purified a CDP-D-glucose oxidoreductase from *Yersinia pseudotuberculosis*, which is also NAD^+ dependent.[9] In view of the central position of this enzyme as a branch point in 3,6-dideoxyhexose biosynthesis and its unusually weak binding of the nicotinamide cofactor, we have carried out a stereochemical analysis of this enzymatic process aimed at elucidating its reaction course in detail. Reported in this paper are the results of this analysis and their implication on this enzyme's mechanism.

Crucial to this study is the availability of the labeled substrates (6*S*)- and (6*R*)-CDP-[4-^{2}H,6-^{3}H]-D-glucose. It is anticipated that the replacement of the hydroxyl group at C-6 by the deuterium migrating from C-4 is intramolecular and stereospecific; therefore, the resulting product will have hydrogen, deuterium, and tritium in a chiral arrangement at C-6 that can be analyzed by the method of Cornforth, Arigoni, and co-workers.[10] The requisite substrates were obtained from the corresponding chirally labeled precursors **1** and **2**, which were synthesized as outlined in Scheme II.[11] The deuterium at C-4 was introduced by repetitive incubation of **3** in a pyridine/D_2O (5:1) solution followed by evaporation.[12] The deuterium content estimated by NMR of the reduced product **4** was greater than 95%. Stereospecific incorporation of tritium labeling into the C-5 hydroxymethyl group was effected according to a method developed by Kakinuma with minor modification.[13] The common precursor, a 5,6-yne derivative **6**, was obtained from the dibromo olefin **5** upon treatment with *n*-butyllithium in THF at −78 °C followed by quenching with $[^3H]H_2O$ (30 mCi, 0.3 mL). Transformation of **6** with a specific radioactivity of 0.46 Ci/mol to the *E* olefin **7** was achieved by reduction using chromous sulfate in aqueous DMF.[14] Dihydroxylation with a catalytic amount of OsO_4 in the presence of *N*-methylmorpholine *N*-oxide (NMO) afforded the desired *cis*-diol **8** in 72% yield.[15] The protected glucose was converted to free (6*S*)-[4-^{2}H,6-^{3}H]-D-glucose (**1**) by hydrogenolysis (10% Pd/C) and subsequent acid hydrolysis. The 6*R*-labeled glucose was prepared analogously from **6** via the *Z* olefin **9**, which was produced by hydrogenation over Lindlar catalyst poisoned with quinoline. Conversion of the 6*S*- and 6*R*-labeled glucose to the corresponding CDP derivatives was accomplished by a sequence commonly used to make nucleoside diphosphohexoses.[16] The specific radioactivities of the final products were 89 and 74 mCi/mol, respectively.[17]

The (6*S*)- and (6*R*)-CDP-[4-^{2}H,6-^{3}H]-D-glucose were each mixed with CDP-[*U*-^{14}C]-D-glucose, diluted with excess unlabeled CDP-glucose (1:9), and then incubated with homogeneous CDP-D-glucose oxidoreductase in the presence of NAD^+. The CDP-4-keto-6-deoxy-D-glucose products isolated by paper chromatography (EtOH/BuOH/H_2O, 5:5:2) were subjected to Kuhn-Roth oxidation. The nascent acetic acid samples were formed in radiochemical yields of 52-54%, and their chiralities were determined by the method of chiral methyl analysis.[10,18] An *F* value of 71 corresponding to a 72% ee *R* configuration and an *F* value of 30 corresponding to a 69% ee *S* configuration were obtained for the two acetates derived from the 6*S*- and 6*R*-labeled glucose, respectively.[19] These results unequivocally show that the hydrogen migration from C-4 to C-6 does proceed intramolecularly and the displacement of the hydroxyl group at C-6 is stereospecific and occurs with inversion.[20] Notwithstanding the high enantiomeric purity of the substrates, the moderate ee found for the acetic acid samples may directly reflect the weak binding of the cofactor to this enzyme. Nevertheless, our general conclusions completely parallel those found for all of the other sugar oxidoreductases characterized so far[5,21] and, thus, suggest that this class of enzymes, regardless of their source, evolved from a common progenitor whose stereochemical course has persevered throughout the enzyme's subsequent diversification.

Acknowledgment. This work is supported by National Institutes of Health Grant GM 35906. H.-w.L. also thanks the National Institutes of Health for a Research Career Development Award (GM 00559).

