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Characterization of $(\eta\text{-}C_5Me_5)Cr(NO)(O\text{-}i\text{-}Pr)_2$: Coordination Saturation from Alkoxide π-Donation

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Treatment of $Cp^*Cr(NO)_2CH_2Cl$ or $Cp^*Cr(NO)_2Cl$ with excess Na(O-*i*-Pr) in 2-propanol gives a volatile, deep blue-green complex that analyzes correctly for the empirical formula $[Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2]$ in 86–94% yield ($Cp^* = \eta^5\text{-}C_5Me_5$). Spectroscopic evidence indicates the new material to be a mononuclear, diamagnetic Cr(II) complex that contains a terminal NO ligand. A single-crystal X-ray structural analysis shows the molecule to adopt a nearly C_s piano-stool structure with the nitrosyl ligand being bound in a terminal (NO^+) mode: monoclinic space group $P2_1/n$, $a = 9.535$ (3) Å, $b = 9.789$ (4) Å, $c = 20.108$ (9) Å, $\beta = 91.89$ (5)°, $Z = 4$, Mo Kα radiation, $T = 294$ K, $R/R_w = 5.71\%/6.49\%$ for 2267 independent reflections ($F > 4\sigma F$) and 190 parameters. The isopropoxide ligands are oriented so as to make use of a pπ-orbital perpendicular to the Cr–O–C plane for donation into an empty Cr d orbital that is nonbonding to the nitrosyl ligand. The Cr–O bond lengths observed average 1.815 (4) Å and are consistent with significant Cr–O π-bonding. Although formally a 16-electron complex, $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ is unreactive in solution with excess alkoxide, CO, or PPh_3, indicating isopropoxide π-donation to essentially render the complex coordinatively saturated.

Introduction

The pace of transition-metal alkoxide investigation has increased significantly over the past several years and is largely due to the importance of metal alkoxides as models for metal oxide-based catalysis.[2] The recent growth in the number of organometallic alkoxide complexes containing the Cp or Cp* ligand has helped bridge the gap between inorganic "alkoxides" and organometallic systems ($Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$).[3] Complexes containing alkoxide or related thiolate ligands together with strong π-accepting ligands have been targeted with regard to characterizing the competitive donor/acceptor interactions around the metal atom.[4] Particular emphasis has been placed on characterizing the π-donor ability of alkoxide and thiolate ligands.

Our present report deals with the unexpected formation of the bis(isopropoxide) complex $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ when we attempted to prepare the still unknown isopropoxymethyl complex $Cp^*Cr(NO)_2CH_2O\text{-}i\text{-}Pr$ from the chloromethyl precursor $Cp^*Cr(NO)_2CH_2Cl$.[5] Our structural characterization of the new $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ complex adds to the relatively small number of structurally characterized mononuclear chromium(II) alkoxide complexes.[6] We compare its chemistry to the dinuclear complexes $[M_2(O\text{-}i\text{-}Pr)_6(NO)_2]$ (M = Cr, Mo, W),[7] which possess fluxional terminal/bridging O-*i*-Pr ligands and are related to our new bis(isopropoxide) complex by the formal replacement of an isopropoxide ligand by the $\eta^5\text{-}C_5Me_5$ ligand. The structural and reactivity data presented here indicates that isopropoxide π-donation to the metal helps to render the $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ complex coordinatively saturated.

Results and Discussion

Synthesis and Characterization of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. Upon heating of a 2-propanol solution of $Cp^*Cr(NO)_2CH_2Cl$ and excess Na(O-*i*-Pr) to reflux, the initial green solution rapidly changes to a deep blue-green color (eq 1). After 1 h an IR absorption

$$Cp^*Cr(NO)_2CH_2CH_2Cl + NaO\text{-}i\text{-}Pr \xrightarrow[\Delta]{HO\text{-}i\text{-}Pr} \underset{86\%}{Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2} \quad (1)$$

at 1670 cm^{-1} completely replaces the initial ν_{NO} bands of $Cp^*Cr(NO)_2CH_2Cl$. Removal of the solvent and extraction of the residue with hexane produces a dark blue solution that can be eluted through Al_2O_3 (III) with 5:1 hexane/ether in order to remove traces of residual isopropoxide. Concentration and crystallization from pentane gives black-blue crystals which analyze correctly for a complex with the empirical formula $[Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2]$. A somewhat more direct and slightly higher yield route to the same material follows from the treatment of $Cp^*Cr(NO)_2Cl$ with excess Na(O-*i*-Pr) in 2-propanol (eq 2).

