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Comparing the Isoelectronic Complexes $[RuTp(CH_3CN)_3]PF_6$ (Tp = Hydridotris(pyrazolyl)borate) and $[RuCp(CH_3CN)_3]PF_6$. Structure and Acetonitrile Exchange Kinetics

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Introduction

The hydridotris(pyrazolyl)borate anion (Tp), introduced as a ligand in transition metal complexes by Trofimenko,[1] is often compared with Cp due to the same charge and number of electrons donated as well as the facial geometry typically adopted. Notwithstanding this, the differences in size and electronic properties may not be neglected in discussing reactivites. Thus, the cone angle of Tp is close to 180°, well above the 100° calculated for Cp.[2] The steric bulk of the Tp ligand disfavors metal coordination numbers higher than six. As a consequence, processes involving a coordination number increase, e.g., oxidative additions and associative substitutions, are rare for Tp systems. With respect to ruthenium, there are so far, to the best of our knowledge, no genuine seven-coordinate Tp compounds known. For instance, di- and polyhydride complexes favor dihydrogen rather than dihydride coordination to maintain octahedral geometry.[3] In addition there are different geometries of the orbitals involved in constructing the complexes, with Cp being a π donor, but Tp being a good σ donor. The π properties of the Tp ligand come into play in the presence of appropriate, i.e., π accepting, coligands such as CO. This interplay is particularly effective in the case of C_{3v} symmetry where all three π orbitals of the metal are equally participating in metal−ligand bonding as in $MoTp(CO)_3$.[2] Here we report the molecular structure and ligand exchange kinetics of trisacetonitrile complex $[RuTp(CH_3CN)_3]^+$ in comparison to its isoelectronic analogue $[RuCp(CH_3CN)_3]^+$.[4]

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[5] RuTp(COD)Cl has been prepared according to the literature.[6] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. FT-IR spectra were recorded on a Mattson RS 2 spectrometer.

Synthesis. $[RuTp(CH_3CN)_3]PF_6$. A solution of RuTp(COD)Cl (100 mg, 0.218 mmol) and NH_4PF_6 (43 mg, 0.262 mmol) in CH_3CN/DMF (1:1, 4 mL) was heated at reflux for 3 h. The solvent was removed under vacuum, and the residue was redissolved in CH_2Cl_2 (3 mL). Insoluble materials were removed by filtration over anhydrous Na_2SO_4. The volume of the filtrate was reduced to about 0.5 mL, and upon addition of Et_2O (3 mL), a bright yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O (5 × 2 mL), and dried under vacuum. Yield: 89 mg (70%). Anal. Calcd for $C_{15}H_{19}BF_6N_9PRu$: C, 30.95; H, 3.29; N, 21.65. Found: C, 30.88; H, 3.32; N, 21.70. ^1H NMR (δ, CD_3NO_2, 20 °C): 7.86 (d, $^3J_{HH} = 2.4$ Hz, 3H, Tp), 7.80 (d, $^3J_{HH} = 1.9$ Hz, 3H, Tp), 6.33 (vt, $^3J_{HH} = 2.4$ Hz, $^3J_{HH} = 1.9$ Hz, 3H, Tp), 5.23 (m, 9H, CH_3CN). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 145.1 (3C, Tp), 137.7 (3C, Tp), 126.0 (3C, $CH_3\mathit{C}N$), 107.9 (3C, Tp), 3.7 (3C, $\mathit{C}H_3CN$). IR (Nujol, cm^{-1}): 2511 (m, ν_{B-H}), 2284 (w, ν_{CN}).

Acetonitrile Exchange Kinetics. The acetonitrile exchange was studied according to eq 1 as a function of temperature and CD_3CN concentration by monitoring the increase in intensity of the proton NMR signal of free CH_3CN (at 1.97 ppm) and the decrease of the bound CH_3CN (at 2.54 ppm) after fast injection of CD_3CN (0.761−3.045 M) to solutions of $[RuTp(CH_3CN)_3]PF_6$ (0.053 M) in CD_3NO_2 (0.4 mL).

$$[RuTp(CH_3CN)_3]PF_6 + 3CD_3CN \xrightarrow{3k_{ex}} [RuTp(CD_3CN)_3]PF_6 + 3CH_3CN \quad (1)$$

The time dependence of the mole fraction $x = [CH_3CN]_c/([CH_3CN]_c + [CH_3CN]_f)$ of coordinated nondeuterated acetonitrile, obtained by integration of the signals, was fitted to eq 2,[7] where x_0 and x_∞ are the values of x at $t = 0$ and ∞ and k_{ex} is the observed first-order rate constant for the exchange of a one-bound solvent molecule.

$$x = x_\infty + (x_0 - x_\infty)\exp[-k_{ex}t/(1 - x_\infty)] \qquad (2)$$

The adjustable parameters were x_0, x_∞, and k_{ex}. Temperature readings were calibrated by using the method of Raiford et al.,[8] corrected to 250.13 MHz by adding a capillary of methanol to the experimental sample. The temperature dependence of the rate constants is given by the Eyring equation (eq 3).

