## Alkyne Addition to a Metal-Stabilized Thiyl Radical: Carbon–Sulfur Bond Formation between 1-Octyne and [Ru(SP)<sub>3</sub>]<sup>+</sup>

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The metal-stabilized thiyl radical complex [Ru(SP)<sub>3</sub>]<sup>+</sup>, [Ru-1]<sup>+</sup>, {SP = 2-(diphenylphosphanyl)benzenethiolate} adds 1octyne across the cis-sulfur sites to yield the S-alkylated dithiolene product [Ru-1·octyne]<sup>+</sup>. The product complex exists as a pair of inseparable geometric isomers, which were char-

### Introduction

We have recently reported a series of studies on the addition of alkenes to the oxidized metal-thiolate complexes  $[M(SP)_3]^+$  {M = Ru, Re; SP = 2-(diphenylphosphanyl)benzenethiolate}.<sup>[1-4]</sup> Although formally in the +4 oxidation state, the complexes are regarded as metal-stabilized thivl radicals because of the delocalization of spin density over the metal and sulfur donors, Scheme 1.<sup>[4]</sup> Two of the S ligands are optimally positioned for C-S bond forming reactions with alkenes, which generate diamagnetic Ru<sup>II</sup>-dithioether complexes. The reaction is initiated by electrochemical (Scheme 2 top) or chemical (Scheme 2 middle) oxidation of [Ru-1]-. Similar alkene additions are reported with other oxidized ruthenium thiolates<sup>[5]</sup> and oxidized metal-dithiolenes.<sup>[6-9]</sup> For [Ru-1]<sup>+</sup>, the alkene addition rate constant varies from  $4.3 \times 10^7 \text{ m}^{-1} \text{ s}^{-1}$  to  $2.9 \times 10^3 \text{ m}^{-1} \text{ s}^{-1}$ , and higher values are observed for "electron-rich" alkenes.<sup>[1]</sup> While alkene addition to [Ru-1]<sup>+</sup> is irreversible, equilibrium binding constants for ethylene to  $[\text{Re-1}]^{n+}$  (n = 0, 1, 2) depend on the complex charge. Three distinct bind-



Scheme 1. Metal-coordinated thiyl radical complex [Ru-1]<sup>+</sup> with calculated spin density values (italics).[4]

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acterized by X-ray crystallography, <sup>31</sup>P NMR spectroscopy, and cyclic voltammetry. By using electrochemical methods, the rate constant for 1-octyne addition was determined as  $8.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

ing regimes with equilibrium constants over 20 orders of magnitude are accessible within a 240 mV potential window.<sup>[2]</sup>



Scheme 2. Reactivity of [Ru-1]+ with alkenes and alkynes.

Herein, we describe carbon-sulfur bond forming reactions between  $[Ru-1]^+$  and 1-octyne (Scheme 2 bottom). Alkyne addition across the thiolate donors of neighboring SP chelates yields a new tetradentate, S-alkylated dithiolene ligand. The intraligand addition of alkynes across sulfur donors of Mo-tris(dithiolene)s was employed by the Fekl group to selectively displace a single dithiolene donor.<sup>[10]</sup> Similarly, Yan and co-workers detected a variety of metalfree alkyne disulfuration and hydrosulfuration products following alkyne addition to a dinuclear Co-thiolate.<sup>[11]</sup> Dis-

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#### **Results and Discussion**

Oxidation of [Ru-1]<sup>-</sup> with ferrocenium hexafluorophosphate (2 equiv.) in the presence of 1-octyne yields the diamagnetic Ru(II) complex [Ru-1·octyne]PF<sub>6</sub> as a dark orange product. Recrystallization from THF/hexane gives pure [Ru-1·octyne]PF<sub>6</sub> as a yellow solid. The ESI-MS spectrum displays a parent peak at m/z = 1091.18, consistent with the theoretical value, m/z = 1091.37, for the desired complex, Figure S1.

Single crystals of [Ru-1·octyne]PF<sub>6</sub> for X-ray diffraction studies were obtained by evaporation of chlorobenzene/hexane mixtures. The asymmetric unit consists of co-crystallized mixtures of two geometric isomers (Scheme 2 bottom). Unlike the related alkene addition product [Ru-1·pmethylstyrene]PF<sub>6</sub>, the isomers of [Ru-1·octyne]PF<sub>6</sub> could not be separated by crystallization or other methods.<sup>[1]</sup> Analyses of multiple crystals consistently reveal co-crystallized products. The isomers differ based on the relative position of the hexyl side chain, which can be located either at the R<sub>1</sub> (nearest S *trans* to S, major) or R<sub>2</sub> (nearest S *trans* to P, minor) position. An ORTEP<sup>[14]</sup> representation of the major [Ru-1·octyne]<sup>+</sup> isomer is provided in Figure 1.



