5160 *Inorg. Chem.* **1992,** *31,* 5160–5161

$[M(SR)_3L_2]$ Complexes of Ruthenium(IV,III) and Osmium(IV): Structural Integrity of the Trigonal $[M(SR)_3]^{+,0}$ Cores

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Received July 17, 1992

In contrast to the considerable chemistry of iron thiolate complexes, the chemistry of ruthenium and osmium thiolate compounds has been less extensively developed.[1–4] We have previously reported the synthesis of ruthenium and osmium compounds with sterically hindered aromatic thiolate ligands.[2] Herein we report that the systematic elaboration of the coordination chemistry of Ru and Os thiolate complexes reveals the integrity of the trigonal $[M(SR)_3]^{+,0}$ cores.

The compounds $[M(SR)_4(CH_3CN)]$ (M = Ru, Os; RS = S-2,3,5,6-Me_4C_6H, S-2,4,6-*i*-$Pr_3C_6H_2$)[5] have trigonal bipyramidal structures with the CH_3CN and a thiolate ligand occupying the axial positions.[2a] The observation that the Ru–S_{ax} bond distance is almost 0.2 Å longer than the Ru–S_{eq} bonds suggested that the axial thiolate could be selectively replaced. The reaction of $[M(SR)_4(CH_3CN)]$ (M = Ru, Os; RS = S-2,3,5,6-Me_4C_6H, S-2,4,6-*i*-$Pr_3C_6H_2$) with HBF_4 (or HPF_6) in CH_3CN gives $[M(SR)_3(CH_3CN)_2][BF_4]$.[6] The X-ray crystal structure of a representative member of this series, $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2][PF_6]$ (**1**), was determined (Figure 1).[7] The structure is similar to that of $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4(CH_3CN)]$ (**2**) but with a CH_3CN molecule replacing the axial thiolate ligand; two of the equatorial thiolate ligands are oriented in the direction of one of the axial CH_3CN ligands, and the third thiolate is directed toward the second CH_3CN ligand (i.e., the 2-up, 1-down conformation).[2b] The Ru–S_{eq} distances (2.200 (8) Å) in **1** are unchanged compared to **2**, but the Ru–N distances in **1** are 0.06 Å shorter than the Ru–N distance in **2**. The ^1H NMR spectrum of **1** indicates that the 2-up, 1-down arrangement of the equatorial thiolates is also present in solution and that rotation about the Ru–S bonds and the S–C bonds is not observed on the NMR time scale from room temperature to >60 °C.[6] This compound is similar in structure to the isoelectronic $[Tc^{III}(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2]$ and to closely related rhenium complexes.[8,9]

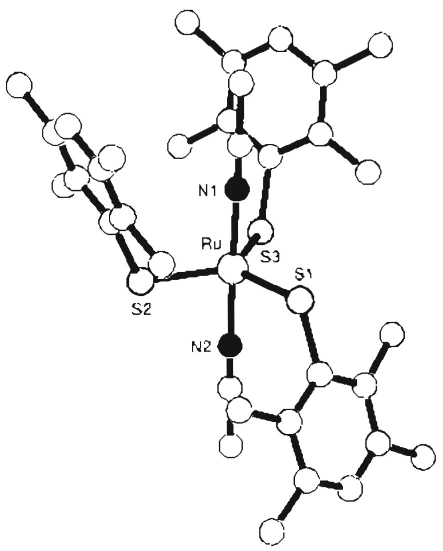

Figure 1. X-ray structure of $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2]^+$. Selected bond distances (Å) and angles (deg): Ru–S1 = 2.195 (8); Ru–S2 = 2.198 (8); Ru–S3 = 2.208 (8); Ru–N1 = 2.03 (2); Ru–N2 = 2.03 (2); S1–Ru–S2 = 118.3 (3); S1–Ru–S3 = 117.7 (3); S1–Ru–N1 = 87.7 (8); S1–Ru–N2 = 92.0 (9); S2–Ru–S3 = 123.9 (3); S2–Ru–N1 = 92.7 (8); S2–Ru–N2 = 88.4 (9); S3–Ru–N1 = 92.7 (7); S3–Ru–N2 = 86.5 (9); N1–Ru–N2 = 179 (1); Ru–S1–C11 = 111.5 (8); Ru–S2–C21 = 111.9 (8); Ru–S3–C31 = 110.7 (8).