$$Cp^*Cr(NO)_2Cl + NaO\text{-}i\text{-}Pr \xrightarrow[\Delta]{HO\text{-}i\text{-}Pr} \underset{94\%}{Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2} \quad (2)$$

In contrast to our earlier successes in converting chromium–halomethyl complexes to their Cr–CH_2–OR derivatives,[5b] we have not been able to produce any detectable quantities of a $Cp^*Cr(NO)_2CH_2O\text{-}i\text{-}Pr$ derivative, even when running the reactions shown in eqs 1 and 2 with substoichiometric amounts of isopropoxide. For the reaction with $Cp^*Cr(NO)_2Cl$, simple metathetical reactivity commonly seen for $CpM(NO)_2X$ complexes does not give any detectable amounts of $Cp^*Cr(NO)_2O\text{-}i\text{-}Pr$.[8] In analogy to the instability observed for the $CpCr(NO)_2OEt$[9] complex, it is possible that the $Cp^*Cr(NO)_2O\text{-}i\text{-}Pr$ complex is unstable, leading to the formation of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ by some oxidation process. The related $CpMo(NO)_2SPh$ complex is also known to be unstable to the formation of $CpMo(NO)(SPh)_2$.[4d]

$Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ is a low-melting, nonpolar material that is freely soluble in common organic solvents. Vacuum sublimation of the solid onto a water-cooled finger at 35 °C gives pure $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ as dark lustrous crystals that are stable for days in the air. However, solutions of the complex are somewhat air-sensitive, leading to the formation of an intractable gray precipitate after a few minutes of air exposure.

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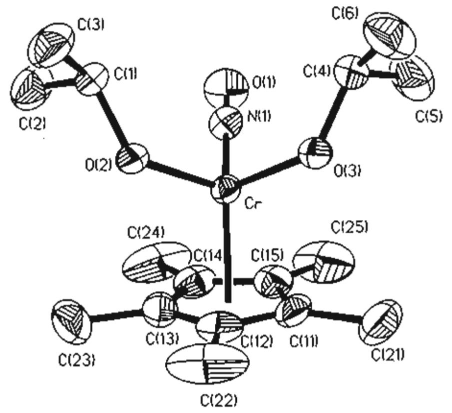

Figure 1. X-ray structure of Cp*Cr(NO)(O-*i*-Pr)$_2$.

Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3)

	x	*y*	*z*	U_{eq}[a]
Cr	1407 (1)	2694 (1)	3760 (1)	44 (1)
N(1)	2131 (4)	2330 (4)	3037 (2)	56 (1)
O(1)	2642 (5)	1870 (4)	2551 (2)	90 (2)
C(11)	1778 (6)	1662 (6)	4772 (3)	70 (2)
C(12)	373 (7)	2050 (5)	4733 (3)	71 (2)
C(13)	−279 (6)	1338 (6)	4216 (3)	77 (2)
C(14)	711 (7)	566 (5)	3903 (3)	76 (2)
C(15)	2001 (6)	761 (6)	4245 (3)	72 (2)
C(21)	2869 (8)	2130 (7)	5268 (4)	141 (4)
C(22)	−320 (9)	3035 (7)	5191 (3)	147 (4)
C(23)	−1808 (6)	1467 (8)	4043 (4)	148 (4)
C(24)	437 (10)	−398 (6)	3335 (3)	169 (5)
C(25)	3329 (8)	35 (7)	4096 (4)	160 (4)
O(2)	−100 (3)	3686 (3)	3471 (1)	52 (1)
C(1)	−258 (5)	4302 (5)	2833 (2)	55 (2)
C(2)	−1067 (7)	3382 (6)	2367 (3)	95 (3)
C(3)	−957 (6)	5663 (5)	2919 (3)	87 (2)
O(3)	2687 (3)	3897 (3)	4100 (1)	54 (1)
C(4)	3702 (5)	4590 (5)	3732 (2)	62 (2)
C(5)	5042 (6)	3801 (8)	3732 (3)	112 (3)
C(6)	3885 (7)	5992 (6)	4017 (3)	98 (3)

[a] Equivalent isotropic *U* defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