Figure 1. ORTEP<sup>[14]</sup> representation of  $[\text{Ru-1-octyne}]^+$  showing a single isomer with the hexyl side chain (C57–C62) extending from C56. For clarity, the co-crystallized isomer with a hexyl side chain originating from C55 is not shown (see Supporting Information).

The [Ru-1·octyne]<sup>+</sup> complex contains a pseudo-octahedral Ru ion in a meridional  $P_3S_3$  donor environment. The Ru–S and Ru–P bond lengths range from 2.3106(15) to 2.3890(14) Å and 2.3294(14) to 2.3823(14) Å, respectively, in accord with related structures, Table 1.<sup>[1,3,15]</sup> The alkynyl carbon atoms of 1-octyene provide a bridge, C55 and C56, between the *cis*-sulfur donors, S2 and S3. The S2–C55 and S3–C56 bond lengths of 1.798(8) and 1.796(7) Å, respectively, confirm covalent attachment of 1-octyne to the metal-stabilized thiyl radical core with values similar to those observed in alkene addition products such as  $[\text{Ru-1}\cdot\text{C}_2\text{H}_4]^+$ . The S2–C55–C56–S3 torsion angle, 8.3(8)°, approaches zero as expected for an *S*-alkylated dithiolene chelate; in contrast to the torsion angle of –47.3(3)° for the dithioether fragment in  $[\text{Ru-1}\cdot\text{C}_2\text{H}_4]^+$ . The C55–C56 bond length, 1.322(10) Å, matches the values of 1.312(9) and 1.394(10) Å reported by Yan in their alkyne addition products and is consistent with a C–C double bond.<sup>[12,13]</sup>

Table 1. Selected bond lengths [Å] and angles [°] of [Ru-1· octyne]<sup>+</sup>, [Ru-1·C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>,<sup>[3]</sup> and [Ru-1]<sup>-,[15]</sup>

	[Ru-1·octyne] <sup>+</sup>	$[\text{Ru-1-}C_2H_4]^+$	[Ru-1] <sup>_</sup>
Ru–S1	2.3890(14)	2.3856(9)	2.402(1)
Ru–S2	2.3663(15)	2.3749(9)	2.445(1)
Ru–S3	2.3106(15)	2.3365(9)	2.394(1)
Ru–P1	2.3294(14)	2.3290(9)	2.295(1)
Ru–P2	2.3422(14)	2.3965(10)	2.353(1)
Ru–P3	2.3823(14)	2.3648(9)	2.340(1)
S2-C55	1.798(8)	1.836(4)	
S3-C56	1.796(7)	1.843(4)	
C55-C56	1.322(10)	1.510(5)	
S2-Ru-S3	86.22(6)	87.71(3)	89.77(2)
Ru-S2-C55	103.1(3)	104.52(12)	
Ru-S3-C56	105.2(3)	103.59(12)	
S2-C55-C56-S3	8.3(8)	-47.3(3)	

The <sup>31</sup>P NMR of crystalline [Ru-1•octyne]<sup>+</sup> displays a pair of second-order spectra, Figure S2. The relative intensities, chemical shifts, and coupling constants for the major (60%) ( $\delta_1 = 57.2$ ,  $\delta_2 = 42.8$ ,  $\delta_3 = 35.8$  ppm;  $J_{12} = J_{13} = 31$ and  $J_{23} = 313$  Hz) and minor (40%) isomers ( $\delta_1 = 57.2$ ,  $\delta_2 = 43.0$ ,  $\delta_3 = 36.2$  ppm;  $J_{12} = J_{13} = 31$  and  $J_{23} = 313$  Hz) are similar to values previously reported for the two isomers of [Ru-1•p-methylstyrene]<sup>+</sup>.<sup>[1]</sup> In that study, the isomer with the substituted carbon positioned nearest the S *trans* to S was identified as the major alkene addition product. This is consistent with the higher calculated spin densities<sup>[4]</sup> on the S *trans* to P (0.31) as compared to the S *trans* to S (0.21) and Tedder's Rules for radical alkene addition.<sup>[16]</sup> Given similar product ratios, we assign the major isomer of [Ru-1•octyne]<sup>+</sup> likewise.

