

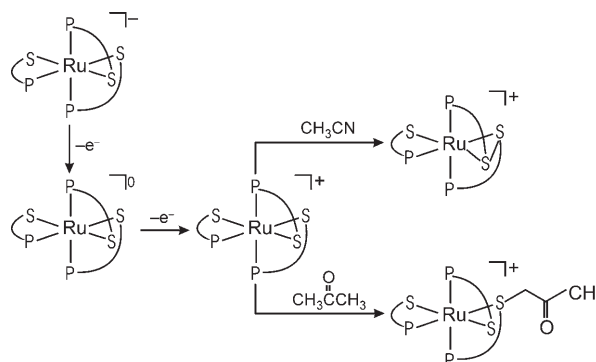
Singlet Diradical Character of an Oxidized Ruthenium Trithiolate: Electronic Structure and Reactivity**

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The nucleophilicity of transition-metal thiolates has been attributed to a metal–sulfur d–p π interaction, which results in high sulfur character for the occupied frontier orbitals.^[1–3] Consequently, oxidation of metal thiolates may be either sulfur- or metal-centered. Recent studies have focused on the stabilization and characterization of metal-coordinated phenylthiyl radicals and related complexes.^[4–17] Unlike their phenoxide counterparts, phenylthiyl radicals tend to localize unpaired spin density on the heteroatom, yielding complexes with a potentially rich sulfur-based reactivity that is fundamentally different than the nucleophilicity of their reduced derivatives.

Elucidation of the electronic structure of metal-coordinated thiyl radicals is instrumental to unlocking their reactive potential. When spectroscopic methods alone are insufficient, density functional theory (DFT) is a vital tool. The spectroscopically observable thiyl-radical intermediate $[\text{Ru}(\text{dppbt})_3]^+$ (dppbt = 2-diphenylphosphinothiaphenolate) displays sulfur-centered reactivity (Scheme 1) and is ideal for DFT investigations.^[18,19]

Figure 1 shows atom positions and coordinates for the family of complexes in this study. To avoid formal oxidation states, a $\{\text{Ru}(\text{SR})_3\}^n$ convention, similar to the Enemark–Feltham notation, is used.^[20,21] The anionic, neutral, and cationic complexes are here referred to as $\{\text{Ru}(\text{SR})_3\}^{12}$, $\{\text{Ru}(\text{SR})_3\}^{11}$, and $\{\text{Ru}(\text{SR})_3\}^{10}$, respectively. The $\{\text{Ru}(\text{SR})_3\}^{12}$ and $\{\text{Ru}(\text{SR})_3\}^{11}$ complexes were analyzed as a singlet ($S = 0$) and doublet ($S = 1/2$), consistent with experiment.^[18,19] The reac-



Scheme 1. Solvent-dependent reactivity of the $[\text{Ru}(\text{dppbt})_3]^+$ ion. $\widehat{\text{SP}}$ = 2-diphenylphosphinothiaphenolate (dppbt).

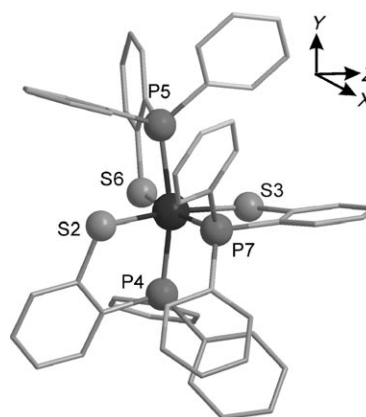


Figure 1. Structure of $[\text{Ru}(\text{dppbt})_3]^n$ ($n = -1, 0, +1$) with numbering scheme and coordinate system.

tive intermediate, $\{\text{Ru}(\text{SR})_3\}^{10}$, possesses a nearly degenerate electronic ground state with respect to frontier orbitals. Consequently, its electronic structure was considered as a singlet diradical, which is consistent with experimental data. This description is in line with oxidized nickel dithiolenes.^[13]

Insight into the complex ground state of $\{\text{Ru}(\text{SR})_3\}^{10}$ can be gained from the qualitative MO diagram of $\{\text{Ru}(\text{SR})_3\}^{12}$ (Figure 2). The HOMO and HOMO–1 have π^* character with significant ruthenium and sulfur contributions. Oxidation to $\{\text{Ru}(\text{SR})_3\}^{11}$ removes an electron from the $\text{Ru } d_{yz}/\text{S } 3p_y$ π^* orbital, while further oxidation to $\{\text{Ru}(\text{SR})_3\}^{10}$ removes an electron from the three-center π interaction between $\text{Ru } d_{xz}$, $\text{S } 2p_x$, and $\text{S } 6p_z$. In each case, the oxidation cannot be considered as strictly metal- or ligand-centered.

