Inorg. Chem. **1996,** *35,* 3431−3433

Stable Cyclohexadienyl Complexes of Ruthenium in a Piano Stool Geometry Containing a Tridentate Nitrogen Donor Ligand. First Structural Characterization of the (η^5-Cyanocyclohexadienyl)ruthenium(II) Complex and Spectroelectrochemical Correlation†

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Received June 15, 1995

Introduction

The reaction of nucleophiles with transition metal π-complexes is of significant interest as a synthetic route to arene functionalization.[2−4] Arene ruthenium complexes play an increasingly important role in organometallic chemistry, and the η^6-arene ruthenium unit offers specific properties for the reactivity of the arene ligand.[5] Although several η^5-cyclohexadienyl complexes of ruthenium have been isolated,[5−10] most of these complexes are derived from only the following three sandwich varieties: bis(arene), arene−cyclopentadienyl, and arene−cyclophane. To fine-tune the electrophilicity of the coordinated arene rings in ruthenium complexes with "piano stool" configuration seem to be of great potential.[12,13] In an attempt to widen the variety of such complexes, three cyclohexadienyl complexes of ruthenium(II) $[(\eta^5\text{-}C_6H_6(Y))RuL]PF_6$ [Y = CN$^-$ (**1**), H$^-$ (**2**), OH$^-$ (**3**); L = {(2-pyridylethyl)(2-pyridylmethyl)methylamine}] having half-sandwich or "piano stool" geometry have been prepared and characterized by physicochemical methods. The complex **1** has been further characterized by an X-ray structure determination. The complexes are among only a handful of isolated η^5-cyclohexadienyl complexes of ruthenium having "piano stool" geometry[8,9] and represent the first examples containing a non-phosphine, tridentate N-donor ligand.[13,14]

Experimental Section

Materials. All chemicals and reagents were procured from commercial sources and used as received, unless otherwise stated. Acetonitrile, dichloromethane, and methanol were purified as before.[13−15] The compound $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$ was prepared as described previously.[13] The supporting electrolyte for electrochemical experiments, tetrabutylammonium perchlorate was prepared/purified as before.[13−15]

Syntheses. $[(\eta^5\text{-}C_6H_6(CN))RuL]PF_6$, 1. To a solution of $[(\eta^6\text{-}C_6H_6)RuL][PF_6]_2$ (0.12 g, 0.17 mmol) in a mixture of CH_3CN-CH_3OH (2:1 v/v; 10 mL) was added solid KCN (0.02 g, 0.3 mmol). The reaction mixture was stirred for 1 h and subsequently evaporated to dryness. The yellow residue thus obtained was washed with methanol and recrystallized from CH_3CN, affording yellow air-stable microcrystals (0.08 g, 79%). X-ray quality crystals were obtained from CH_3CN-CH_3OH mixture. Mp: 295 °C. Anal. Calcd for $C_{21}H_{23}N_4RuPF_6$: C, 43.64; H, 3.98, N, 9.70. Found: C, 43.55; H, 4.00; N, 9.67. IR (KBr, cm^{-1}, selected peaks): 2210 (s, ν(CN)), 2920 (m, ν(C−H$_{endo}$), 830 (s, $\nu(PF_6^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 132\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H NMR (80 MHz, CD_3CN, 298 K), δ: 9.04 (2 H, br, H^6) and 7.84−7.16 (6 H, unresolved m, H^{3,4,5}) (pyridine ring protons); 4.45−4.25 (6 H, br, NCH$_2$ and NCH$_2$CH$_2$), 3.06 (3 H, s, NCH$_3$); 5.88 (1 H, t, J = 5 Hz, H^4), 3.59 (2 H, t, J = 5 Hz, H^{3,5}), 3.00 (1 H, m, H$_{endo}$) (overlaps with NCH$_3$), 2.45 (2 H, t, J = 6.25 Hz, H^{2,6}) (η^5-cyclohexadienyl ring protons).[16] Absorption spectrum [in CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 245 (12 450) and 312 (8230). Cyclic voltammetry (CH_3CN, platinum working electrode, SCE, scan rate: 100 mV s^{-1}): 0.96 V (E_{pa}, anodic peak potential), $E_{1/2}$ = 1.20 V and 1.48 V.

