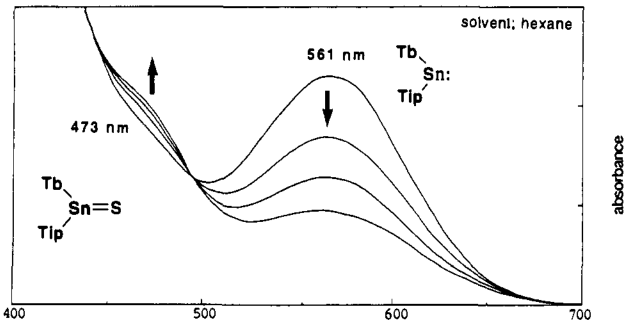
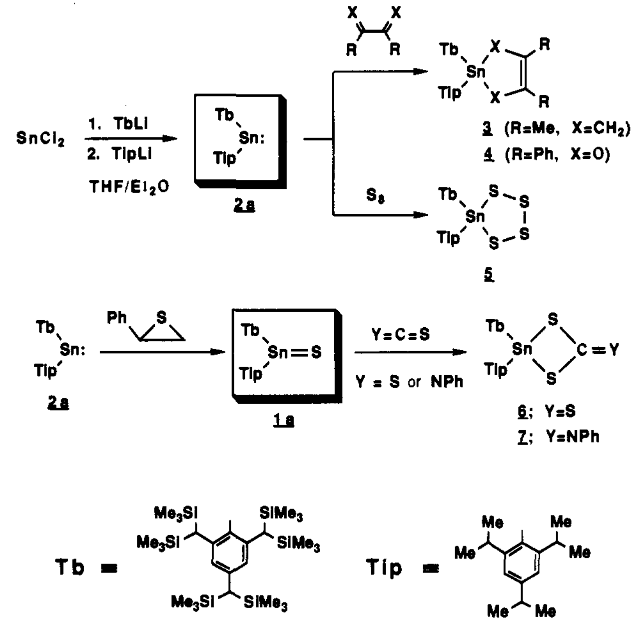


Figure 1. UV-vis spectral change in the reaction of Tb(Tip)Sn: (**2a**) with styrene episulfide in hexane.

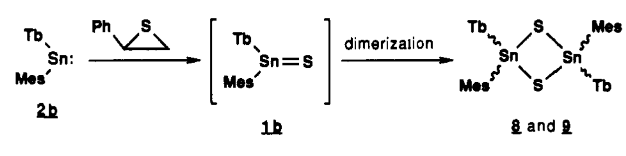
Scheme I



In contrast to the successful formation of germanium-sulfur double-bond compounds by the reactions of thermodynamically stabilized germylene with elemental sulfur,[2] only 1,2,3,4,5-tetrathiastannolane **5**[6,9] was isolated (9%) as a sulfurized product upon treatment of stannylene **2a** with elemental sulfur (Scheme I). On the other hand, when the deep purple solution of **2a** in hexane was treated with styrene episulfide at room temperature, the solution turned yellow, suggesting the formation of stannanethione **1a**.[6] Monitoring of the reaction using UV-vis spectroscopy showed an appearance of a new absorption at 473 nm (shoulder) at the expense of the absorption of stannylene **2a** at 561 nm, as shown in Figure 1, the absorption of 473 nm being assignable to the n-π^* transition of the tin-sulfur double bond of stannanethione **1a**.

Furthermore, the formation of stannanethione **1a** was chemically evidenced by the fact that treatment of the yellow solution thus obtained with an excess amount of thiocumulenes such as carbon disulfide and phenyl isothiocyanate at room temperature afforded 1,3,2-dithiastannetane derivatives **6**[6,10] and **7**[6] in 19 and 38% yields, respectively. The formation of adducts **6** and **7** is worthy of note from the standpoint of the first examples of [2 + 2] cycloaddition of a tin-sulfur double-bond compound except for self-dimerization.[11]

Scheme II



Since the reaction of less hindered diarylstannylene Tb(Mes)Sn: (**2b**; Mes = mesityl) with styrene episulfide in THF at -78 °C gave no monomeric products but a mixture of cis and trans isomers of 1,3,2,4-dithiadistannetanes **8** and **9** (total 11%, cis/trans = ca. 1:1)[6,10] (Scheme II), which are the dimerization products of the intermediary stannanethione Tb(Mes)Sn=S (**1b**), the prominent stability of the stannanethione **1a** is obviously due to the steric demand of the combination of Tb and Tip groups.