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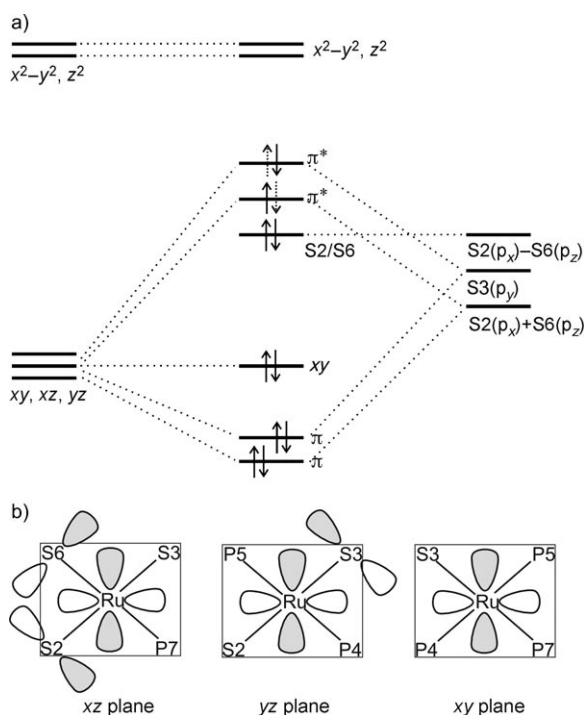


Figure 2. a) Qualitative MO diagram for $[\text{Ru}(\text{dppbt})_3]^n$ ($n = -1, 0, +1$) showing π interactions of Ru d orbitals and S p orbitals. b) Views of the xz, yz, and xy planes highlighting π interactions between Ru d orbitals and S p orbitals.

Mulliken atomic spin densities are consistent with these expectations (Table 1). For $\{\text{Ru}(\text{SR})_3\}^{11}$, large spin densities at Ru (0.62), S2 (0.17), and S6 (0.20) are observed, suggesting

Table 1: Mulliken atomic spin densities.

Complex (total spin) ^[a]	Ru	S2	S3	S6
$\{\text{Ru}(\text{SR})_3\}^{10}$ ($S=0$) ^[b]	0.84	0.21	0.47	0.31
$\{\text{Ru}(\text{SR})_3\}^{11}$ ($S=1/2$)	0.62	0.17	0.02	0.20
$\{\text{Ru}(\text{SR})_3\}^{12}$ ($S=0$)	0.19	0.10	0.03	-0.06

[a] The total spin includes additional ligand contributions not included in the table. [b] Values reported were calculated for the triplet ground state and are assumed to represent the absolute value of the spin density for the singlet diradical ground state.^[13]

that the ground state is best described as a resonance of Ru^{III} thiolate and Ru^{II} thiyl radical. The location and magnitude of spin densities for the singlet diradical $\{\text{Ru}(\text{SR})_3\}^{10}$ were taken from calculations for the triplet ground state as in previous studies.^[13] Spin localization is observed on Ru (0.84), S2 (0.21), S3 (0.47), and S6 (0.31). These results are consistent with a delocalized Ru^{III} thiyl radical with contributions from states including Ru^{IV} thiolate and Ru^{II} dithiyl radical.

Partial quantitative molecular orbital diagrams for $\{\text{Ru}(\text{SR})_3\}^{10}$ and $\{\text{Ru}(\text{SR})_3\}^{11}$ are shown in Figure 3 and Figure S1 in the Supporting Information, respectively. For both complexes, orbitals 239 and 240 are metal-centered ($d_{x^2-y^2}$ and d_{z^2}) virtual orbitals. Both complexes also have occupied S-centered orbitals (out-of-phase $S2 p_x$ and $S6 p_z$); in $\{\text{Ru}(\text{SR})_3\}^{10}$, these are 237 α and 236 β . The $\alpha \pi^*$ orbitals $\text{Ru} d_{yz}/$