$[(\eta^5\text{-}C_6H_6(H))RuL]PF_6$, 2. To a methanolic solution (15 mL) of $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$ (0.15 g, 0.22 mmol) was added solid NaBH$_4$ (0.15 g, 3.95 mmol) slowly to avoid vigorous effervescence. The mixture was stirred for 1 h at room temperature. The color of the solution changed from yellow to greenish yellow. Then water (5 mL) was added to destroy excess NaBH$_4$ and CH$_2$Cl$_2$ (20 mL) was added and the organic layer was separated and dried over MgSO$_4$. It was then filtered and evaporated to dryness. The mass thus obtained was then extracted into acetone, and diethyl ether was then added to commence precipitation. The compound was recrystallized from CH_3CN/CH_3OH solution (0.072 g, yield 60%). Mp: 310 °C. Anal. Calcd for $C_{20}H_{24}N_3RuPF_6$: C, 43.44; H, 4.16; N, 7.60. Found: C, 43.52; H, 4.25; N, 7.57. IR (KBr, cm^{-1}, selected peaks): 2920 (m, ν(C−H$_{endo}$), 2790 (s, ν(C−H$_{exo}$), 830 (s, $\nu(PF_6^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 150\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H NMR (80 MHz, CD_3CN, 298 K), δ: 9.01 (2 H, br, H^6) and 7.82−7.11 (6 H, unresolved m, H^{3,4,5}) (pyridine ring protons); 4.54−3.98 (6 H, br, NCH$_2$ and NCH$_2$CH$_2$); 3.06 (3 H, s, NCH$_3$); 5.62 (1 H, t, J = 5 Hz, H^4), 3.16 (1 H, m, H$_{endo}$) (overlaps with NCH$_3$), 2.77 (2 H, br, H^{3,5}), 2.44 (2 H, dd, J = 6.25 Hz, H^{2,6}), 1.63 (1 H, d, J = 12.5 Hz) (η^5-cyclohexadienyl ring protons).[16,17] Absorption spectrum [in CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 248 (12 250) and 333 (8100). Cyclic voltammetry (CH_3CN, platinum working electrode, SCE, scan rate: 100 mV s^{-1}): 0.71 V (E_{pa}, anodic peak potential), $E_{1/2}$ = 1.20 and 1.50 V.

$[(\eta^5\text{-}C_6H_6(OH))RuL]PF_6$, 3. To the solution of $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$ (0.1 g, 0.14 mmol) in acetone (20 mL) was added an aqueous

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† Dedicated to Professor Animesh Chakravorty on his 60th birthday.

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(10) Addition of acid to a ruthenium(0)-bound, cyclophane−benzene ring converts it to a cyclohexadienyl moiety which has been characterized by X-ray crystallography.[11]

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S0020-1669(95)00750-6 CCC: $12.00

Table 1. Crystallographic Data for $[(\eta^5\text{-}C_6H_6(CN))RuL](PF_6)$ (**1**)

chem formula	$RuC_{21}H_{23}F_6N_4P$	V, Å^3	2263.0(2)
fw	577.5	Z	4
temp, K	295	d_{calc}, g cm^{-3}	1.695
space group	$P2_1/c$ (No. 14)	μ, cm^{-1}	8.30
a, Å	12.816(7)	λ, Å	0.71073
b, Å	12.761(5)	R,[a] %	3.05
c, Å	14.134(7)	R_w,[b] %	4.13
β, deg	101.77(4)		

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$.

solution (10 mL) of NaOH (0.32 g, 0.8 mmol). The mixture was stirred for 1 h at room temperature and filtered. On concentration, the bright yellow precipitate which came out was filtered and washed with water and diethyl ether and dried in vacuo. The complex was recrystallized from CH_3CN-CH_3OH solution (0.06 g, yield 71%). Mp: 253 °C. Anal. Calcd for $C_{20}H_{24}N_3ORuPF_6$: C, 42.22; H, 4.22; N, 7.39. Found: C, 42.20; H, 4.25; N, 7.30. IR (KBr, cm^{-1}, selected peaks): 3450 (m, br, ν(OH)), 2950 (m, $\nu(C-H_{endo})$), 830 (s, $\nu(PF_6^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 130\ \Omega^{-1}$ cm^2 mol^{-1}. ^{1}H NMR (80 MHz, CD_3CN, 298 K), δ: 9.08 (2 H, br, H^6) and 7.79−7.08 (6 H, unresolved m, $H^{3,4,5}$) (pyridine ring protons); 4.17−3.96 (6 H, br, NCH_2 and NCH_2CH_2); 2.97 (3 H, s, NCH_3) (overlaps with H_{endo}); 5.59 (1 H, t, $J = 5$ Hz, H^4), 3.19 (1 H, m, H_{endo}), 2.78 (2 H, unresolved, $H^{3,5}$), 2.42 (2 H, t, $J = 6.25$ Hz, $H^{2,6}$), 2.16 (OH) (3.67, on addition of D_2O) (η^5-cyclohexadienyl ring protons).[16] Absorption spectrum [in CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 248 (10 100) and 329 (6800). Cyclic voltammetry (CH_3CN, platinum working electrode, SCE, scan rate: 100 mV s^{-1}): 0.79 V (E_{pa}, anodic peak potential), $E_{1/2} = 1.22$ and 1.49 V.