Further investigation on the reactivity of the novel stannanethione is currently in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 02231101) from the Ministry of Education, Science and Culture, Japan. We also thank Shin-etsu Chemical Co., Ltd. and Toso Akzo Co., Ltd. for the generous gift of chlorosilanes and alkyllithiums, respectively.

Supplementary Material Available: Experimental details for the formation of **1a**, **2a**, and **7**, and spectral and analytical data of **3**-**9** (5 pages). Ordering information is given on any current masthead page.

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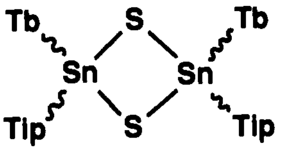
(9) For similar 1,2,3,4,5-tetrathiametallolanes of group 14 metals, see Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047.

(10) The structures of **6**, **8**, and **9** were firmly established by X-ray crystallographic analysis, whose details will be described in a full paper in the near future.

(11) The possibility that a chemical species involved in these cycloadditions is a dimer instead of a monomer (**1a**) or a monomer dissociated to a minor extent from a dimer can be eliminated by the fact that both *cis*- and *trans*-dithiadistannetanes **10**, the dimers of **1a**, are totally inert to the thiocumulenes under the reaction conditions (i.e., room temperature). Although **1a** is stable at room temperature, it undergoes dimerization, giving **10** (*cis*-**10** 2%, *trans*-**10** 6%) at 90 °C in the absence of a tapping reagent.



10

Practical, High-Yield, Regioselective, Rhodium-Catalyzed Hydroformylation of Functionalized α-Olefins

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Received August 10, 1992

Hydroformylation has been an industrially important process for several decades.[2] In general, the harsh reaction conditions required and/or the lack of selectivity observed has limited the utility of hydroformylation in the preparation of functionalized organic molecules.[3] The report in 1988 of a catalytic system which

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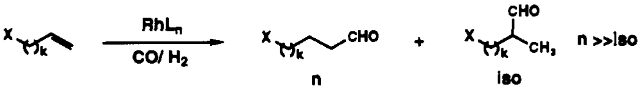
(1) National Science Foundation Predoctoral Fellow 1989-1992.

(2) (a) Claus, R. E.; Schreiber, S. L. *Org. Synth.* **1986**, *64*, 150 and references therein. (b) Webster, F. X.; Rivas-Enterrios, J.; Silverstein, R. M. *J. Org. Chem.* **1987**, *52*, 689. (c) Ogawa, H.; Chihara, T.; Taya, K. *J. Am. Chem. Soc.* **1985**, *107*, 1365.

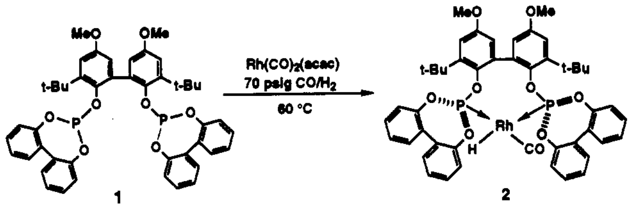
(3) (a) Siegel, H.; Himmele, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 178 and references therein. (b) Markó, L. *J. Organomet. Chem.* **1991**, *404*, 325 and references therein. (c) Alper, H. *Aldrichimica Acta* **1991**, *24*, 3 and references therein. (d) Stille, J. K. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 913. (e) Burke, S. D.; Cobb, J. E.; Takeuchi, K. *J. Org. Chem.* **1990**, *55*, 2138. (f) Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horváth, I. T. *J. Am. Chem. Soc.* **1988**, *110*, 150. (g) Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Tetrahedron Lett.* **1989**, *30*, 233. (h) Anastasiou, D.; Jackson, W. R. *Tetrahedron Lett.* **1990**, *31*, 4795.

gave high n:iso ratios and operated under mild conditions[4] prompted us to examine the use of this system with functionalized substrates.