Electrochemical studies revealed that the $[M(SR)_3(CH_3CN)_2]^+$ complexes can be reversibly reduced by one electron to the analogous M(III) complexes: $[M(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2]^+$ (Ru, –0.30 V; Os, –0.62 V); $[M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]^+$ (Ru, –0.23 V).[10] Chemical reduction of $[Ru(SR)_3(CH_3CN)_2]^+$ (SR = S-2,3,5,6-Me_4C_6H, S-2,4,6-*i*-$Pr_3C_6H_2$) was achieved by reaction with 1 equiv of Cp_2Co in THF.[11] $[Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]$ (**3**) was structurally characterized (Figure 2).[12] The structure of **3** is similar to that of **1** but with a significantly (0.08 Å) longer Ru–S bond distance (2.28 (2) Å) and a slightly decreased Ru–N distance (1.995 (6) Å). The RuS_3 unit is distorted from 3-fold symmetry; the S–Ru–S angles vary from 137 to 104°. The ^1H NMR spectrum of **3** shows paramagnetically shifted resonances; the assignment of three peaks in the –40 °C spectrum at δ 28.5, 23.4, and 17.8 to *m*-H of the thiolate ligands is consistent with the 2-up, 1-down arrangement

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(6) Preparation of $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2][PF_6]$: Compound **2** (1.5 g, 1.87 mmol) and HPF_6 (60% aqueous; 0.81 g, 6 mmol) were refluxed in 150 mL of CH_3CN under N_2 for 3 h. The CH_3CN was removed under vacuum, and the residue was crystallized from THF/hexane to give red crystals in 73% yield. FABMS(+) (*m/z*): 678 (parent); 596 ($Ru(SR)_3$); 430 ($Ru(SR)_2$). ^1H NMR ($CDCl_3$): δ 7.19 (s, 1 H, Ar *H*), 7.13 (s, 2 H, Ar *H*), 2.28 (s, 6 H, $ArCH_3$), 2.19 (s, 6 H, $ArCH_3$), 2.13 (s, 6 H, $ArCH_3$), 2.09 (s, 6 H, $ArCH_3$), 2.08 (s, 6 H, $ArCH_3$), 2.01 (s, 3 H, CH_3CN), 1.32 (s, 3 H, CH_3CN).

(7) $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2][PF_6]\cdot 2THF$ crystal data: triclinic space group, $P\bar{1}$ with a = 13.870 (7) Å, b = 15.922 (7) Å, c = 11.406 (5) Å, α = 95.66 (4)°, β = 101.85 (4)°, γ = 101.26 (4)°, V = 2392 (4) $Å^3$, and Z = 2. Final least-squares refinement gave R (R_w) = 0.073 (0.084) for 1510 unique data with $I > 3\sigma(I)$.

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(10) Cyclic voltammetry: $[n\text{-}Bu_4N][BF_4]$ (0.1 M in CH_3CN) as the supporting electrolyte, platinum as the working electrode, platinum wire as the counter electrode, and SCE as the reference electrode.

(11) Preparation of $[Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]$ (**3**): $[Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]BF_4$ (0.50 g, 0.50 mmol) and Cp_2Co (0.10 g, 0.5 mmol) were stirred in 20 mL of THF for 2 h. The reaction mixture was filtered, and the filtrate was concentrated, layered with ethanol, and cooled at –20 °C. Red microcrystals which separated were filtered off to give 0.36 g (79% yield).

(12) $[Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]$ (**3**) crystal data: monoclinic space group $P2_1/c$ with a = 19.219 (9) Å, b = 17.09 (2) Å, c = 16.50 (1) Å, β = 111.53 (5)°, V = 5043 $Å^3$, and Z = 4. R (R_w) = 0.044 (0.056) for 4159 unique reflections with $I > 3\sigma(I)$.