(8) (a) Han, O.; Liu, H.-w. *J. Am. Chem. Soc.* **1988**, *110*, 7893. (b) Han, O.; Miller, V. P.; Liu, H.-w. *J. Biol. Chem.* **1990**, *265*, 8033. (c) Shih, Y.; Yang, D.-y.; Weigel, T. M.; Liu, H.-w. *J. Am. Chem. Soc.* **1990**, *112*, 9652.

(9) Although *Pasturella pseudotuberculosis* has now been reclassified as *Yersinia pseudotuberculosis*, comparison of the enzymes isolated from these two strains suggested that the bacterial stain used in Strominger's studies was different from that used in our current research.

(10) (a) Cornforth, J. W.; Redmond, J. W.; Eggerer, H.; Buckel, W.; Gutschow, C. *Eur. J. Biochem.* **1970**, *14*, 1-13. (b) Luthy, J.; Rétey, J.; Arigoni, D. *Nature (London)* **1969**, *221*, 1213. (c) Floss, H. G.; Tsai, M.-D. *Adv. Enzymol.* **1979**, *50*, 243.

(11) Compounds **1** and **2** had been prepared heretofore by methods based on complex enzymatic manipulations (see ref 5a and references cited therein).

(12) Ritchie, R. G. S.; Cyr, N.; Korsch, B.; Koch, H. J.; Perlin, A. S. *Can. J. Chem.* **1975**, *53*, 1424.

(13) (a) Kakinuma, K. *Tetrahedron* **1984**, *40*, 2089. (b) Kakinuma, K. *Tetrahedron Lett.* **1971**, 4413.

(14) Castro, C. E.; Stephens, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 4358.

(15) The minor 5*S*,6*R* isomer was readily removed by flash chromatography on silica gel (30% acetone/hexane). The stereochemical assignments of this compound and the following products were made by comparing the NMR spectra of these samples with those of the respective unlabeled and/or deuterated standards that were prepared in parallel.

(16) This sequence involved the treatment of each of the labeled free glucose with hexokinase, phosphoglucomutase, glucose 1,6-diphosphate, and inorganic pyrophosphatase to furnish glucose 1-phosphate, which was then incubated with CTP and CDP-D-glucose pyrophosphorylase to form the requisite substrates, (6*S*)- and (6*R*)-CDP-[4-^{2}H,6-^{3}H]-D-glucose in an 18-20% overall yield. The pyrophosphorylase used in these incubations was partially purified from the same strain of *Y. pseudotuberculosis*.

(17) Since cold carrier was added to increase the sample mass at the later stage of the synthesis, the specific radioactivities of the final products were lower than that of **6**. However, every tritiated molecule still carries a deuterium at C-4.

(18) The standard (*S*)-[2-^{2}H,^{3}H]acetate was synthesized chemically from *pro-S*-tritium-labeled glycine (Kajiwara, M.; Lee, S.-F.; Scott, A. I.; Akhtar, M.; Jones, C. R.; Jordan, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 967), which was generated by the incubation of [2-^{3}H]glycine with alanine aminotransferase (Besmer, P. Ph.D. Dissertation No. 4435, ETH, Zürich, 1970). An identical sequence using deuterated buffer afforded the (*R*)-[2-^{2}H,^{3}H]-acetate. Chiral methyl analysis performed on these standards gave *F* values of 30 and 74 for the (*S*)- and (*R*)-acetates, respectively.

(19) Malate synthetase was purified (Durchschlag, H.; Biedermann, G.; Eggerer, H. *Eur. J. Biochem.* **1981**, *114*, 255) using freshly pressed bakers' yeast kindly donated by Pillsbury Company (Minneapolis, MN).

(20) In view of the large dilution of the labeled precursor by the unlabeled species, the methyl group of the resulting acetic acid will be chiral only if the migration of deuterium from C-4 to C-6 is strictly intramolecular and stereospecific.

(21) (a) Snipes, C.; Chang, C.-J.; Floss, H. G. *J. Am. Chem. Soc.* **1979**, *101*, 701. (b) Otsuka, H.; Mascaretti, O. A.; Hurley, L. H.; Floss, H. G. *J. Am. Chem. Soc.* **1980**, *102*, 6817. (c) Lee, J.-J.; Lee, J. P.; Keller, P. J.; Cottrell, C. E.; Chang, C.-J.; Zahner, H.; Floss, H. G. *J. Antibiot.* **1986**, *39*, 1123.