The cyclic voltammogram of  $[Ru-1 \cdot octyne]^+$  reveals a single, reversible redox event at +300 mV (vs. ferrocenium/ ferrocene) [Figure 2 (top)] assigned to the Ru<sup>III/II</sup> couple. No other redox couples are observed, which indicates that both isomers have the same potential. Further, the Ru<sup>II/I</sup> couple lies outside the solvent window, which precludes the possibility of reduction promoted release of 1-octyne. As shown in Table 2, the redox couple is shifted by +1130 mV with respect to the Ru<sup>III/II</sup> couple in the thiolate precursor [Ru-1]<sup>-,[17]</sup> Similar large shifts are observed for the related dithioether derivatives.<sup>[1,3,4,15]</sup>

The addition of 1-octyne to electrochemically generated  $[Ru-1]^+$  was monitored by cyclic voltammetry. As shown in Figure 2 (bottom), the cyclic voltammogram of  $[Ru-1]^-$  recorded in the presence of 1-octyne displays anodic peaks associated with the oxidation of  $[Ru-1]^-$  to [Ru-1] at -830 mV and of [Ru-1] to  $[Ru-1]^+$  at -60 mV. Following the second oxidation, 1-octyne rapidly adds to  $[Ru-1]^+$  to yield  $[Ru-1\cdotoctyne]^+$ , as identified by its  $Ru^{III/II}$  redox couple at





Figure 2. (top) Cyclic voltammogram of  $[Ru-1 \circ ctyne]^+$  (1.0 mM in CH<sub>3</sub>CN with 0.1 M TBAHFP) at a scan rate of 200 mV/s. (bottom) Cyclic voltammogram of  $[Ru-1]^-$  (2.0 mM in CH<sub>3</sub>CN with 0.1 M TBAHFP) in the presence of 1-octyne (200 mM) at a scan rate of 200 mV/s. Potentials are referenced vs. the ferrocenium/ferrocene couple.

Table 2. Electrochemical comparison of  $[Ru-1]^-$ ,  $[Ru-1 \cdot octyne]^+$ , and  $[Ru-1 \cdot C_2H_4]^+$ .

Redox couple	$\frac{E_{1/2} (\Delta E)}{\mathrm{mV^{[a]}}} /$	Formal oxidation states	Ref.
$\frac{[\text{Ru-1}]^{0/-}}{[\text{Ru-1}\cdot\text{octyne}]^{2+/+}}$ $[\text{Ru-1}\cdot\text{C}_2\text{H}_4]^{2+/+}$	-830 (95)	Ru <sup>III/II</sup>	[17]
	+300 (75)	Ru <sup>III/II</sup>	this work
	+285 (80)	Ru <sup>III/II</sup>	[3]

[a] Potentials vs. ferrocenium/ferrocene reference.  $\Delta E = E_{\rm pc} - E_{\rm pa}$  at a scan rate of 200 mV/s. Measurements were recorded in dry, degassed acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

+300 mV. The rapid, irreversible binding of 1-octyne to  $[Ru-1]^+$  is also evident by the decrease in cathodic current for the  $[Ru-1]^{+/0}$  and  $[Ru-1]^{+/0}$  couples.

The rate constant for 1-octyne addition to  $[Ru-1]^+$  was evaluated by using methods previously described for alkene addition. A series of cyclic voltammograms were recorded over a range of scan rates, 100-1000 mV/s, for solutions containing [Ru-1]<sup>-</sup> and 1-octyne. The data were simultaneously fitted over all scan rates by using the Digisim software package<sup>[18]</sup> to determine a second-order rate constant of  $8.7 \times 10^3 \,\mathrm{m}^{-1} \,\mathrm{s}^{-1}$  for the alkyne addition reaction. This value is two orders of magnitude lower than the corresponding alkene addition rate constant for 1-hexene to [Ru-1]<sup>+</sup>, 7(2)  $\times 10^{5}$  m<sup>-1</sup>s<sup>-1</sup>.<sup>[1]</sup> A 100–1000-fold decrease in rate constant is typical for electrophilic substitutions of comparable alkynes and alkenes. This corroborates our previous observation based on substituent effects of alkene addition to [Ru-1]<sup>+</sup> that our metal-stabilized thiyl radical complex is electrophilic.