Physical Measurements. Conductivity, spectroscopic (IR, UV/vis, and ^{1}H NMR), and electrochemical data were obtained as described previously.[13−15]

X-ray Crystallography. A yellow crystal of $[(\eta^5\text{-}C_6H_6(CN))RuL]PF_6$ (**1**) with the approximate dimensions 0.62 × 0.48 × 0.22 mm was mounted on the diffractometer and intensity data (295 K) were collected using a Siemens R3m/V single-crystal X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The intensities of two standard reflections, recorded after every 98 reflections, remained unchanged during the period of data collection. A total of 4435 reflections were collected in the range $3 < 2\theta < 50°$; among which 3995 were unique. Corrections for extinction and a semiempirical absorption on the basis of azimuthal scans[18] were applied. The structure was successfully solved in the space group $P2_1/c$ by Patterson and Fourier methods and refined using full-matrix least-squares analysis. At convergence, $R = 0.0305$ and $R_w = 0.0413$ for the 3297 observed reflections [$F > 6.0\ \sigma(R)$]. Atomic scattering factors were taken from ref 19. All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer using the programs of SHELXTL-Plus.[20] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at their calculated positions with fixed isotropic thermal parameters in the final cycle of refinement. The PF_6^- anion was disordered. The two axial fluorines were unique (i.e. refined with a site occupation factor of 1.0 each); however, eight peaks were located on the equatorial plane as possible fluorine positions, all of which were refined with a site occupation factor of 0.5.

Crystal data and a symmetry of experimental results are presented in Table 1 while selected bond distances and angles are collected in Table 2. The rest of the crystallographic data have been submitted as Supporting Information.

Results and Discussion

Synthesis and Characterization of the Cyclohexadienyl Complexes of Ruthenium(II). The present complexes **1**−**3** were synthesized following the reactions between the recently reported "piano stool" complex $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$[13] and the nucleophiles CN$^-$, H$^-$, and OH$^-$. These air-stable bright yellow complexes were characterized by solution electrical conductivity (1:1 electrolyte in MeCN solution)[21] and IR[6,11] and ^{1}H NMR[6−9,13,22] spectral measurements. The three legs for the "piano stool" geometry (vide infra) are provided by a tridentate ligand[13,14] containing an aliphatic nitrogen donor atom in combination with two pyridine groups. The fact that this is a neutral ligand with good σ-donor properties seems to be essential for the stabilization of the present complexes.

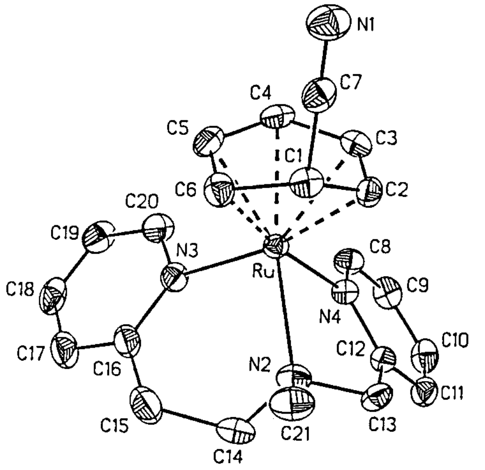

Figure 1. Structure of the cation of $[(\eta^5\text{-}C_6H_6(CN))RuL]PF_6$ (**1**). All atoms are represented by their 30% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) in the Cationic Part of $[(\eta^5\text{-}C_6H_6(CN))RuL]PF_6$ (**1**)

Ru−N(2)	2.208(3)	Ru−N(3)	2.162(3)	Ru−N(4)	2.128(3)
Ru−C(2)	2.186(3)	Ru−C(3)	2.142(3)	Ru−C(4)	2.164(3)
Ru−C(5)	2.131(4)	Ru−C(6)	2.182(4)		
C(1)−C(2)	1.523(5)	C(1)−C(6)	1.517(5)	C(2)−C(3)	1.398(5)
C(3)−C(4)	1.418(5)	C(4)−C(5)	1.419(6)	C(5)−C(6)	1.399(5)
C(1)−C(7)	1.487(4)	N(1)−C(7)	1.136(4)		

N(2)−Ru−N(3)	91.7(1)	N(2)−Ru−N(4)	76.1(1)
N(2)−Ru−C(2)	96.1(1)	N(2)−Ru−C(3)	128.9(1)
N(2)−Ru−C(4)	164.1(1)	N(2)−Ru−C(5)	138.3(1)
N(2)−Ru−C(6)	102.6(1)		