The NMR characteristics of Cp*Cr(NO)(O-*i*-Pr)$_2$ are consistent with the material being a diamagnetic Cr(II) complex. In the ^{1}H NMR spectrum, a sharp resonance at δ 1.78 ppm is assignable to the η^5-C_5Me_5 ligand. An equal intensity pair of doublets between δ 1.2 and 1.3 ppm can be assigned to the diastereotopic isopropoxide ligand methyl groups and are coupled to the isopropoxide C–H proton at δ 5.28 ppm. The ^{13}C NMR spectrum shows signals at δ 118.0 and 9.8 ppm, consistent with the Cp* ring skeletal and CH_3 carbons, respectively. The diastereotopic methyl groups of the isopropoxide ligands appear at δ 27.9 and 26.5 ppm, and the ipso isopropyl carbon resonance appears at δ 82.8 ppm.

The presence of a strong absorption at 1670 cm^{-1} in the IR spectrum is consistent with the presence of a single terminal nitrosyl ligand in the complex. The ν_{NO} band for Cp*Cr(NO)(O-*i*-Pr)$_2$ is 50 cm^{-1} lower than that observed for [$Cr_2(NO)_2$(O-*i*-Pr)$_6$].[7b] The mononuclear nature of the complex is supported by the presence of a low intensity parent ion at *m*/*e* 335 as the largest fragment in the CI mass spectrum. Other major fragments arise from loss of NO (*m*/*e* 305) and combined loss of NO and O-*i*-Pr (*m*/*e* 246).

Table II. Selected Bond Lengths (Å) for Cp*Cr(NO)(O-*i*-Pr)$_2$

Cr–N(1)	1.668 (4)	C(12)–C(22)	1.500 (9)
Cr–C(11)	2.290 (5)	C(13)–C(14)	1.377 (9)
Cr–C(12)	2.308 (6)	C(13)–C(23)	1.493 (8)
Cr–C(13)	2.299 (6)	C(14)–C(15)	1.402 (9)
Cr–C(14)	2.208 (5)	C(14)–C(24)	1.497 (8)
Cr–C(15)	2.195 (6)	C(15)–C(25)	1.492 (9)
Cr–O(2)	1.815 (3)	O(2)–C(1)	1.422 (5)
Cr–O(3)	1.814 (3)	C(1)–C(2)	1.494 (7)
N(1)–O(1)	1.194 (6)	C(1)–C(3)	1.502 (7)
C(11)–C(12)	1.392 (9)	O(3)–C(4)	1.412 (6)
C(11)–C(15)	1.400 (8)	C(4)–C(5)	1.493 (8)
C(11)–C(21)	1.488 (9)	C(4)–C(6)	1.494 (8)
C(12)–C(13)	1.381 (8)	Cp*$_{ct}$–Cr[a]	1.927

[a] Ct = centroid.

Table III. Selected Bond and Torsion Angles and Least-Squares Planes (deg)

Bond Angles			
Cr–N(1)–O(1)	170.1 (4)	O(3)–C(4)–C(6)	108.3 (4)
Cr–O(2)–C(1)	125.1 (3)	C(5)–C(4)–C(6)	112.7 (5)
Cr–O(3)–C(4)	125.4 (3)	C(12)–C(11)–C(15)	107.4 (5)
N(1)–Cr–O(2)	100.4 (2)	C(11)–C(12)–C(13)	108.3 (5)
N(1)–Cr–O(3)	100.0 (2)	C(12)–C(13)–C(14)	108.8 (5)
O(2)–Cr–O(3)	106.8 (1)	C(13)–C(14)–C(15)	107.7 (5)
O(2)–C(1)–C(2)	110.3 (4)	C(11)–C(15)–C(14)	107.7 (5)
O(2)–C(1)–C(3)	107.9 (4)	Cp*$_{ct}$–Cr–N(1)	121.4
C(2)–C(1)–C(3)	112.6 (4)	Cp*$_{ct}$–Cr–O(2)	112.7
O(3)–C(4)–C(5)	110.6 (4)	Cp*$_{ct}$–Cr–O(3)	113.6

Torsion Angles			
Cp*$_{ct}$–Cr–N(1)–O(1)	0.2	N(1)–Cr–O(2)–C(1)	−17.2
Cp*$_{ct}$–Cr–O(2)–C(1)	−147.9	N(1)–Cr–O(3)–C(4)	17.0
Cp*$_{ct}$–Cr–O(3)–C(4)	148.3		