Functionalized α-olefins are attractive starting materials due to their ready availability.[5] The development of practical routes to produce terminally differentiated bifunctional organic molecules is of considerable interest.[6] The regioselective hydroformylation of terminal olefins would provide a new source of ω-functionalized aldehydes. We now report our results in which we have used an in situ generated rhodium complex to effect the hydroformylation of terminal olefins under mild reaction conditions, with typical n:iso ratios of ≥40:1.

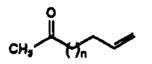
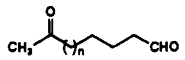
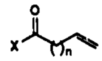
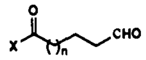
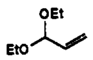
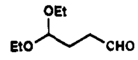
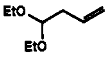
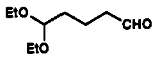
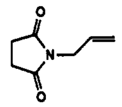
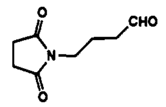
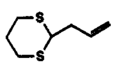
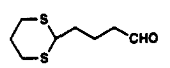
The active hydroformylation catalyst, presumably **2**, used in this study was generated in situ, in the presence of substrate, by the addition of the bis-organophosphite ligand **1**[4,7] to dicarbonylacetylacetonatorhodium(I) (0.54 mol %) in THF under 70 psig[8] of CO/H_2 (1:1 mixture) at 60 °C.



1 **2**

In order to probe the applicability of this catalyst system for organic synthesis we determined its compatibility with a large number of important functional groups, as is shown in Table I.[9] To this end, we were pleased to find that a wide variety of carbonyl-containing substrates—ketones, esters, acids, and amides—produced dicarbonyls in good to excellent yield. Olefinic alcohols, nitriles, and halides were also efficiently hydroformylated. It is of interest that olefins containing unprotected alcohols and even carboxylic acids could be efficiently converted to ω-aldehyde products. Although potentially susceptible to oxidative addition processes, alkyl halides were also tolerated, with alkyl bromides appearing to be superior to alkyl iodides.[10] Unsaturated acetals underwent hydroformylation to produce the monoprotected dialdehydes, which have been shown to be synthetically useful intermediates.[11] Although amines and primary and secondary amides have not, to date, yielded the desired products,[12] *N*-allylsuccinimide was hydroformylated to the imide aldehyde in excellent yield (entry 14). This transformation is of considerable interest as 4-imide aldehydes can be readily converted to 2-pyrrolidone or proline derivatives.[13] While the observed regioselectivity using **1** as ligand was excellent, typically with n:iso ≥ 40:1,[14] substrates with an allylic functional group showed a decrease in regioselectivity (entry 12, n:iso = 10:1; entry 14, n:iso = 18:1; entry 15, n:iso = 2.8:1).[15] These results may be attributed to favorable coordination of the heteroatom to the metal center.

Table I

Entry	Substrate	Product	% Yield[18]
			
1	n=1	n=1	86
2	n=3	n=3	87
			
3	X=OMe, n=8	X=OMe, n=8	91
4	X=OH, n=8	X=OH, n=8	68
5	X=OBz, n=2	X=OBz, n=2	73
6	X=N(Et)$_2$, n=2	X=N(Et)$_2$, n=2	93
			
7	X=CN, n=1	X=CN, n=1	84
8	X=Br, n=1	X=Br, n=1	71
9	X=I, n=1	X=I, n=1	64
10	X=OH, n=7	X=OH, n=7	53
11	X=OTBDMS, n=2	X=OTBDMS, n=2	86
12			80 (n:iso = 10 : 1)
13			75
14			95 (n:iso = 18 : 1)
15			65 (n:iso = 1.8 : 1)

The critical importance of ligand **1** was demonstrated by comparing the regioselectivity observed for the hydroformylation of 5-oxo-1-hexene, **3**, using ligand **1**, triphenyl phosphite, and triphenylphosphine under the conditions described herein.[16] The

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[4] Billig, E.; Abatjoglou, A. G.; Bryant, D. R. U.S. Patents 4,668,651 (1987) and 4,769,498 (1988). The catalyst system employing **1** as ligand gave the highest n:iso ratios for the hydroformylation of propene.

