Angewandte
Chemie

Electronic-Structure Calculations

DOI: 10.1002/anie.200700297

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

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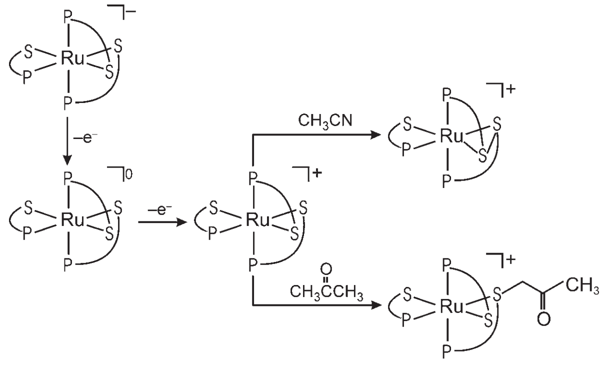
The nucleophilicity of transition-metal thiolates has been attributed to a metal–sulfur d–p π interaction, which results in high sulfur character for the occupied frontier orbitals.[1–3] Consequently, oxidation of metal thiolates may be either sulfur- or metal-centered. Recent studies have focused on 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 [Ru-(dppbt)$_3$]$^+$ (dppbt = 2-diphenylphosphinothiaphenolate) displays sulfur-centered reactivity (Scheme 1) and is ideal for DFT investigations.[18,19]



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

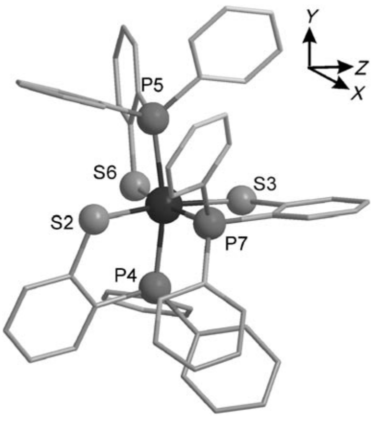


Figure 1. Structure of [Ru(dppbt)$_3$]^n (n = −1, 0, +1) with numbering scheme and coordinate system.

Figure 1 shows atom positions and coordinates for the family of complexes in this study. To avoid formal oxidation states, a {Ru-(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 {Ru-(SR)$_3$}^{12}, {Ru-(SR)$_3$}^{11}, and {Ru-(SR)$_3$}^{10}, respectively. The {Ru-(SR)$_3$}^{12} and {Ru-(SR)$_3$}^{11} complexes were analyzed as a singlet ($S = 0$) and doublet ($S = 1/2$), consistent with experiment.[18,19] The reactive intermediate, {Ru-(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 {Ru-(SR)$_3$}^{10} can be gained from the qualitative MO diagram of {Ru-(SR)$_3$}^{12} (Figure 2). The HOMO and HOMO−1 have π* character with significant ruthenium and sulfur contributions. Oxidation to {Ru-(SR)$_3$}^{11} removes an electron from the Ru d$_{yz}$/S3 p$_y$ π* orbital, while further oxidation to {Ru-(SR)$_3$}^{10} removes an electron from the three-center π interaction between Ru d$_{xz}$, S2 p$_x$, and S6 p$_z$. In each case, the oxidation cannot be considered as strictly metal- or ligand-centered.

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[**] This research was supported in part by the National Science Foundation (CHE-0238137) and by the National Center for Supercomputing Applications utilizing the University of Kentucky High Performance Computing System. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (43917-AC3) for partial support of this work.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

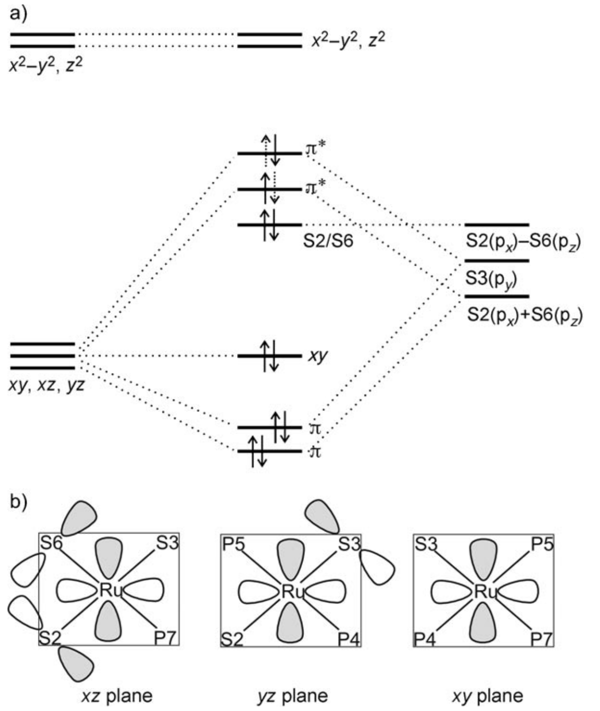


Figure 2. a) Qualitative MO diagram for [Ru(dppbt)$_3$]^n ($n=-1$, 0, $+1$) showing π interacations of Ru d orbitals and S p orbitals. b) Views of the *xz*, *yz*, and *xy* planes highlighting π interactions between Ru d orbitals and S p orbitals.

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

Table 1: Mulliken atomic spin densities.