X-ray Structural Characterization. In order to confirm the identity of **1**−**3** and establish the coordination geometry at the metal, a single-crystal X-ray study of a representative complex, **1**, was undertaken. The study revealed that the certain consists of a RuL^{2+} unit that is bonded to a cyclohexadienyl ring system (Figure 1), in a "piano stool" configuration.[12,13,23] The X-ray analysis also reveals the *exo*-stereochemistry of the cyanide group. Comparison of X-ray metric parameters of **1** (Table 2) with the parent compound $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$[13] reveals evidence for mutual *trans* influence of the tridentate ligand. The average Ru−C distances (C_2-C_6) in **1** are shorter by 0.04 Å and Ru−N distances longer by 0.032 Å (pyridine N) and 0.037 Å (amine N). However, the mean N−Ru−N angle is not significantly different from that found in the parent complex.

Of principal interest are the various structural distortions to the coordinated cyclohexadienyl ring. The Ru atom is bonded to five unsaturated carbon atoms (Figure 1). The methylene carbon C_1 lies ∼ 0.65 Å above and the Ru atom is ∼1.66 Å away from this plane. Thus the cyclohexadienyl ring is

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nonplanar in an envelope conformation bent across the C_2- - -C_6 axis such that the plane defined by $C_2-C_1-C_6$ makes a dihedral angle of 42.5° with the planar five-membered π-dienyl system. Both the pyridine rings of the tridentate ligand are planar; however, they are tilted to each other by an angle of 85.0°. The average carbon−carbon distance around the delocalized system is 1.408 Å.

Absorption Spectra. The electronic nature of **1**−**3** was probed with UV/vis spectroscopy. We assign the absorption band in the range 310−330 nm as due to metal-to-ligand charge-transfer (MLCT) transition. We believe that the acceptor orbital is predominantly of cyclohexadienyl origin since the band positions shift systematically as a function of the nature of the nucleophile. The highest energy bands are due to metal-perturbed intraligand transitions.

Electrochemistry. Unlike the parent compound $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$ which exhibits a reductive response,[13] the present complexes display three oxidative responses, when examined by cyclic voltammetry. The responses at less positive potential were irreversible[24] and the anodic peak potentials (E_{pa}) were found to shift with the nature of the nucleophile. We assign this process as due to the $Ru^{III}-Ru^{II}$ redox couple. Interestingly, the other two reversible responses (the concentration of species responsible for the responses at ~1.20 V is very much reduced) were invariant as to the nature of the nucleophile. We believe that these two highest potential responses are associated with species like "$RuL(MeCN)_3$" and related species, without any organometallic ring.[25]

Spectroelectrochemical Correlation. The extent of electrophilicity of the coordinated benzene ring in $[(\eta^6\text{-}C_6H_6)RuL](PF_6)_2$ toward the nucleophile Y (CN^-, H^-, and OH^-) follows an interesting pattern. In fact, a linear trend is observed (Figure S1, Supporting Information) between the E_{pa} values for the $Ru^{III}-Ru^{II}$ couple and the energies of the MLCT transition. This trend reflects that the stronger the nucleophile the better the stabilization of the ruthenium(II) state and hence the higher the energy of its MLCT transition. It must be noted that the peak potentials (in this case the E_{pa} values) are unrelated to the thermodynamic $E_{1/2}$ values; however, these are valuable quantities for discussing similarities and disparities within a given group of compounds.[26,27] This trend reveals, within the present group of complexes, the following order of the strength of the nucleophiles: $CN^- > OH^- > H^-$. The significance of this result with a larger variety of nucleophiles will be reported in due course.

Acknowledgment. We are grateful to the Department of Science and Technology, Government of India, and the Council of Scientific and Industrial Research, New Delhi, India for support. Crystallographic studies were done at the National Single Crystal Diffractometer Facility, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta, India. We deeply appreciate the help provided by Professor A. Chakravorty. We also thank Mr. A. K. Patra for providing us preliminary data for **3**.

Supporting Information Available: Tables of crystal data and structure determination summary (Table S1), atomic positional parameters (Table S2), intramolecular bond distances and angles (Tables S3 and S4), anisotropic thermal parameters (Table S5), hydrogen atom coordinates (Table S6) and figures showing a linear correlation between the E_{pa} values (mV) and metal-to-ligand charge transfer energy (cm^{-1}) for **1**, **2**, and **3** (Figure S1) and ^1H NMR spectra of **1** (Figure S2), **2** (Figure S3), and **3** (Figure S4; with D_2O, Figure S5) (13 pages). Ordering information is given on any current masthead page.

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[24] The Ru^{III}/Ru^{II} response remains irreversible even at a scan rate of 1 V/s and at −20 °C.

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