[5] Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; pp 105–282.

[6] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 621–632. (b) Szmant, H. H. *Organic Building Blocks of the Chemical Industry*; John Wiley & Sons: New York, 1989. (c) Davies, J. A. *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, pp 361–389.

[7] See supplementary material for the experimental procedure for the preparation of **1**.

[8] The reaction vessel is initially pressurized at room temperature to 60 psig with CO/H_2 (1:1 mixture). However, at 60 °C the pressure rises to approximately 70 psig.

[9] For a review of hydroformylation of functionalized olefins, see: Botteghi, C.; Ganzerla, R.; Lenarda, M.; Moretti, G. *J. Mol. Catal.* **1987**, *40*, 129.

[10] When 5-iodo-1-pentene was stored over copper prior to use, no hydroformylation was observed.

[11] Botteghi, C.; Soccolini, F. *Synthesis* **1985**, 592.

[12] The hydroformylation reactions proceed (starting material is consumed and no loss of active catalyst complex was observed by ^{31}P NMR); however, the amino aldehydes and amide aldehydes produced are susceptible to secondary reactions. Attempts to trap the aldehydes through various means are ongoing.

[13] (a) Delogu, G.; Faedda, G.; Gladiali, S. *J. Organomet. Chem.* **1984**, *268*, 167. (b) Becker, Y.; Eisenstadt, A.; Stille, J. K. *J. Org. Chem.* **1980**, *45*, 2145.

[14] The n:iso ratios were determined by ^1H NMR and/or GC analysis of the crude reaction mixtures.

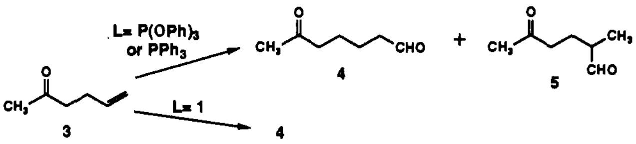
[15] Other substrates with sulfur-containing functional groups in the allylic position also show a decrease in the n:iso ratios. Further details concerning the effect of allylic functionality on the hydroformylation of olefins will be addressed in a subsequent full paper.

[16] General procedure for the hydroformylation of 5-hexen-2-one (entry 1): Into a Fisher-Porter bottle (purchased from Aerosol Lab Equipment, Walton, NY 13856), properly fitted with a pressure coupling closure complete with gas inlet, pressure gauge, and pressure release valve, was added dicarbonylacetylacetonatorhodium(I) (28 mg, 0.109 mmol, 0.54 mol %), **1** (320 mg, 0.408 mmol), THF (36 mL), and 5-hexen-2-one (2.32 mL, 20 mmol). The reaction vessel was degassed three times and sparged with CO/H_2 (1:1 mixture) for several minutes. The reaction vessel was pressurized at room temperature to 60 psig with CO/H_2 (1:1 mixture) and then heated at 60 °C for 18 h. After cooling to room temperature, the pressure was released and the solution concentrated. The resulting oil was purified by Kugelrohr distillation to give a colorless oil, 6-oxoheptanal[17] (2.21 g, 86% yield). **CAUTION**: The hydroformylation reactions should be performed behind an appropriate blast shield.

[17] Karim, M. R.; Sampson, P. *Org. Prep. Proced. Int.* **1990**, *22* (5), 648.