$$k_{ex} = (k_BT/h)(\exp(-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT) \qquad (3)$$

X-ray Structure Determination of $[RuTp(CH_3CN)_3]PF_6$. Pale yellow needlelike crystals of $[RuTp(CH_3CN)_3]PF_6{\cdot}solv$ were obtained by diffusion of Et_2O into CH_3CN solutions. Crystal data: $C_{15}H_{19}BF_6N_9PRu$ (solvent omitted here and in fw, D_x, and μ), fw = 582.24, hexagonal, space group $P\bar{6}c2$ (no. 188), $a = 18.726(8)$ Å, $c = 13.944(6)$ Å, $V = 4235(3)$ Å^3, $Z = 6$, $D_x = 1.370$ Mg/m^3, $\mu = 0.67$ mm^{-1}, $T = 295(2)$ K. X-ray data were collected on a Siemens SMART CCD area detector diffractometer (sealed X-ray tube, graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å, 0.3° ω scan frames covering the entire reciprocal space up to $\theta_{max} = 25°$, 41 300 reflections collected, 2595 independent, corrections for absorption by the multiscan method).

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Table 1. Structure and Acetonitrile Exchange Kinetics of $[RuTp(CH_3CN)_3]^+$, $[RuCp(CH_3CN)_3]^+$, and $[Ru(CH_3CN)_6]^{2+}$

	$[RuTp(CH_3CN)_3]^+$	$[RuCp(CH_3CN)_3]^{+\,a}$	$[Ru(CH_3CN)_6]^{2+\,b}$
$Ru-N_{av}(CH_3CN)$, Å	2.045(7)	2.083(1)	2.028(1)
$N-Ru-N_{av}(CH_3CN)$, deg	89.9(2)	86.0(7)	89.8(1)
$C\equiv N_{av}$, Å	1.12(1)	1.131(3)	1.137(1)
$\Delta H^{\ddagger}$, kcal mol^{-1}	37.2 ± 0.7	20.7 ± 0.5	33.5 ± 0.5
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	30.2 ± 1.8	14.2 ± 1.7	7.9 ± 1.4
k^{298}, s^{-1}	1.2×10^{-8}	5.6	8.9×10^{-11}

[a] Reference 4. [b] Reference 11.

The structure was solved by direct methods using the program SHELXS97.[9] Structure refinement on F^2 was carried out with the program SHELXL97.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Final refinement gave R1 = 0.051 and wR2 = 0.110 for 2021 reflections ($F^2 > 2\sigma(F^2)$) and R1 = 0.0757 for all data, 163 parameters. Excursions in the final difference Fourier map were between −0.46 and +0.33 e Å^{-3}. $[RuTp(CH_3CN)_3]PF_6$·solv adopts an interesting host−guest structure of hexagonal symmetry with six Ru complexes and four PF_6 anions per unit cell forming a framework in which large channels of about 9 Å diameter extend at 0, 0, *z* along the *c*-axis and are filled with disordered two PF_6 anions and with solvent molecules Et_2O/CH_3CN in unknown proportions. Due to disorder in these channels no assignment of the encountered electron densities to specific molecular species was possible, and six carbon atom sites refined in *x, y, z* and population parameters were used to model this part of the structure.

Results and Discussion

The cationic trisacetonitrile complex $[RuTp(CH_3CN)_3]PF_6$ has been obtained in 70% isolated yield by the reaction of RuTp(COD)Cl with NH_4PF_6 in boiling DMF/CH_3CN (1:1 mixture). This yellow, air-stable complex has been characterized by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy as well as elemental analysis. The complex is characterized by one set of equivalent pyrazolyl rings and one set of equivalent CH_3CN ligands in the ^1H NMR spectrum. This simplicity is indicative of a complex that has C_{3v} symmetry. This is also supported by the $^{13}C\{^1H\}$ NMR data giving rise to three resonances for the Tp and two for the CH_3CN ligands. The resonance of the nitrile group is found at 126.0 ppm, compared to 118.0 ppm in free CH_3CN. The solid-state structure of $[RuTp(CH_3CN)_3]PF_6$·solv has been determined by X-ray crystallography. An ORTEP diagram of the $[RuTp(CH_3CN)_3]^+$ complex is depicted in Figure 1, with selected bond distances and angles reported in the caption. The coordination geometry of $[RuTp(CH_3CN)_3]^+$ is approximately octahedral, with all angles at ruthenium being close to 90° (the bite angle of the Tp ligand produces an average N−Ru−N angle of 87.1(2)°), and thus the molecule closely approximates C_{3v} symmetry. The bond distances within the Tp ligand are unremarkable. The $Ru-N^4$ and $Ru-N^2$ bond distances are 2.062(8) and 2.045(6) Å, respectively. The mean $Ru-NCCH_3$ bond distance is 2.045(7) Å with a N−Ru−N angle of 89.9(2)°. For comparison,[4] in $[RuCp(CH_3CN)_3]^+$ this angle is somewhat smaller, being 86.0(7)°, whereas the mean Ru−N bond distance has increased by 0.038 Å to 2.083(1) Å. The decrease in the $Ru-NCCH_3$ bond lengths of the RuTp complex relative to that in the RuCp analogue may be ascribed to increased $d \rightarrow \pi^*$ bonding in the former. Noteworthy, π bonding effects are even more pronounced in the octahedral dicationic complex $[Ru(CH_3CN)_6]^{2+}$ where the $Ru-NCCH_3$ bond distance is 2.028(1) Å.[11]