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

Partial quantitative molecular orbital diagrams for {Ru-(SR)$_3$}^{10} and {Ru-(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 {Ru-(SR)$_3$}^{10}, these are 237α and 236β. The α π* orbitals Ru d_{yz}/S3 p_y and Ru d_{xz}/S2 p_x/S6 p_z are identified as 236α (occupied) and 238α (virtual). The β π* orbitals are linear combinations of their α counterparts. The Ru d_{xz}/S2 p_x/S6 p_z contribution is largest in 237β (occupied), while 238β (virtual) is predominately Ru d_{yz}/S3 p_y in character. Thus, orbitals 236α and 238α (or a linear combination of the two) represent magnetic orbitals of the {Ru-(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 {Ru-(SR)$_3$}^{11}, the odd electron lies in orbital 237α, a π* orbital (Figure S1 in the Supporting Information).

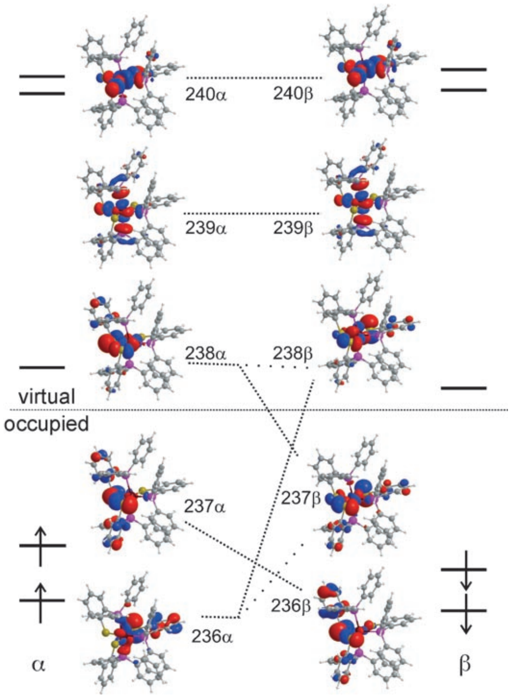
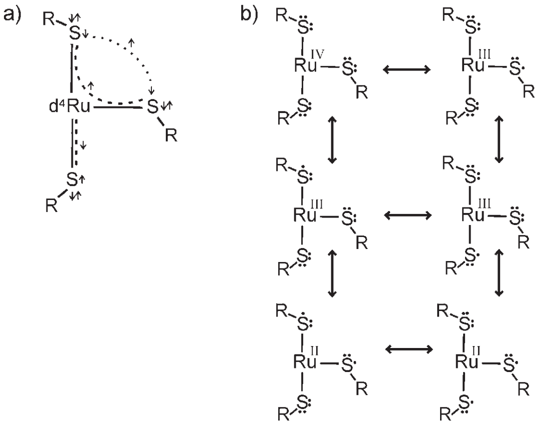


Figure 3. Partial MO diagram of {Ru-(SR)$_3$}^{10}.

Metal-coordinated thiyl radicals typically display a low-energy charge-transfer band in solution.[13] The lowest 20 excited states of singlet {Ru-(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 237α to 238α and 236β to 238β at an energy of 9200 cm^{-1}. A pair of intense transitions with large ligand-to-ligand contributions are also observed at 11 300 and 12 100 cm^{-1} (excitations 6 and 7). Experimentally, {Ru-(SR)$_3$}^{10} displays a band at 11 600 cm^{-1} in acetonitrile or acetone.[18,19]

The electronic structure of {Ru-(SR)$_3$}^{10} is best described as a diradical with unpaired electrons delocalized about Ru d_{yz}/S3 p_y and 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 {Ru-(SR)$_3$}^{10} to disulfide is slow with a large entropic barrier,[18] facilitating reactivity with other substrates.

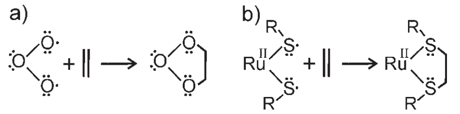
When {Ru-(SR)$_3$}^{10} is generated in the presence of methyl ketones, C–S bond formation occurs.[19] The reaction is presumed to involve the enol tautomer; S-based reactivity



Scheme 2. a) Representation of the singlet diradical ground state of $\{\text{Ru-(SR)}_3\}^{10}$. 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 $\{\text{Ru-(SR)}_3\}^{10}$.

of oxidized Ru thiolates with alkenes was reported by Goh, Webster, and co-workers.[22] As such, $\{\text{Ru-(SR)}_3\}^{11}$ 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 mV, assigned as Ru$^{\text{III}}$/Ru$^{\text{II}}$. This is a shift of +1150 mV from [Ru(dppbt)$_3$] and is consistent with a Ru$^{\text{II}}$ 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 dithiother product, [Ru(dppbt)(dppbt$_2$){CH$_2$CH(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 $\{\text{Ru-(SR)}_3\}^{10}$ is akin to the generally accepted ground state of ozone. To a first approximation, the Ru$^{\text{II}}$ dithiyl radical fragment and O$_3$ are isoelectronic. Ozone reacts with alkenes to initially generate a primary ozonide,[26] whereas $\{\text{Ru-(SR)}_3\}^{10}$ adds alkenes to generate a dithioether (Scheme 3).



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

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, [PPN][Ru(dppbt)$_3$] (PPN$^+$ = (PPh$_3$)$_2$N$^+$)

Synthetic methods: Solutions of [Ru(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.

[PPN][Ru(dppbt)(dppbt$_2$){CH$_2$CH(Ph)}]: Styrene(2.0 ml) was added to a solution of freshly prepared [Ru(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 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 V vs. Ag/Ag$^+$.

Received: January 22, 2007
Published online: April 20, 2007

Keywords: density functional calculations · diradicals · electronic structure · oxidation · sulfur

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

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