A New Catalytic Reaction Involving Oxidative Addition of Iodotrimethylsilane (Me_3SiI) to Pd(0). Synthesis of Stereodefined Enynes by the Coupling of Me_3SiI, Acetylenes, and Acetylenic Tin Reagents

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Oxidative addition reactions of a carbon-halogen (C-X) bond to a low valent transition metal complex are essential in catalytic and stoichiometric application of transition-metal reagents for organic synthesis.[1] Oxidative addition of a hydrogen-silicon bond (H-Si) is known for a number of transition metals and is an obligatory step in catalytic reactions such as hydrosilylation of olefins.[2] Recently, important advances have been made in the

(1) For general reviews, see: (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis. Practical Applications of Transition Metals*; Plenum Press: New York, NY, 1984. (c) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980.

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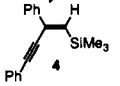
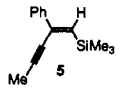
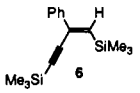
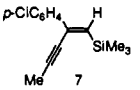
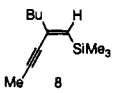
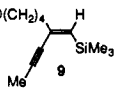
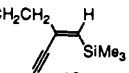
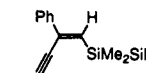
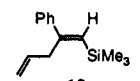
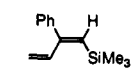
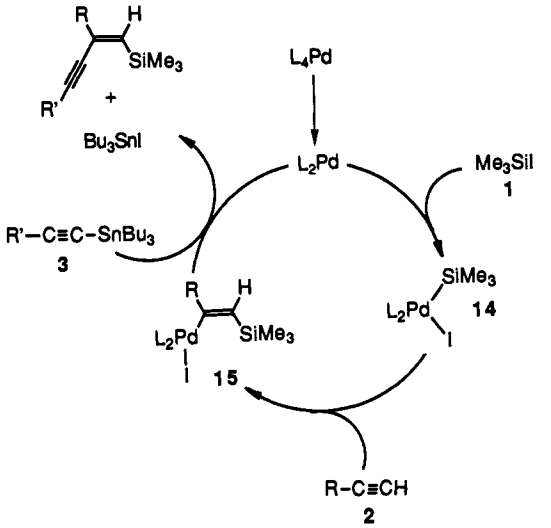
Table I. Palladium-Catalyzed Coupling of Acetylenes, Me_3SiI, and Organostannanes[a]

entry	acetylene (1b)	organostannane (1c)	enyne (1d)	yield[b] (time) (1e)	stereoselectivity[c] (1f)
1	Ph–C≡CH **2a**	Ph–C≡C–$SnBu_3$ **3a**	 **4**	71 % (2 h)	>98 %
2	**2a**	Me–C≡C–$SnBu_3$ **3b**	 **5**	97 % (2.5 h)	>98 %
3	**2a**	Me_3Si–C≡C–$SnBu_3$ **3c**	 **6**	79 % (3 h)	87 %
4	*p*-ClC_6H_4–C≡CH **2b**	**3b**	 **7**	70 % (2.5 h)	>98 %
5	Bu–C≡CH **2c**	**3b**	 **8**	71 % (3.5 h)	>98 %
6	*t*-$BuMe_2SiO(CH_2)_4$–C≡CH **2d**	**3b**	 **9**	76 % (3 h)	94 %
7	*o*-$BrC_6H_4CH_2CH_2$–C≡CH **2e**	**3b**	 **10**	70 % (2 h)	93 %
8[d]	**2a**	**3b**	 **11**	72 % (2 h)	>98 %
9[e]	**2a**	 **3d**	 **12**	73 % (7 h)	56 %
10[e,f]	**2a**	 **3e**	 **13**	80 % (7 h)	70 %

[a] Reaction conditions: acetylene (2.5 mmol), Me_3SiI (5 mmol), organostannane (3.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), dioxane (5 mL) at 60 °C under N_2. [b] Isolated yields. [c] Determined by GC. [d] $Me_3SiSiMe_2I$ was used in place of **1**. [e] $Pd(PPh_3)_4$ (0.2 mmol) was used. [f] Organostannane (5 mmol) was used.

