[**2**]$Cl_6 \cdot 16H_2O$: To a solution of $Na[AuCl_4]$ (0.10 g, 0.28 mmol) in water (2 mL) was added 2,2′-thiodiethanol (0.16 mL). The resulting colorless solution was added to a solution of [**1**]$Cl_2 \cdot 5H_2O$ (0.20 g, 0.24 mmol) in water (40 mL). The mixture was stirred at RT for 30 min, followed by addition of several drops of a saturated NaCl aqueous solution. The reaction solution was allowed to stand at RT for 5 days, which gave dark green-brown microcrystals. Yield: 0.22 g (82 %); elemental analysis for $[Au_2\{Pd[Co(C_6H_{18}N_3S_3)_3]_2\}_2]Cl_6 \cdot 16H_2O$: calcd C 12.77, H 4.64, N 7.45; found: C 12.71, H 4.69, N 7.43; ^{13}C NMR (500 MHz, D_2O, DSS): $\delta = 34.86$, 35.55, 40.40 (CH_2S), 48.44, 56.00, 57.22 (CH_2N); UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\log\varepsilon$) = 18.36 (3.05), 26.91 (4.63), 30.56 (4.76), 33.6 (4.7 sh), 43.6 cm^{-1} (4.8 $M^{-1}cm^{-1}$ sh).

[**3**]$(NO_3)_6 \cdot 9H_2O$: To a solution of [**1**]$(NO_3)_2 \cdot 1.5H_2O$ (0.20 g, 0.24 mmol) in water (40 mL), $AgNO_3$ (0.04 g, 0.24 mmol) was added. The mixture was stirred at RT for 30 min, followed by addition of several drops of a saturated aqueous $NaNO_3$. The reaction solution was allowed to stand at RT for 5 days, which gave dark green-brown microcrystals. Yield: 0.20 g (80 %); elemental analysis for $[Ag_2\{Pd[Co(C_6H_{18}N_3S_3)_3]_2\}_2](NO_3)_6 \cdot 9H_2O$: calcd: C 13.65, H 4.29, N 11.94; found: C 13.44, H 4.28, N 11.71; ^{13}C NMR (500 MHz, D_2O, DSS): $\delta = 33.03$, 35.21, 39.27 (CH_2S), 50.02, 55.98, 57.25 (CH_2N); UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\log\varepsilon$) = 17.82 (3.00), 27.1 (4.6 sh), 30.56 (4.85), 33.8 (4.7 sh), 43.7 cm^{-1} (4.8 $M^{-1}cm^{-1}$ sh).

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[9] Crystal structure analysis: General: Bruker CCD area detector, $T = 203$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), semiempirical absorption correction with SADABS. The structures were solved by direct methods (SIR 92) and refined with full-matrix least-squares procedures on F^2 using SHELXL-93. [**2**]$Cl_6 \cdot 16H_2O$: crystal size $0.10 \times 0.09 \times 0.08$ mm, orthorhombic, space group *Pbcn*, $a = 18.888(2)$, $b = 13.397(1)$, $c = 28.211(2)$ Å, $V = 7138.6(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.100$ g cm^{-3}, $\mu = 61.40$ cm^{-1}, ω scan mode, $2\theta_{max} = 55.18$, 7869 reflections collected, 7869 independent reflections, 5102 observed reflections ($F > 4\sigma(F)$), 352 parameters, semiempirical absorption correction with SADABS, max./min. transmission 0.647/0.547, R_1 ($F > 4\sigma(F)$) = 0.038, wR_2 (all data) = 0.133, residual electron density 2.22/−1.43 e Å^{-3} (the peaks larger than 1.0 e Å^{-3} were found in the vicinity of heavy atoms). Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined. [**3**]$(NO_3)_6 \cdot 9H_2O$: crystal size $0.25 \times 0.13 \times 0.10$ mm, monoclinic, space group *Pn*, $a = 22.3703(4)$, $b = 13.9570(7)$, $c = 23.4220(4)$ Å, $\beta = 107.633(1)°$, $V = 6969.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.013$ g cm^{-3}, $\mu = 24.23$ cm^{-1}, ω scan mode, $2\theta_{max} = 55.28$, 22 370 reflections collected, 16 071 independent reflections, 13 955 observed reflections ($F > 4\sigma(F)$), 352 parameters, semiempirical absorption correction with SADABS, max./min. transmission 0.746/0.473, R_1 ($F > 4\sigma(F)$) = 0.042, wR_2 (all data) = 0.127, residual electron density 1.15/−0.83 e Å^{-3} (the peaks larger than 1.0 e Å^{-3} were found in the vicinity of heavy atoms and nitrate anions). The asymmetric unit contained two crystallographically independent, yet nearly identical, complex cations [**3**]$^{6+}$. Hydrogen atoms were not included in the calculations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144580 ([**2**]$Cl_6 \cdot 16H_2O$) and -144581 ([**3**]$(NO_3)_6 \cdot 9H_2O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Proton-Coupled Electron Transfer from Sulfur: A S-H/S-D Kinetic Isotope Effect of ≥ 31.1**