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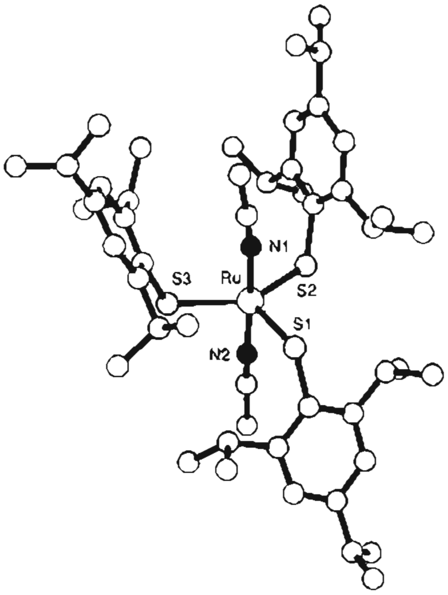

Figure 2. X-ray structure of $Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(CH_3CN)_2]$. Selected bond distances (Å) and angles (deg): Ru–S1 = 2.257 (8); Ru–S2 = 2.286 (6); Ru–S3 = 2.290 (2); Ru–N1 = 1.996 (6); Ru–N2 = 1.994 (5); S1–Ru–S2 = 104.3 (3); S1–Ru–S3 = 118.7 (1); S1–Ru–N1 = 88.5 (2); S1–Ru–N2 = 92.5 (2); S2–Ru–S3 = 136.9 (2); N1–Ru–N2 = 177.7 (2); S2–Ru–N1 = 94.4 (2); S2–Ru–N2 = 87.3 (2); S3–Ru–N1 = 89.8 (2); S3–Ru–N2 = 88.0 (2); Ru–S1–C11 = 112.8 (2); Ru–S2–C21 = 108.8 (2); Ru–S3–C31 = 112.6 (2).

of the equatorial thiolate ligands. At room temperature these three peaks coalesce into a broad resonance at δ 20.0 consistent with rotation about the Ru–S bonds. The ^1H NMR spectrum of a 1/1 mixture of $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(CH_3CN)_2]^n$ (n = 0, 1+) displays averaged resonances indicating that electron self-exchange is fast on the NMR time scale.

The short Ru–S bond distance, the orientation of the equatorial thiolate ligands, and the high barrier for Ru–S bond rotation in the $[Ru^{IV}(SR)_3(CH_3CN)_2]^+$ compounds are consistent with a $(e'')^4$, $(e')^0$, $(a_1')^0$ electron configuration in which there is significant π overlap between the $3p\pi$ orbital on sulfur and the empty $e'(d_{xy},d_{x^2-y^2})$ orbitals on the ruthenium. In the reduced compound, $[Ru^{III}(SR)_3(CH_3CN)_2]$, the added electron occupies the e′orbital and thus weakens the $p\pi$–$d\pi$ bonding between S and Ru.

The reaction of $[M(SR)_4(CH_3CN)]$ (M = Ru, Os; SR = $S\text{-}2,3,5,6\text{-}Me_4C_6H$, $S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$) with HCl in THF gives $[M(SR)_3Cl(CH_3CN)]$ in which chloride replaces the axial thiolate ligand. $[Ru(SR)_3Cl(CH_3CN)]$ is converted to $[Ru(SR)_3(CH_3CN)_2]^+$ by reaction with $TlPF_6$ in CH_3CN. The reaction of $[Ru(SR)_3(CH_3CN)_2]^+$ with NEt_4Cl in CH_3CN regenerates $[Ru(SR)_3Cl(CH_3CN)]$. Further studies of the reactivity of the $[M(SR)_3L_2]$ compounds are in progress.

Acknowledgment. We thank Michelle Millar for discussion and the NSF and NIH for partial funding.

Supplementary Material Available: For 1 and 3, tables of crystallographic data, fractional atomic coordinates, and isotropic and isotropic thermal parameters and figures showing ORTEP diagrams with atom labeling (22 pages). Ordering information is given on any current masthead page.