Least-Squares Planes

plane 1: Cp*[C(11)→C(15)]
plane 2: Cp*$_{ct}$–Cr–N(1)–O(1)

∠plane 1/plane 2 = 91.1°

X-ray Structure of Cp*Cr(NO)(O-*i*-Pr)$_2$. The molecular structure of Cp*Cr(NO)(O-*i*-Pr)$_2$ as determined by single-crystal X-ray diffraction methods is shown in Figure 1. Table I lists the atomic coordinates and equivalent isotropic displacement parameters. Tables II and III list selected bond distances and bond angles, respectively. With no crystallographically imposed symmetry, the three-legged stool complex adopts nearly C_s molecular symmetry. A least-squares plane containing the Cp*$_{ct}$–Cr–N(1)–O(1) positions (ct = centroid) nearly divides the molecule into two equal halves and lies at nearly right angles to the plane described by the skeletal Cp* carbon atoms. The ∠Cr–N–O of 170.1 (4)° constitutes an essentially linear nitrosyl (NO$^+$) coordination mode.

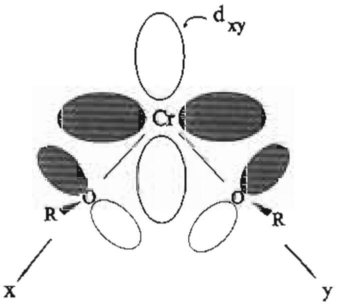

Figure 2. Alkoxide π-interactions with the empty Cr d$_{xy}$ orbital as viewed down the *z* axis containing the nitrosyl ligand.

The most important structural feature regards the orientation of the isopropoxide ligands to the {CrNO}^{4} center in pseudooctahedral coordination.[10] The important issue here is whether the Cp*Cr(NO)(O-*i*-Pr)$_2$ complex should be considered as a 16-electron system, with the O-*i*-Pr ligands functioning as only as 2-electron donors or whether it should be considered coordinatively saturated by the addition of pπ-donation from the isopropoxide O atoms. For the case of the closely related CpMo(NO)(SR)$_2$ complex, thiolate π-donation is argued as the cause of shortened Mo–S bonds and an overall stabilization of the complex as a monomer.[4d] Using an orthogonal pseudooctahedral geometry coordinate reference framework consistent with previous discussions (Figure 2), alkoxide π-donation to the empty metal d$_{xy}$ level

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would be maximized when the torsion angles N(1)–Cr–O(2)–C(1) and N(1)–Cr–O(3)–C(4) are 0 or 180°. These torsion angles are found to be 17.2 and 17.0°, respectively, thus suggesting the isopropoxide ligands to have significant π-interactions with the Cr(II) d_{xy} orbital. The variation of the torsion angles from 0° is likely the result of nonrigorous orthogonal geometry observed between the three *fac*-coordination sites occupied by the alkoxide and nitrosyl ligands. Solid-state packing forces may also contribute to the nonzero torsion angles. For the case of $CpMo(NO)(SPh)_2$, the N–Mo–S–C torsion angles are 12 and 186°.[4d] Interestingly, the geometry of the $Mo(NO)(O\text{-}i\text{-}Pr)_2$ moiety in $[Mo_2(NO)_2(O\text{-}i\text{-}Pr)_6]$ is quite similar to what we observe for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. From the X-ray data reported by Chisholm et al.,[7a] we calculate the N–Mo–O–C torsion angles for the terminal (O-*i*-Pr) ligands in $[Mo_2(NO)_2(O\text{-}i\text{-}Pr)_3]_2$ to be 4.0 and 5.2°.

Another indication of Cr–O π-bonding for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ comes from the comparison of its Cr–O bond lengths to other crystallographically characterized Cr complexes possessing terminal alkoxide ligands. Next to the 1.771 (3) and 1.774 (3) Å Cr–O distances reported for $[Cr(OCH\text{-}t\text{-}Bu_2)_4]$,[11] the average Cr–O bond length of 1.815 (4) Å in $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ is among the shortest Cr–O alkoxide distances of which we are aware.[12] Similarly short are the 1.83 (1) Å Cr–O distances reported for the terminal alkoxide ligands in the Cr(II) complex $[Cr(\mu\text{-}OCH\text{-}t\text{-}Bu_2)(OC\text{-}t\text{-}Bu)]_2$[13] and the 1.823 (4) and 1.828 (4) Å Cr–O distances reported for the Cr(III) complex $Li[Cr(O\text{-}t\text{-}Bu_2)_4]THF$.[11] For these latter cases, significant Cr–O π-bonding is invoked to explain the short Cr–O bonds.