[18] Unless otherwise indicated, n:iso > 40:1. Yields, unless otherwise stated, refer to isolated yields of compounds of greater than 95% purity as determined by capillary GC and/or ^1H NMR.

latter two ligands produced aldehydes **4** and **5** in ratios of 3:1 and 2.4:1, respectively. In contrast, when the bis-organophosphite ligand **1** was used under identical reaction conditions, **4** was the only observable product as determined by ^{1}H NMR.



In summary, we have shown that the bis-organophosphite rhodium(I) complex prepared from **1** can effect the regioselective hydroformylation of terminal olefins under mild reaction conditions to produce a variety of ω-functionalized aldehydes. That this catalyst system operates under significantly milder conditions, demonstrates notably increased regioselectivity, and is tolerant of a variety of potentially reactive functional groups bodes well for its use in organic synthesis. We are currently investigating the extension of this methodology to the syntheses of various acyclic, carbocyclic, and heterocyclic systems.

Acknowledgment. We thank Union Carbide for financial support. Preliminary work was funded, in part, by the National Institutes of Health. G.D.C. thanks the National Science Foundation for a graduate fellowship. S.L.B. acknowledges additional support as a Fellow of the Alfred P. Sloan Foundation and a Camille & Henry Dreyfus Teacher-Scholar. We thank Dr. Chang Byon for carrying out some preliminary work and Dr. James Babin of Union Carbide for technical advice and stimulating discussions.

Supplementary Material Available: Experimental section containing the preparations and spectroscopic and analytical characterization of compounds (6 pages). Ordering information is given on any current masthead page.

Syntheses, Properties, and Crystal Structures of Thiolate-Bridged Ruthenium Complexes $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_n$ (*n* = 0, 4) and Their Novel Electrochemical One-Step Four-Electron Redox Reactions

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Received August 27, 1992

Multielectron redox reactions in biological and catalytic chemistry have been continuously attractive topics.[1] Our ultimate goal is to design multielectron-transfer reagents for the activation of inactive molecules such as N_2 and RCN. In general, one-electron-transfer reactions are widely known in natural metalloenzymes and synthetic metal complexes, but one-step two-electron-transfer reactions have been found only in several transition-metal complexes.[2] Little is known about one-step four-electron-transfer reactions, although such process is important, e.g., in reduction of O_2 to H_2O in fuel cells.[3] We have synthesized electron-rich binuclear Ru(II,II) complexes and their oxidized forms with unusually high oxidation state Ru(IV,IV), $[Ru(\mu\text{-}SR)(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_n$ (R = Ph, Et; *n* = 0, 4). The compound with R = Ph has been found to exhibit unprecedented reversible one-step 4e redox reaction corresponding to Ru(II,II)/Ru(IV,IV).

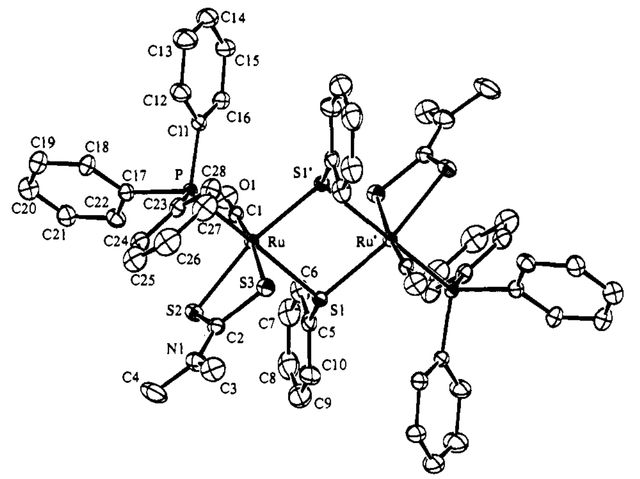

Figure 1. Molecular structure of $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2\cdot CH_2Cl_2$ (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru–Ru', 3.683(1); Ru–S1, 2.458(1); Ru-S1', 2.413(1); Ru–S2, 2.409(1); Ru–S3, 2.469(1); Ru–C1, 1.844(5); Ru–P, 2.326(1); C1–O1, 1.148(6); C2–N1, 1.319(6); S1–Ru–S1', 81.80(4); Ru–S1–Ru', 98.21(4); S2–Ru–S3, 71.61(5).

