yield: 25 mg (75%). ^{1}H NMR (500 MHz, CD_2Cl_2): 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)}$(PF_6)^+$; 1631 {$[Cp^*Ru]_3$(NiPcOEt) − 2H}$^+$.

{Cp*Ru[η^6-Ni(PcO-*i*-Pr)]}PF_6. A solution of 48 mg (0.096 mmol) of [Cp*Ru$(CH_3CN)_3$]PF_6 in 20 mL of CH_2Cl_2 was added dropwise to a solution of 0.100 g (0.096 mmol) of Ni(PcO-*i*-Pr) in 20 mL of CH_2Cl_2. The resulting solution was stirred at room temperature for 3 h, and the solvent was removed under vacuum. The resulting green powder was dissoled in a minimum volume (∼4 mL) of CH_2Cl_2 and loaded onto a 22 × 2.5 cm silica gel column. Unreacted **3** was removed by eluting with Et_2O. 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 CH_2Cl_2 by addition of THF. Yield: 0.052 g (38%). ^{1}H NMR (500 MHz, CD_2Cl_2): 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 (CH_2Cl_2), 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)}PF_6 were grown from CH_2Cl_2 by layering with THF. Single-crystal structural analysis was performed at 190 K using a Stoe-IPDS diffractometer (Mo Kα radiation) equipped with an imaging plate detector and a rotating anode (Siemens). Structure solution and refinement were carried out using SHELXS 86[34] and SHELXTL 97[35] 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.

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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.

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