The Cr–O–C bond angles for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ average 125.3° and are quite similar to the Mo–O–C angles observed for the terminal isopropoxide ligands in $[Mo_2(NO)_2(O\text{-}i\text{-}Pr)_6]$.[7a] Recent work has pointed out that M–O–C or M–S–C angles for alkoxide and thiolate complexes are largely dictated by steric effects and not necessarily an indication of metal–oxygen π-bonding.[6,14]

Inert Nature of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. In comparison to the previously characterized group VI $[M_2(NO)_2(O\text{-}i\text{-}Pr)_6]$ complexes,[7] where bridging and terminal O-*i*-Pr ligands are fluxional, $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ does not dimerize in solution. Furthermore, unlike the reactivity of dinuclear $[CpM(NO)(halide)_2]_2$ complexes[15] and 16-electron $CpM(NO)(alkyl)_2$ complexes[16] with a variety of ligands to give $CpM(NO)X_2L$ adducts, $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ is unreactive with added alkoxide, CO, iodide, and PPh_3. A similar lack of reactivity is observed for $CpMo(NO)(SPh)_2$.[4d] Thus, it is perhaps an oversimplification to call $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ a pure 16-electron complex, since the structural evidence suggests that the alkoxide ligands are able to serve as π- and σ-donors. The monomeric nature of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ may also be partially due to the combined steric demands of the isopropoxide and the Cp* ligands. Previous investigations have shown that sterically less demanding alkoxides tend to favor the formation of dinuclear complexes, whereas bulky alkoxides favor mononuclear structures.[7b] Accordingly, where the $CpCr(NO)_2Cl$ reacts to give the paramagnetic complex $[CpCr(NO)(\mu\text{-}OMe)]_2$ (eq 3),[17] we have not detected the formation of $[Cp^*Cr(NO)(\mu\text{-}O\text{-}i\text{-}Pr)]_2$.

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl + NaOMe \xrightarrow{MeOH} [(\eta^5\text{-}C_5H_5)Cr(NO)(\mu\text{-}OMe)]_2 \quad (3)$$

In closing, we note that the only significant reactivity we could find for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ arises when the compound is heated to 100 °C above its melting point. Under these conditions we observe the formation 2-propanol, acetone, and uncharacterized metal decomposition products. The formation of acetone may indicate an irreversible β-H elimination of the isopropoxide ligand, leading to unstable Cr–H byproducts.[18] We are currently looking closer at this form of reactivity in $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ and related isopropoxide complexes.

Experimental Section

General Information. Standard Schlenk techniques employing an N_2 atmosphere were used throughout the synthesis and purification measures. The Al_2O_3 (III) chromatography support was prepared from neutral alumina (Aldrich) by the addition of 6% H_2O followed by evacuation (10^{-5} Torr) for 2 h at room temperature to remove residual air. Reagent grade 2-propanol (J. T. Baker) was saturated with N_2 before use. The ether, hexane, and pentane solvents were saturated with N_2 and distilled from Na/K alloy, and CH_2Cl_2 was distilled from CaH_2. [PPN]I was prepared from the metathesis of [PPN]Cl and NaI.[19] The starting $Cp^*Cr(NO)_2Cl$ and $Cp^*Cr(NO)_2CH_2Cl$ complexes were prepared by published methods.[5] The ^1H and ^{13}C NMR spectra were recorded on a Bruker WP-270 spectrometer at 270 and 67.9 MHz, respectively. NMR spectra are referenced to the residual proton solvent peaks in $CDCl_3$: δ 7.24 ppm (^1H); δ 77.0 ppm (^{13}C). Mass spectra were obtained with a Finnigan 4610 mass spectrometer using chemical ionization (CH_4). The melting point was determined in an open capillary and is uncorrected. Combustion analysis was performed by Robertson Laboratories, Madison, NJ.