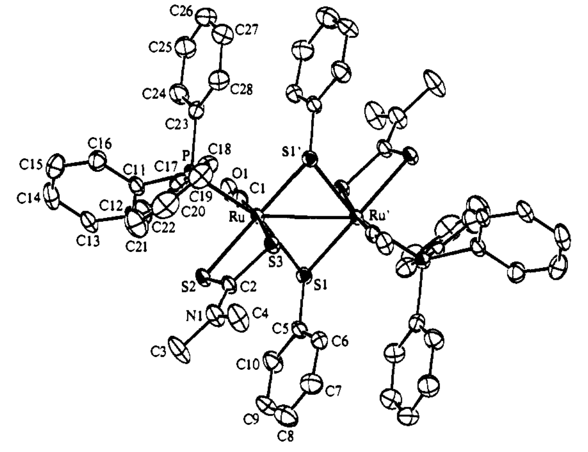

Figure 2. Molecular structure of $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2^{4+}$ (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru–Ru', 2.876(2); Ru–S1, 2.405(3); Ru–S1', 2.310(3); Ru–S2, 2.404(3); Ru–S3, 2.425(3); Ru–C1, 1.891(10); Ru–P, 2.409(3); C1–O1, 1.145(10); C2–N1, 1.297(11); S1–Ru–S1', 104.83(9); Ru–S1–Ru', 75.17(8); S2–Ru–S3, 72.0(1).

$RuH(S_2CNMe_2)(CO)(PPh_3)_2$[4] (1.0 g) was reacted with excess RSH (R = Ph (1.5 mL), Et (5 mL)) in 50 mL of benzene (65 °C) for 2 h (R = Ph) or 24 h (R = Et) under nitrogen with H_2 evolution to produce suspensions of yellow powders. The suspensions were filtered, and $[Ru(\mu\text{-}SR)(S_2CNMe_2)(CO)(PPh_3)]_2$ (R = Ph (**1**)[5], Et (**2**)[6]) were obtained as yellow powders which

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[1] (a) Nakamura, A.; Ueyama, N. *Adv. Inorg. Chem.* **1989**, *44*, 39. (b) Chang, I. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 4901. (c) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (d) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.

[2] (a) $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomethane): Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429. (b) $[Pt_2^{III}(NH_3)_4(C_5H_4NO)_2(NO_3)_2]^{2+}$: Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. (c) $[Mo_2^{0}(CO)_8(SR)_2]^{2-}$ (R = Ph, *t*-Bu): Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Organometallics* **1984**, *3*, 943. (d) $[Fe_2^{I}(PPh_2)_2(CO)_6]^{2}$: Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146. (e) *trans*-$(O)_2Re^{V}(py\text{-}X)_4^+$ (py-X = substituted pyridine), *cis*-$(O)_2Re^{V}(bpy\text{-}Y_2)(py\text{-}X)_2^+$ (bpy-Y = doubly substituted 2,2'-bipyridine ligand): Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y.-H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928.

[3] (a) Yeager, B. *Electrochim. Acta* **1984**, *29*, 1527. (b) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847.

[4] Critchlow, P. B.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1367–1372.

[5] Anal. Calcd for $C_{57}Cl_2H_{54}N_2O_2P_2Ru_2S_6$ (MW = 1326.42): C, 51.62; H, 4.10; N, 2.11. Found: C, 51.22; H, 4.49; N, 2.14. IR ν(CO) = 1940, 1916; ν(CN) = 1516 cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 85% H_3PO_4 as the external standard) 47.6 ppm. The ^{31}P NMR spectrum for the component soluble in benzene is observed at 45.7 ppm. UV–Vis (CH_2Cl_2) 445(1080), 328 (sh) (22 800), 274 (sh) nm (51 800 M^{-1} cm^{-1}).

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