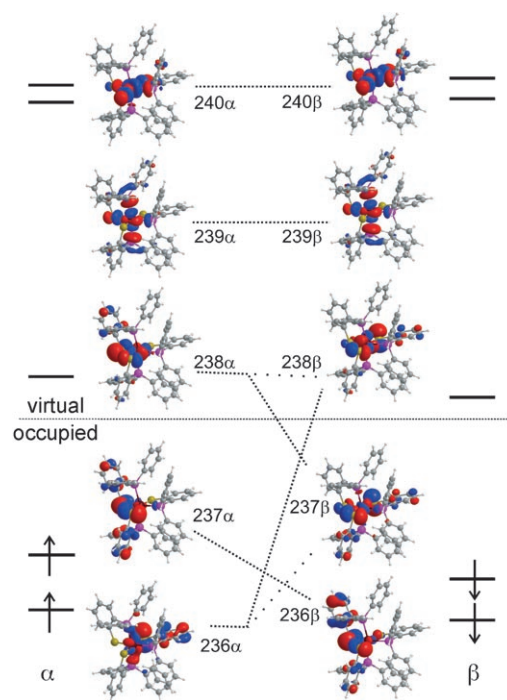


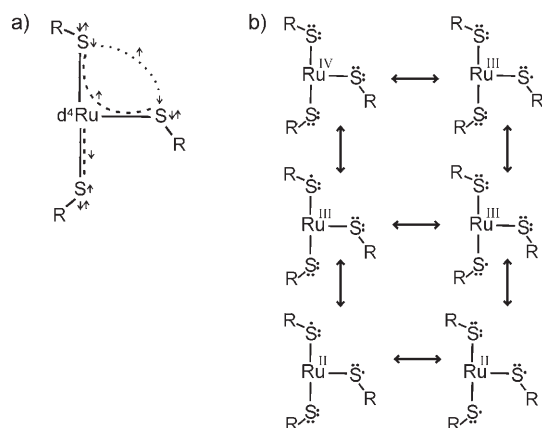
Figure 3. Partial MO diagram of $\{\text{Ru}(\text{SR})_3\}^{10}$.

$S3 p_y$ and $\text{Ru} d_{xz}/S2 p_x/S6 p_z$ are identified as 236 α (occupied) and 238 α (virtual). The $\beta \pi^*$ orbitals are linear combinations of their α counterparts. The $\text{Ru} d_{xz}/S2 p_x/S6 p_z$ contribution is largest in 237 β (occupied), while 238 β (virtual) is predominately $\text{Ru} d_{yz}/S3 p_y$ in character. Thus, orbitals 236 α and 238 α (or a linear combination of the two) represent magnetic orbitals of the $\{\text{Ru}(\text{SR})_3\}^{10}$ diradical. The partial overlap of the magnetic orbitals may be responsible for the preference for a singlet, rather than triplet, ground state. For $\{\text{Ru}(\text{SR})_3\}^{11}$, the odd electron lies in orbital 237 α , a π^* orbital (Figure S1 in the Supporting Information).

Metal-coordinated thiyl radicals typically display a low-energy charge-transfer band in solution.^[13] The lowest 20 excited states of singlet $\{\text{Ru}(\text{SR})_3\}^{10}$ were determined by time-dependent DFT (Table S3 in the Supporting Information). Excitation 4 is the most intense band, with large contributions from 237 α to 238 α and 236 β to 238 β at an energy of 9200 cm^{-1} . A pair of intense transitions with large ligand-to-ligand contributions are also observed at 11300 and 12100 cm^{-1} (excitations 6 and 7). Experimentally, $\{\text{Ru}(\text{SR})_3\}^{10}$ displays a band at 11600 cm^{-1} in acetonitrile or acetone.^[18,19]

The electronic structure of $\{\text{Ru}(\text{SR})_3\}^{10}$ is best described as a diradical with unpaired electrons delocalized about $\text{Ru} d_{yz}/S3 p_y$ and $\text{Ru} d_{xz}/S2 p_x/S6 p_z$, as shown in Scheme 2. The half-occupied orbitals overlap slightly, but the major components are orthogonal. This orientation precludes rapid combination to the disulfide. In fact, decay of $\{\text{Ru}(\text{SR})_3\}^{10}$ to disulfide is slow with a large entropic barrier,^[18] facilitating reactivity with other substrates.