Synthesis of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. Method A. Freshly cut Na metal (0.10 g, 4.3 mmol) was added to a Schlenk flask containing 10 mL of N_2-saturated 2-propanol and a stir bar. After the metal was completely consumed, $Cp^*Cr(NO)_2CH_2Cl$ (0.10 g, 0.34 mmol) was added and the vessel was equipped with a reflux condenser. Upon heating of the reaction mixture to a gentle reflux (oil bath), the solution changed from an initial green color to deep blue-green. After the solution was stirred for 1 h at reflux, the solvent was removed in vacuo and the dry residue was extracted three times with 25-mL portions of hexane. The combined extracts were concentrated to 10 mL and transferred to the top of a 2 × 3 cm column of Al_2O_3 (III). Elution of the column with a 5:1 hexane/ether mixture produced a dark blue-green zone that was collected and taken to dryness. Recrystallization of the residue in pentane at −80 °C produced $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ as dark blue-black crystals (0.10 g, 0.29 mmol, 86% yield).

Method B. $Cp^*Cr(NO)_2Cl$ (1.0 g, 3.5 mmol) was dissolved in 80 mL of ca. 0.20 M Na(O-*i*-Pr) in 2-propanol and heated gently at reflux for 1 h. Workup of the deep blue green solution as described in method A gave 1.1 g (3.3 mmol, 94% yield) of **2**. ^1H NMR ($CDCl_3$): δ 5.28 (septet, 2 H, $OC\mathit{H}Me_2$), $^3J_{HH}$ = 6.0 Hz; δ 1.78 (s, 15 H, $C_5\mathit{Me}_5$); δ 1.28 (d, 6 H, ($OCH\mathit{Me}_aMe_b$), $^3J_{HH}$ = 6.0 Hz; δ 1.22 (d, 6 H, ($OCHMe_a\mathit{Me}_b$), $^3J_{HH}$ = 6.0 Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 118.0 (C_5Me_5); δ 82.5 ($O\mathit{C}HMe_2$); δ 27.9 ($OCH\mathit{Me}_aMe_b$); δ 26.5 ($OCHMe_a\mathit{Me}_b$); δ 9.8 ($C5\mathit{Me}_5$). IR (KBr): ν_{NO} 1670 cm^{-1} (vs). Mass spectrum (*m/e* [assignment] (relative intensity): 335 [M^+] (3%), 305 [M − NO] (80%), 276 [M − $OCHMe_2$] (87%), 246 [M − NO − $OCHMe_2$] (100%), 217 [M − 2($OCHMe_2$) (16%). Mp: 41–42 °C. Anal. Calcd for $C_{16}H_{29}NO_3Cr$ (M_r = 335.4): C, 57.30; H, 8.72; N, 4.18. Found: C, 57.28; H, 8.67; N, 4.22.

Attempted Addition of CO to $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. A 5-mm NMR tube containing ca. 0.005 g of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ and 0.7 mL of $CDCl_3$ was flushed with CO gas. No change in the initial ^1H NMR spectrum was observed after agitating the mixture for several hours at ambient temperature. Monitoring the same reaction by IR spectroscopy

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Table IV. Crystallographic Data for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$

chem formula $C_{16}H_{29}NO_3Cr$
$a = 9.535$ (3) Å
$b = 9.789$ (4) Å
$c = 20.108$ (9) Å
$\beta = 91.89$ (5)°
$V = 1875.8$ (13) Å^3
$Z = 4$
$T = 21$ °C

space group $P2_1/n$ (No. 14)
fw 335.4
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.188$ g/cm^3
$\mu = 0.602$ mm^{-1}
$R^a = 0.0571$
$R_w{}^b = 0.0649$

$^a R = |\sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

in CH_2Cl_2 showed no appearance of a carbonyl-containing product or disappearance of starting material.

Attempted Addition of PPh_3 or Iodide to $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. A benzene solution containing an equimolar amount of PPh_3 and $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ was heated at reflux for 30 min. A separate tube containing an equimolar amount of [PPN]I and $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ was treated similarly. Monitoring these reactions by ^1H NMR and IR spectroscopy did not show the appearance of any new species or the disappearance of starting material.

Thermolysis of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. A 5-mm NMR tube containing ca. 0.01 g of $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$ was attached to a vacuum manifold and placed under an N_2 atmosphere. The tube was heated at 150 °C using a preheated oil bath for 1 min, and then the oil bath was replaced by a Dewar vessel containing liquid N_2. After cooling, the system was evacuated and $CDCl_3$ was vacuum transferred to the cold tube. After thawing, the tube was examined by ^1H NMR spectroscopy.