Pd- or Pt-catalyzed double silylation of olefins,[3] acetylenes,[4] and isonitriles.[5] The reaction mechanism invoked the addition of disilane (Si–Si) to Pd(0) or Pt(0) complexes. In contrast, there has been almost no example of oxidative addition of halosilanes (Si–X) to a transition metal. In 1988, the observation of oxidative addition of a silicon–halogen bond [Me_3SiBr and Me_3SiI (**1**)] to $Pt(PEt_3)_n$ (n = 3 and 4) was reported by Tanaka.[6] He proposed

Scheme I



a similar path in Pd-catalyzed Heck-type conversion of styrene with Me_3SiI to a vinylsilane.[7] Although interesting, the reaction lacks substrate generality and is not so useful as an organic transformation. In this context, transition-metal-catalyzed synthetic reaction in which oxidative addition of halosilanes is a key step still remains unexploited. We now report the Pd-catalyzed three-component coupling reaction[8] of acetylenes, iodotrimethylsilane (Me_3SiI), and acetylenic tin reagents leading to silyl-substituted conjugated enynes (eq 1). The reaction exhibited high regio- and stereoselectivities.

$$\text{R–C≡CH} + \text{Me}_3\text{SiI} + \text{R'–C≡C–SnBu}_3 \xrightarrow[\text{dioxane}]{\text{Pd(PPh}_3)_4} \underset{\text{R'}}{\overset{\text{R}}{\overset{\text{H}}{\text{=}}}}\!\!\text{SiMe}_3 \quad (1)$$

The results are summarized in Table I. A typical procedure is as follows. In a 10-mL reaction flask were placed phenylacetylene (**2a**) (2.5 mmol, 255 mg), (phenylethynyl)tributylstannane (**3a**) (3.5 mmol, 1.37 g), $Pd(PPh_3)_4$ (0.05 mmol, 58 mg), and dioxane (5 mL). To the reaction mixture was added **1** (5 mmol, 0.71 mL), and the mixture was stirred at 60 °C for 2 h under N_2. To the mixture was added aqueous NH_4F to remove Bu_3SnI, which was formed through the coupling reaction. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give a brown oil, which was purified by column chromatography (silica gel, hexane) to give (*Z*)-2,4-diphenyl-1-(trimethylsilyl)-1-buten-3-yne (**4**)[9] (490 mg, 71%) as a colorless oil.

Both aromatic and aliphatic terminal acetylenes undergo the coupling reaction. Most importantly, the coupling reaction proceeds regio- and stereoselectively. The assignment of the regiochemistry of **4** was confirmed by protodesilylation of **4** (treatment of **4** with *p*-TsOH in wet CH_3CN)[10] leading to 2,4-diphenyl-1-

(2) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1989; Chapter 25.

(3) Hayashi, T.; Kobayashi, T.-a.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.-a.; Tanaka, M. *J. Chem. Soc. Chem. Commun.* **1990**, 563. Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987.

(4) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.

(5) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.

(6) (a) Yamashita, H.; Hayashi, T.; Kobayashi, T.-a.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417. (b) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

(7) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1991**, 761.

(8) For recent papers on Pd-catalyzed three-component coupling reactions, see: Kosugi, M.; Tamura, H.; Sano, H.; Migita, T. *Tetrahedron* **1989**, *45*, 961. Catellani, M.; Chiusoli, G. P.; Concari, S. *Tetrahedron* **1989**, *45*, 5263.

(9) All new compounds were characterized by NMR, IR, and mass spectral data and elemental analyses. See supplementary material.

(10) Deuterodesilylation of **4** should be a good way to confirm both the regio- and stereochemistry. However, the reaction did not proceed with retention and a stereoisomeric mixture of monodeuterio-2,4-diphenyl-1-buten-3-yne was obtained, in contrast to earlier reports. Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825. Wüest, H. *Tetrahedron Lett.* **1977**, 4305.

buten-3-yne,[11] not 1,4-diphenyl-1-buten-3-yne. The assignment of the stereochemistry of **4** was made on the basis of its ^1H NMR spectra.[12] Solvents like toluene, CH_3CN, CH_2Cl_2, or THF were less efficient (data not shown) than dioxane. When the reaction was conducted by using Me_3SiBr or Me_3SiOTf instead of **1**, no reaction took place. The reaction with propynyltributylstannane (**3b**) gave 1-silyl-1-penten-3-ynes with high stereoselectivity (entries 2, 4, and 5-7). Use of [(trimethylsilyl)ethynyl]tributylstannane (**3c**) led to a slightly lower stereoselectivity (entry 3).[13] It is noteworthy that the bromine atom in **2e** remained intact under the reaction conditions (entry 7), although Pd-catalyzed coupling reaction of bromobenzene with organostannanes is well-known.[14] The reaction using $Me_3SiSiMe_2I$ in place of **1** gave (*Z*)-2-phenyl-1-[(trimethylsilyl)dimethylsilyl]-1-penten-3-yne (**11**) (entry 8) without the cleavage of the Si-Si bond.[4,6b] Although other organostannanes such as allyl- and vinylstannane were also applicable to the present coupling reaction, the stereoselectivity was low (entries 9 and 10). The decrease in stereoselectivity[13] may reflect the relative rates of transmetalation (organic group transfer) for organostannanes, as has been observed by Stille.[14a]