My-Hang V. Huynh,* Peter S. White, and Thomas J. Meyer*

There is an extensive redox chemistry of high oxidation state ruthenium(IV) oxo,[1] and osmium(VI) nitrido,[2] and osmium(IV–VI) hydrazido[3] complexes based on multiple electron/atom transfers such as O atom,[4] N^- ion,[3] and H^-

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[*] Dr. M.-H. V. Huynh,[+] Dr. T. J. Meyer,[++] Dr. P. S. White
Department of Chemistry, Venable and Kenan Laboratories
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599–3290 (USA)
E-mail: huynh@lanl.gov
tjmeyer@lanl.gov

[+] Present address:
Los Alamos National Laboratory
Chemistry Division MS J514
Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-9905

[++] Present address:
Los Alamos National Laboratory
ALDSSR MS A127
Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-5450

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ion[5] transfer. Kinetic studies have uncovered reactions which occur with large H/D kinetic isotope effects[6–8] including $k_{\text{O-H}}/k_{\text{O-D}} = 30 \pm 1$ for the oxidation of hydroquinone (H_2Q) to benzoquinone (Q) by *cis*-$[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$, bpy = 2,2′-bipyridine and py = pyridine, [Eq. (1)],[6a] and $k_{\text{N-H}}/k_{\text{N-D}} \geq 41.4 \pm 1.3$ for the reduction of Q to H_2Q by *trans*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{N(H)N(CH}_2)_4\text{O}\}]^+$, tpy = terpyridine, [Eq. (2)].[7]

$$cis\text{-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+} + \text{H}_2\text{Q} \longrightarrow cis\text{-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{py})(\text{H}_2\text{O})]^{2+} + \text{Q} \quad (1)$$

$$2\, trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{N(H)N(CH}_2)_4\text{O}\}]^+ + \text{Q} \longrightarrow 2\, trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2\{\text{NN(CH}_2)_4\text{O}\}]^+ + \text{H}_2\text{Q} \quad (2)$$

The latter two reactions occur by proton-coupled electron transfer with an electron transferred to or from a largely metal-based dπ orbital and a proton to or from a coordinated O or N atom. Herein we report what appears to be the first proton-coupled electron transfer from a S-atom. Its existence may have important implications for the electron-transfer reactivity of Fe–S proteins.[9]

A rapid reaction occurs between the *cis* and *trans* isomers of the osmium(VI) nitrido complex, $[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2(\text{N})]\text{PF}_6$, and 3,5-dimethylbenzenethiol under argon at room temperature to give the corresponding osmium(IV) sulfimido products, *cis*- and *trans*-**1** ([**1A**]PF$_6$ = *trans* and [**1B**]PF$_6$ = *cis*). The net reaction is given in [Eq. 3].

$$[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2(\text{N})]^+ + \text{Me}_2\text{C}_6\text{H}_3\text{SH} \longrightarrow \underset{\mathbf{1}}{[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+} \quad (3)$$