X-ray Structure Determination for $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$. Crystals suitable for X-ray analysis were grown by vacuum sublimation at 35 °C onto a water-cooled finger. A dark plate measuring 0.10 mm × 0.35 mm × 0.45 mm was selected and flame sealed inside a 0.5-mm glass X-ray capillary. The centering of 20 reflections in the range $35° < 2\theta < 10°$ lead to the selection of a primitive monoclinic cell. An axial photograph indicated symmetry along the unique (*b*) axis. The θ–2θ data set was collected at room temperature. The structure was solved by direct methods, and remaining non-hydrogen atoms were located by subsequent difference maps. The data solution and refinement procedures utilized the SHELXTL or SHELXTL PLUS package of programs (formerly Nicolet, presently Siemens Corp., Madison, WI). Table IV lists a summary of the crystallographic data. The small variation of ψ-scan intensity data indicated that an absorption correction was unnecessary.

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Supplementary Material Available: For $Cp^*Cr(NO)(O\text{-}i\text{-}Pr)_2$, complete listings of the X-ray data collection and refinement parameters, final anisotropic thermal parameters, and H atom coordinates (4 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Mono- and Dinuclear Complexes of a New Binucleating Porphyrin, α,α-5,15-Bis(*o*-(nicotinoylamino)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin. Crystal Structures of a Mononuclear Nickel(II) Complex and a Binuclear Cu–Pt Complex

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The synthesis and characterization of a new binucleating porphyrin ligand, α,α-5,15-bis(*o*-(nicotinoylamido)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, $[H_2(DPE)]\text{-}(py)_2$ is reported. Treatment of $[H_2(DPE)]\text{-}(py)_2$ with methanol solutions of Ni(II) or Cu(II) leads to the formation of mononuclear metal complexes, $[M(DPE)]\text{-}(py)_2$, in which the metal has inserted into the porphyrin core, leaving the pyridine binding site free. Addition of a second metal to form a binuclear complex, $[M(DPE)]\text{-}(py)_2M'Cl_2$, can be accomplished using the reagent $M'(DMSO)_2Cl_2$, M′ = Pd, Pt, and Zn. $[Ni(DPE)]\text{-}(py)_2$ and $[Cu(DPE)]\text{-}(py)_2PtCl_2$ have been characterized by single-crystal X-ray analysis. Crystal data for $[Ni(DPE)]\text{-}(py)_2$: $NiO_2N_8C_{56}H_{52}\cdot 2CHCl_3$, triclinic, $P\bar{1}$, $a = 14.306$ (4) Å, $b = 14.719$ (5) Å, $c = 14.296$ (5) Å, $\alpha = 94.86$ (3)°, $\beta = 96.38$ (3)°, $\gamma = 63.45$ (2)°, $Z = 2$, $R = 0.049$, and $R_w = 0.064$. Crystal data for $[Cu(DPE)]\text{-}(py)_2PtCl_2$: $CuPtO_2N_8C_{56}H_{52}$, triclinic, $P\bar{1}$, $a = 19.333$ (1) Å, $b = 23.74$ (1) Å, $c = 12.984$ (5) Å, $\alpha = 103.28$ (4)°, $\beta = 108.29$ (3)°, $\gamma = 76.47$ (3)°, $Z = 4$, $R = 0.073$, and $R_w = 0.085$. Pt–Pt distances between the two molecules in the asymmetric unit are 3.766 (3) Å.

Multinuclear transition-metal complexes have been intensely studied as active-site models[1] of enzymes whose functions are believed to require the presence of more than one metal. Additional interest in multimetallic systems derives from the possibility of developing special chemical and physical properties as a result of the mutual interaction of two or more metal centers.[2] The potential for developing new catalysts or catalytic reactions also provides a strong driving force for continuing research in this field.[3] Particularly intriguing is the possibility of discovering new processes which cannot be mediated by the individual metal components alone.

Preparation of discrete multinuclear complexes relies heavily on ligand design. For binuclear metal systems, important ligand features include the presence of two distinct, well-defined binding sites which position the metals in close proximity. The ability to vary the identity of the two metals and the metal–metal separation is also a desirable attribute. For these reasons, we have utilized porphyrins as the basis of our binucleating ligand systems. The porphyrin ligand can bind a wide range of metals and is easily

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