#### Conclusions

The previously reported addition reaction of alkenes to the metal-stabilized thiyl radical [Ru-1]<sup>+</sup> has been extended to alkynes. By using similar chemical oxidation strategies, 1octyne is efficiently added to [Ru-1]<sup>+</sup> to yield an *S*-alkylated dithiolene ligand that remains coordinated to the metal center. As with alkenes, the addition of alkyne to the Ru core is irreversible, which is attributable to the stability of the Ru<sup>II</sup> oxidation state in a pseudo-octahedral environment. The rate constant for 1-octyne addition was found to be approximately 100 times lower than those of the corresponding alkenes, in line with the electrophilic character of our metal-stabilized thiyl radical. We are currently exploring the addition of other alkynes and related unsaturated compounds to establish the scope and limits of this reactivity.

#### **Experimental Section**

All reactions were performed under an inert nitrogen or argon atmosphere by using standard Schlenk techniques. Solvents were purified, dried, and freshly distilled and degassed immediately prior to use. The ruthenium thiolate precursors HNEt<sub>3</sub>[Ru-1]<sup>[19]</sup> and PPN[Ru-1]<sup>[15]</sup> were prepared as described previously. All other chemicals were purchased from Aldrich and used as received. Elemental analyses were obtained from Midwest Microlab, LLC in Indianapolis, Indiana. Electrochemical measurements were performed with a PAR 273A potentiostat/galvanostat in dry, degassed acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte. Additional details of the electrochemical measurements are described in the Supporting Information.

**Crystallographic Studies:** Crystals of [Ru-1·octyne]PF<sub>6</sub> adequate for X-ray diffraction studies were grown from chlorobenzene/hexane. [Ru(C<sub>62</sub>H<sub>55</sub>P<sub>3</sub>S<sub>3</sub>)]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>: yellow prism, monoclinic, space group  $P_{2_1}/n$ , a = 12.0367(4), b = 24.2458(10) Å, c = 20.1572(9) Å,  $\beta = 98.291(3)^\circ$ , V = 5821.2(7) Å<sup>3</sup>,  $r_{calcd.} = 1.409$  g/cm<sup>3</sup>, Z = 4. Data were collected on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer at 100 K by using Mo- $K_a$  radiation. For 8452 reflections,  $I > 2\sigma(I)$  [R(int) 0.061], the final anisotropic full-matrix least-squares refinement on  $F^2$  for 679 variables converged at R1 = 0.078 and wR2 = 0.133 with a GOF of 1.06. Full details of the data collection and structure refinement are provided in the Supporting Information. CCDC-844993 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**[Ru-1·octyne]PF<sub>6</sub>:** To a yellow solution of HNEt<sub>3</sub>[Ru-1] (100 mg, 0.0935 mmol) in dry acetonitrile (40 mL) was added 1-octyne (1.38 mL, 9.35 mmol) by a syringe. The solution was cooled to 0 °C in an ice bath, and a blue solution of ferrocenium hexafluorophosphate (61.9 mg, 0.0187 mmol) in acetonitrile (30 mL) was slowly added by a cannula. The resulting solution was stirred overnight, during which time the solution gradually developed a dark orange color. The solvent was removed by rotary evaporation to yield an oily orange residue. The crude product was washed with an excess of hot water ( $\approx$ 300 mL) and diethyl ether (100 mL). The crude product was recrystallized from THF/hexane. Yield: 49 mg (0.040 mmol, 43%). X-ray quality crystals were obtained by slow evaporation of a 1:2 chlorobenzene/hexane mixture.  $E_{1/2}$  (Ru<sup>III</sup>/

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Ru<sup>II</sup>) = +356 mV. +ESI-MS: calcd. for C<sub>62</sub>H<sub>56</sub>P<sub>3</sub>S<sub>3</sub>Ru *m/z* (*Z* = 1) = 1091.37; found: 1091.18. C<sub>62</sub>H<sub>56</sub>F<sub>6</sub>P<sub>4</sub>RuS<sub>3</sub> (1236.26): calcd. C 60.23, H 4.57; found C 58.03, H 3.72. Electronic absorption:  $\lambda_{max}$ (ε [cm<sup>-1</sup>], M<sup>-1</sup>) = 305 (9527), 361 nm (shoulder). FTIR (KBr pellet):  $\tilde{v}$  = 3052, 2929, 2852, 1434, 1086, 837, 559, 531 cm<sup>-1</sup>.

**Supporting Information** (see footnote on the first page of this article): Details of X-ray diffraction and electrochemical methods, ESI-MS and <sup>31</sup>P NMR spectra, and cyclic voltammograms are presented.

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