Complex [**1A**]PF$_6$ has been isolated and characterized by X-ray crystallography (Figure 1). In the structure, the distorted octahedral arrangement of ligands around the Os atom in the parent nitrido complex is retained. The Os–N$_{\text{tpy}}$ bond lengths range from 2.015(10) Å to 2.129(9) Å with the shortest Os–N$_{\text{tpy}}$ bond *trans* to the sulfimido ligand. Angle N1-S1-C41 = 101.6(5)° is consistent with pseudo sp^3-hybridization and protonation at the S atom.[10] The bond lengths Os1–N1 = 1.906(10) Å and N1–S1 = 1.706(9) Å and the angle Os1-N1-S1 = 130.4(6)° are consistent with an osmium(IV) complex with an Os1–N1 double bond and a N1–S1 single bond. There are clear structural similarities with known osmium(IV) phosphoraniminato (*trans*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2(\text{NPPh}_3)]^+$)[2b] and dialkylhydrazido complexes ($[\text{Os}^{\text{IV}}(\text{tpy})(\text{bpy})\{\text{NN(CH}_2)_4\text{O}\}]^{2+}$,[11] *cis*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NCCH}_3)\{\text{NN(CH}_2)_4\text{O}\}]^+$, and *cis*-$[\text{Os}^{\text{IV}}(\text{tpy})(\text{NCCH}_3)_2\{\text{NN(CH}_2)_4\text{O}\}]^{2+}$).[4]

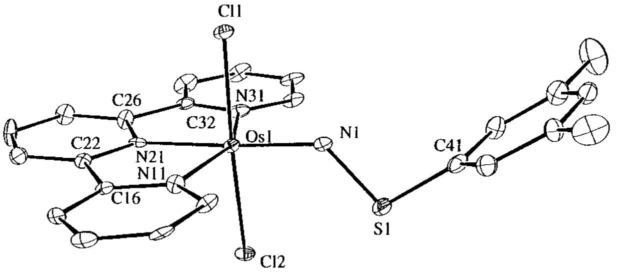


Figure 1. ORTEP plot (thermal ellipsoids set at 30%) of the ion [**1A**]$^+$.

Cyclic voltammetric measurements in 1:1 (v/v) CH$_3$CN:H$_2$O ($\mu = 1.0\,\text{M}$ HNO$_3$, scan rate = 200 mV s^{-1}) reveal that $E_{1/2}$ for the osmium(V/IV) couple decreases by 59 mV pH unit^{-1} from pH = 0 to 1.3 and is pH independent above pH 1.3. From these data, p$K_a = 1.31 \pm 0.03$ for the acid–base equilibrium in Equation (4), (Supporting Information Figure 1).

$$trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+ \xrightleftharpoons{K_a} trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2(\text{NSC}_6\text{H}_3\text{Me}_2)] + \text{H}^+ \quad (4)$$

As found for the hydrazido Os$^{\text{V}}$/Os$^{\text{IV}}$ couple of [Eq. 2], there is also evidence for proton-coupled electron transfer in the redox chemistry of the sulfur-based couple [**1A**]$^+$/[**2A**]$^+$ in [Eq. 5]. When [**1A**]$^+$ and Q are mixed, a rapid reaction occurs in which [**1A**]$^+$ is oxidized to [**2A**]$^+$, and Q is reduced to H$_2$Q, [Eq. (5)].

$$2\, \underset{[\mathbf{1A}]^+}{trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2\{\text{NS(H)C}_6\text{H}_3\text{Me}_2\}]^+} + \text{Q} \xrightarrow{\Delta G^{\circ} = -0.27\,\text{eV}} 2\, \underset{[\mathbf{2A}]^+}{trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NSC}_6\text{H}_3\text{Me}_2)]^+} + \text{H}_2\text{Q} \quad (5)$$

The kinetics of this reaction were studied in 1:1 (v/v) CH$_3$CN:H$_2$O and CH$_3$CN:D$_2$O ([H$^+$] = $1.4 \times 10^{-1}\,\text{M}$, $\mu = 1.0\,\text{M}$ KNO$_3$, and $T = 25.0 \pm 0.1\,^{\circ}\text{C}$) by following characteristic changes in the absorption spectra as [**1A**]$^+$ was converted into [**2A**]$^+$ under pseudo-first-order conditions in Q. At low [Q] ($< 2.80 \times 10^{-3}\,\text{M}$) but with [Q] in pseudo-first-order excess, the kinetics are first order in both [Os$^{\text{IV}}$] and [Q] with the observed rate constants $k_{\text{obs}}(\text{H}_2\text{O}) = (1.44 \pm 0.02) \times 10^1\,\text{M}^{-1}\text{s}^{-1}$ and $k_{\text{obs}}(\text{D}_2\text{O}) = (4.63 \pm 0.09) \times 10^{-1}\,\text{M}^{-1}\text{s}^{-1}$ (Supporting Information Figure 2). A plot of k_X/k_D versus χ_D in