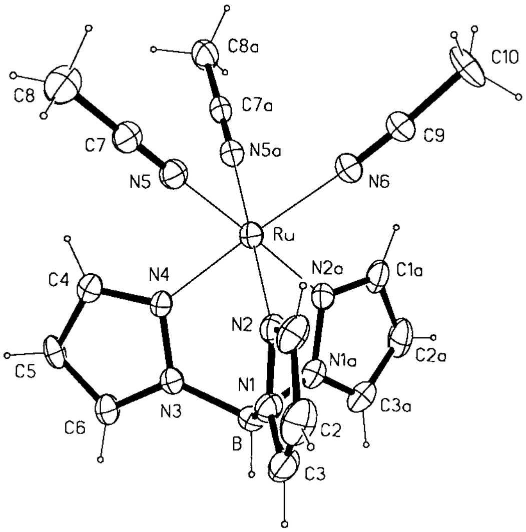

Figure 1. Structural view of the Ru complex in $[RuTp(CH_3CN)_3]PF_6$·solv showing 20% thermal ellipsoids. The complex is mirror-symmetric, with Ru, N3, N4, B, N6, etc. defining the crystallographic mirror plane. Selected bond lengths (Å) and angles (deg): $Ru-N^2$ 2.045(6), $Ru-N^4$ 2.062(8), $Ru-N^5$ 2.040(7), $Ru-N^6$ 2.056(8), N^5-C^7 1.128(9), N^6-C^9 1.117(12), N^2-Ru-N^4 87.1(2), N^2-Ru-N^6 91.4(2), N^2-Ru-N^5 92.4(2), N^4-Ru-N^5 91.5(2), N^5-Ru-N^6 89.9(2).

The CH_3CN ligand in $[RuTp(CH_3CN)_3]^+$ is substitutionally inert and is not replaced by CD_3CN (20 equiv) in a solution of $[RuTp(CH_3CN)_3]^+$ in CD_3NO_2 at room temperature over several days. The kinetics of this process has been studied in detail by ^1H NMR spectroscopy as a function of $[CD_3CN]$ and temperature. The results of the kinetic measurements at various temperatures evaluated by eq 2 are summarized in Table 1. It is remarkable that the CH_3CN exchange is more than 8 orders of magnitude slower in $[RuTp(CH_3CN)_3]^+$ than in the isoelectronic complex $[RuCp(CH_3CN)_3]^+$,[4] mainly due to the much higher activation enthalpy. The kinetic trans effect thus correlates with the trans influence of the ligands in the order Cp > Tp. Since the reaction rate is not affected by $[CD_3CN]$, a unimolecular process (dissociative mechanism, D) is indicated. This is also reflected by the large and positive entropy of activation. The great thermodynamic stability of $[RuTp(CH_3CN)_3]^+$ results from appreciable back-bonding from the electron-rich Ru^{2+} center into the π^* orbital of the coordinated acetonitrile. This is seen by the short $Ru-NCCH_3$ bond distances. This effect is however not apparent from the $\nu_{(CN)}$ absorption of $[RuTp(CH_3CN)_3]^+$ observed at 2281 cm^{-1}, which is comparable to those of $[RuCp(CH_3CN)_3]^+$ (2284 cm^{-1}) and free CH_3CN (2283 and 2246 cm^{-1}).

In summary, the acetonitrile exchange kinetics further supports the fact that the Tp ligand strongly prefers a six-coordinate environment around Ru, promoting substitution reactions to follow a dissociative pathway. The large cone angle may be

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responsible for this preference, but electronic effects may also play an important role particularly in the case of C_{3v} symmetry, where all three π orbitals of the RuTp fragment are equally participating in the metal−ligand bondings.

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Supporting Information Available: Listings of crystallographic data, atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for [RuTp(CH_3CN)$_3$]PF_6·solv as well as kinetic data (Tables S1−S6 and Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Additions and Corrections

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Belén Albela, Eberhard Bothe, Oliver Brosch, Katsura Mochizuki, Thomas Weyhermüller, and Karl Wieghardt*: Redox Chemistry of (1,4,7-Tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane)ruthenium(III), [$Ru^{III}L$]: Synthesis and Characterization of [Ru^{II}_2(L−L)](BPh_4)$_4$·10CH_3CN and [LRuRuRuL](PF_6)$_2$·H_2O.

Pages 5137. Equation 4 is incomplete. The correct eq 4 is provided.

$$[L_2Ru_3]^{3+} \underset{+e}{\overset{-e}{\rightleftharpoons}} [L_2Ru_2]^{2+} \underset{+e}{\overset{-e}{\rightleftharpoons}} [L_2Ru_3]^{+} \underset{+e}{\overset{-e}{\rightleftharpoons}} [L_2Ru_3]^{0} \quad (4)$$

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