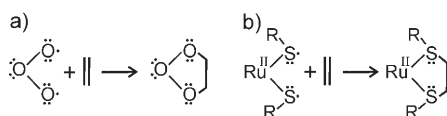
When $\{\text{Ru}(\text{SR})_3\}^{10}$ is generated in the presence of methyl ketones, C–S bond formation occurs.^[19] The reaction is presumed to involve the enol tautomer; S-based reactivity



Scheme 2. a) Representation of the singlet diradical ground state of $\{\text{Ru}-(\text{SR})_3\}^{10}$. Electrons on the dashed lines are delocalized between Ru and S. The electron on the dotted line is delocalized between S2 and S6. b) Resonance depictions of the singlet diradical ground state of $\{\text{Ru}-(\text{SR})_3\}^{10}$.

of oxidized Ru thiolates with alkenes was reported by Goh, Webster, and co-workers.^[22] As such, $\{\text{Ru}-(\text{SR})_3\}^{11}$ was oxidized in the presence of styrene by bulk electrolysis. The voltammogram after oxidation (1 e^- ; Figure S2 in the Supporting Information) reveals a product with a single redox event at $+800\text{ mV}$, assigned as $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$. This is a shift of $+1150\text{ mV}$ from $[\text{Ru}(\text{dppbt})_3]$ and is consistent with a Ru^{II} dithioether.^[23] Electrospray ionization mass spectrometry (ESI-MS) of the product (Figure S3 in the Supporting Information) reveals a parent-ion peak at m/z 1085.132 with an isotopic envelope consistent with the anticipated 1-phenylethyl dithioether product, $[\text{Ru}(\text{dppbt})(\text{dppbt}_2)\text{-}\{\text{CH}_2\text{CH}(\text{Ph})\}]^+$. Alkene addition to oxidized nickel dithiolenes has been reported, although recent studies indicate intraligand as opposed to interligand alkene addition.^[24,25] In our system, only interligand addition is possible.

Based on the current analysis, the singlet diradical ground state of $\{\text{Ru}-(\text{SR})_3\}^{10}$ is akin to the generally accepted ground state of ozone. To a first approximation, the Ru^{II} dithiyl radical fragment and O_3 are isoelectronic. Ozone reacts with alkenes to initially generate a primary ozonide,^[26] whereas $\{\text{Ru}-(\text{SR})_3\}^{10}$ adds alkenes to generate a dithioether (Scheme 3).



Scheme 3. a) Ozonolysis of alkenes to the initial primary ozonide. b) Alkene addition to $\{\text{Ru}-(\text{SR})_3\}^{10}$.

Experimental Section

Calculations: The initial structure analysis was performed by using Jaguar^[27] and the LACVP(Fe)/6-31G(d)(rest) basis set. The final geometry optimization and analysis of electronic states were carried out with the B3LYP functional and the mixed basis set (6-31g(d) for carbon and hydrogen atoms, 6-311g(d,p) for sulfur and phosphorus

atoms, and LanL2DZ for ruthenium) as implemented in Gaussian 03.^[28] Initial Cartesian coordinates were taken from the crystallographic coordinates of the anionic complex, $[\text{PPN}][\text{Ru}(\text{dppbt})_3]$ ($\text{PPN}^+ = (\text{PPh}_3)_2\text{N}^+$).

Synthetic methods: Solutions of $[\text{Ru}(\text{dppbt})_3]$ were prepared as described previously.^[23] Mass spectra were recorded at the Mass Spectrometry Application and Collaboration Facility in the Chemistry Department at Texas A&M University.

$[\text{PPN}][\text{Ru}(\text{dppbt})(\text{dppbt}_2)\{\text{CH}_2\text{CH}(\text{Ph})\}]$: Styrene (2.0 ml) was added to a solution of freshly prepared $[\text{Ru}(\text{DPPBT})_3]$ in acetonitrile (2 mm, 10 ml) containing *n*-tetrabutylhexafluorophosphate (0.100 M) chilled to -20°C in a foil-wrapped spectroelectrochemical cell. Bulk oxidation at $+0.620\text{ V}$ resulted in a one-electron oxidation and formation of the desired product as an air- and thermally stable yellow solution. ESI-MS obsd (calcd): m/z : 1085.132 (1085.133). $E_{1/2} = +0.80\text{ V}$ vs. Ag/Ag^+ .

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thiyl radicals donate one electron, and sulfenylium cations donate zero electrons.

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