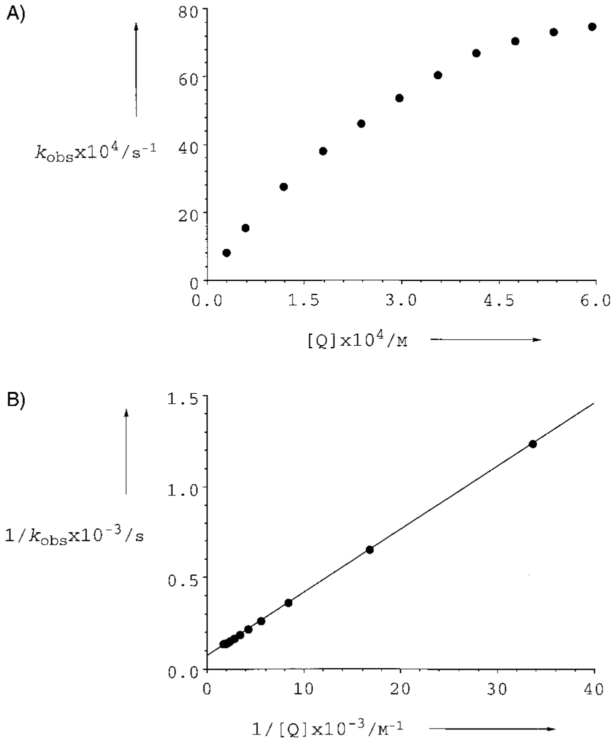
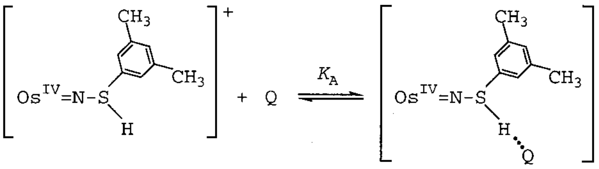


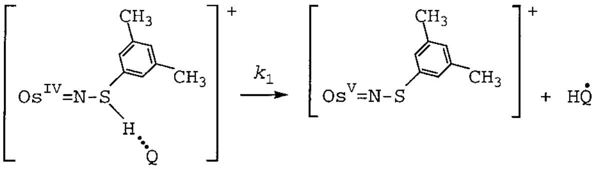
Figure 2. A) Plot of k_{obs} versus [Q] for the reaction between Q and [**1A**]PF$_6$ in 1:1 (v/v) CH$_3$CN:H$_2$O ($25.0 \pm 0.1\,^{\circ}$C, [H$^+$] = $1.4 \times 10^{-1}\,\text{M}$, and $\mu = 1.0\,\text{M}$ KNO$_3$). B) An inverse–inverse plot ($1/k_{\text{obs}}$ versus 1/[Q]) of the plot shown in (A).

$CH_3CN:H_2O/D_2O$ mixtures in which k_X is the rate constant (k_{obs}) at mole fraction D (χ_D) was linear (Supporting Information Figure 3) which reveals that a single proton is involved in the reaction.[12] From the intercept of the plot at $\chi_D = 0$, the H_2O/D_2O kinetic isotope effect $k_{obs}(H_2O)/k_{obs}(D_2O)$ is 31.1 ± 0.2 under these conditions.

When studied over a more extended range, the concentration dependence in [Q] is more complex. As illustrated in Figure 2A and by the linear plot of $1/k_{obs}$ versus $1/[Q]$ (Figure 2B), there is evidence for saturation kinetics with the [Q] dependence consistent with the expression $k_{obs} = \{(2k_1[Q]/([Q]+K_A)\}$ and the mechanism summarized in Eqs. (6)–(8).[7]



(6)



(7)

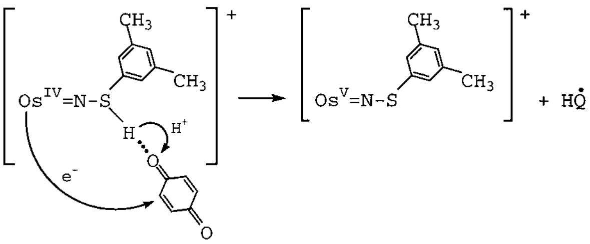
$$[Os^{IV}\{NS(H)C_6H_3Me_2\}]^+ + H\dot{Q} \xrightarrow{\text{rapid}} [Os^{V}(NSC_6H_3Me_2)]^+ + H_2Q \quad (8)$$