The proposed reaction mechanism is shown in Scheme I. A first step of the catalytic cycle would be the oxidative addition of **1** to the palladium(0) catalyst to give a silylpalladium iodide **14**. Silylpalladation[15] of an acetylene with **14** yields vinylpalladium species **15**. The transmetalation of an organostannane followed by reductive elimination gives the coupled product,[14] regenerating the palladium(0) catalyst. Silylpalladation of acetylene with **14** would be the regio- and stereodetermining step, since it is established that the succeeding step of reductive elimination proceeds with a retention of configuration.[14] The results shown in entries 7 and 8 suggest that oxdative addition of the Si-I bond in **1** predominated, interestingly, over that of C-Br and Si-Si under the present reaction conditions.

These results suggest new possibilities of designing various catalytic reactions on the basis of oxidative addition of halosilanes and of silylmetalation. The present reaction offers a new synthetic method for stereodefined conjugated enynes, which are important in the synthesis of a wide range of natural products and other complex organic molecules.[16] A search for other coupling reactions along these lines is in progress.

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Supplementary Material Available: Spectral data and elemental analyses for the products (5 pages). Ordering information is given on any current masthead page.

(11) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480.

(12) The signal due to a vinyl proton of the *Z* isomer of **4** appeared downfield from that of the *E* isomer by ca. 0.2 ppm. See supplementary material.

(13) This suggests that the slight loss of stereochemistry took place in the intermediate **15**.

(14) For reviews, see: (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (c) Harrison, P. G. *Chemistry of Tin*; Blackie: London, 1989.

(15) Recently, some Pd-catalyzed reactions were reported that might involve silylpalladation of acetylene. $Me_3SiSnMe_3$: Mitchell, T. N.; Killing, H.; Dickie, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354. Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561. Me_3SiCN: Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539. $Me_3SiSiMe_3$: Ref 4.

(16) For recent papers on silyl-substituted enynes, see: Kusumoto, T.; Nishide, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1947. Kusumoto, T.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3103. For recent papers on the synthesis of conjugated enynes, see: Trost, B. M.; Matsubara, S.; Caring, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8745. Oshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277. Trost, B. M.; Kottirsch, G. *J. Am. Chem. Soc.* **1990**, *112*, 2816. Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330.

Preparation of the Thiosulfinato Complexes $CpRu(PPh_3)(CO)SS(O)R$, Where R = C_3H_7, $CHMe_2$, and 4-C_6H_4Me, and the Structure for R = $CHMe_2$. Oxygen Transfer To Give the Thiosulfonato Complex $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me and Its Structure

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Transition-metal complexes containing thiosulfinato ligands, $RS(O)S^-$, are practically unknown. They have been the subject of speculation[1] as possible precursors to organic thiosulfinate esters, which have a broad spectrum of biological activity.[2] The complexes $CpW(CO)_3SS(O)R$ have been prepared,[3] but they were unstable, and no X-ray structure was reported.[4] Transition-metal thiosulfonato complexes are also unknown.[5] They would contain the $MSS(O)_2R$ moiety and, thus, would be homologues of the well-known metal sulfonates $MS(O)_2R$.[6] The coordinating ability of small sulfur oxide ligands is well documented[1,7] and of interest with respect to SO_2-pollution abatement.[8] We have prepared a number of complexes containing rare polysulfano ligands of the type RS_x^-, where $x = 2, 3$.[3,9] Therefore, oxidized ligands of the type $RS_x(O)_y^-$ became natural targets of preparative studies. We report the rational synthesis of ruthenium thiosulfinato complexes and an unexpected conversion via a novel oxygen transfer to give a ruthenium thiosulfonato complex.

The preparation of organic thiosulfinate esters ($RSS(O)R'$) via oxidation of the disulfides is not practical.[5d] Unsymmetrical esters can readily be prepared via reaction of a thiol with a sulfinyl transfer reagent of the type RS(O)(phth), where phth = phthalimido.[10] Similarly, oxidation of the tungsten disulfano moiety in $CpW(CO)_3SSR$ gave a complex mixture of several products.[3] However, treatment of the metal thiol $CpRu(PPh_3)(CO)SH$[11] with RS(O)(phth) in THF, under N_2, at room

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