Direct evidence was obtained for the putative intermediate at $[Q] = 2.17 \times 10^{-4} - 2.60 \times 10^{-3}\,\text{M}$ by a shift in λ_{max} (a characteristic band of $[\mathbf{1A}]^+$) from 456 nm to 428 nm which subsequently disappeared to give the spectrum of the final product (Supporting Information Figure 4). This mechanism is similar in detail to mechanisms proposed for the oxidation of H_2Q by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$[6a] and for the reduction of Q by *trans*-$[Os^{IV}(tpy)(Cl)_2\{N(H)N(CH_2)_4O\}]^+$ in which an intermediate has also been observed.[7]

As calculated from the intercept, slope, and intercept-to-slope ratios in Figure 2B, $K_A(H_2O) = (1.02 \pm 0.02) \times 10^3\,\text{M}^{-1}$ and $k_1(H_2O) = (1.42 \pm 0.04) \times 10^{-2}\,\text{s}^{-1}$. The kinetics were also measured in 1:1 (v/v) $CH_3CN:H_2O/D_2O$ mixtures. From the [Q] dependence in $CH_3CN:D_2O$, $K_A(D_2O)$ and $k_1(D_2O)$ are $(9.91 \pm 0.15) \times 10^2\,\text{M}^{-1}$ and $(4.71 \pm 0.18) \times 10^{-4}\,\text{s}^{-1}$, respectively (Supporting Information Figure 5). From these data, $K_A(H_2O)/K_A(D_2O) = 1.03 \pm 0.03$ and $k_1(H_2O)/k_1(D_2O) = 30.2 \pm 0.3$.

The kinetic analysis reveals a mechanism involving pre-association to form a detectable intermediate, probably stabilized by hydrogen bonding. The magnitude of the kinetic isotope effect points to synchronous electron–proton transfer and a proton-coupled electron-transfer mechanism, [Eq. (9)].

Because of a possible contribution from a parallel electron-transfer pathway between Q and the deprotonated form of $[\mathbf{1A}]^+$, *trans*-$[Os^{IV}(tpy)(Cl)_2\{NS(C_6H_3)Me_2\}]$, the kinetic isotope effect of 31.1 is a lower limit. It should be possible to unravel the contribution, if any, of a second pathway by the pH-dependent kinetic study currently under investigation.



(9)

Our study appears to provide the first documented example of two phenomena: 1) proton-coupled electron transfer involving a S atom, and 2) proton-coupled electron transfer from an atom not directly bonded to the metal. The reaction is also notable for the large magnitude of the kinetic isotope effect. The observation of S-based, proton-coupled electron transfer could have important implications for the electron-transfer chemistry of iron-sulfur proteins. Related pathways could provide a mechanism for converting complex redox equivalents, involving the transfer of both electrons and protons, into the electron-transfer equivalents available in electron transfer reactions.

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[10] In the deprotonated form, *trans*-[$Os^{IV}(tpy)(Cl)_2(NSC_6H_3Me_2)$], the angle Os1-N1-S1 (129.5(2)°) and bond Os1-N1 (1.890(3) Å) are relatively unchanged while there are significant changes in the angle N1-S1-C41 (104.3(2)°), and the bonds N1-S1 (1.596(4) Å), and S1-C41 (1.784(4) Å cf. with Os1-Cl1 (2.4139(10), Os1-Cl_2 (2.4007(10), Os1-N11 (2.057(3), Os1-N21 (2.012(3), Os1-N31 (2.065(3)) Å in [**1A**]$^+$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141160 (**1A**) and -149866. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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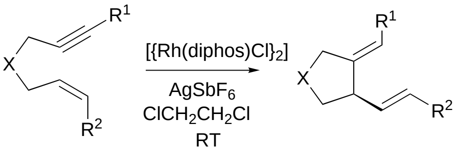
The First Highly Enantioselective Rh-Catalyzed Enyne Cycloisomerization[**]

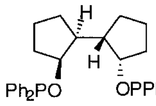
Ping Cao and Xumu Zhang[*]

The development of efficient asymmetric cyclizations is of great interest in organic synthesis due to the existence of many biologically active and naturally occurring cyclic compounds.[1] However, efficient enantioselective transition metal catalyzed cyclization reactions are rare and remain relatively unexplored.[2, 3] In contrast, the racemic variants of these reactions have been extensively studied. For example, transition metal catalyzed cycloisomerization of 1,6-enynes have been explored in depth.[4] An asymmetric variant of this transformation would be significant for the synthesis of enantiomerically pure five-membered carbo- and heterocycles. So far, only limited progress has been made in this important enantioselective transformation.[5] We reasoned that a key to developing such highly enantioselective metal-catalyzed reaction is to find a highly active catalyst for cycloisomerization under mild conditions. Recently, we made a significant advance in developing the first Rh^I-catalyzed enyne cycloisomerization reaction at room temperature. Excellent chemo-, regio-, and diastereoselectvities were achieved (Scheme 1).[6] Here we report on the first asymmetric Rh-catalyzed enyne cycloisomerizations facilitated by Rh^I complexes with Me-DuPhos (DuPhos = 1,2-bis(phospholano)benzene),[7] BICP (2*R*,2′*R*)-bis(diphenylphosphanyl)-(1*R*,1′*R*)-dicyclopentane (**1**) [8] and the phosphinite (*R*,*R*,*R*,*R*)-BICPO ligands.[9]



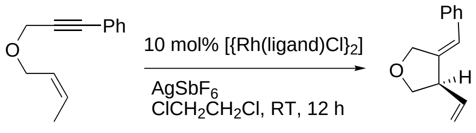
Scheme 1. Rh-catalyzed enyne cycloisomerization.

Using some commercially available chiral phosphane ligands and ligands developed in our laboratory, we screened the asymmetric enyne cycloisomerization reaction with **1a** as a prototypical substrate (Table 1). The highest *ee* was achieved with a Rh/Me-DuPhos catalyst, while no reactivity was observed with a Rh/BINAP system (BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-dinaphthyl). We found that both the activity and enantioselectivity of this asymmetric C–C bond-forming reaction are sensitive to the structure of the chiral ligand. For example, both activity and enantioselectivity were low with the Et-BPE (BPE = 1,2-bis(phospholano)ethane) ligand, and the enantioselectivity dropped significantly on changing from Me-DuPhos to Et-DuPhos. Good enantioselectivities were also obtained with BICP and Me-PennPhos (Me-PennPhos = *P*,*P*′-1,2-diphenylenebis(endo-2,5-dimethyl-7-phosphabicyclo[2.2.1]heptane).



(*R*,*R*,*R*,*R*)-BICPO

Table 1. Ligand effects on Rh-catalyzed enantioselective enyne cycloisomerization [Eq. (1)].[a]



1a **2a**

(1)

Entry	Ligand	Conversion [%][b]	*ee* [%][c]
1	Me-DuPhos	100	95
2	Et-DuPhos	<5	63
3	BICP	100	74
4	Me-PennPhos	100	71
5	BINAP	0	–
6	Et-BPE	<5	5

[a] All reactions were carried out with 10 mol% [{Rh(ligand)Cl}$_2$] in $ClCH_2CH_2Cl$ with 0.1 M enyne substrate at room temperature for 2–12 h. The cationic Rh^I catalyst was generated by adding $AgSbF_6$ to the solution of [{Rh(ligand)Cl}$_2$] in the presence of the substrate. [b] Conversion was determined by GC. [c] The *ee* was determined by GC on a 15 m Supelco *β*-390 column with a chiral phase.

On the basis of these results, Me-DuPhos was selected as the preferred ligand for the Rh-catalyzed cycloisomerization of **1a**. We found that the optimal catalyst loading for achieving high reactivity and enantioselectivity is 5–10 mol%. The cationic Rh^I catalyst must be generated in situ by adding one equivalent of $AgSbF_6$ to the reaction mixture after the substrate has been introduced. Higher catalyst loading

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[*] Prof. X. Zhang, P. Cao
Department of Chemistry
The Pennsylvania State University
University Park, PA 16802 (USA)
Fax: (+1) 814-863-8403
E-mail: xumu@chem.psu.edu

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