

monoxide, hydrogen peroxide was formed at a low, steady rate through the first two catalytic reactions and was used efficiently for alkane oxidation. On the other hand, starting with dihydrogen, hydrogen peroxide was formed rapidly (as evidenced by a relatively rapid drop in gas pressure), but most of it underwent subsequent metal-catalyzed decomposition at the reaction temperature (85–100 °C).

Ethanol was the primary product in the Pd-catalyzed oxidation of ethane by hydrogen peroxide and was detected when the overall catalytic reaction was carried out at a lower temperature (Table I). The subsequent metal-catalyzed oxidation of alcohol to carboxylic acid by dioxygen is well precedented.<sup>4,5</sup> A significant amount of formic acid was invariably formed in the oxidation of ethane. Experiments using acetic acid as substrate under the same reaction conditions indicated that formic acid was indeed derived from the former through a further oxidation step involving C–C bond cleavage. Free methyl radical, formed by a possible decarboxylation step, appeared *not* to be an intermediate in this transformation since, in the presence of <sup>13</sup>CO, CH<sub>3</sub><sup>13</sup>CO<sub>2</sub>H was not observed as a product. Note that carbon monoxide was an efficient trapping agent for methyl radical (rate constant in water:<sup>6</sup> 2 × 10<sup>6</sup> L mol<sup>-1</sup> s<sup>-1</sup> at 25 °C), and we have observed the formation of acetic acid in good yields from methyl radical and carbon monoxide in water under oxidizing conditions.<sup>7</sup> Interestingly, like ethane, the further oxidation of acetic acid also required the presence of carbon monoxide (therefore, hydrogen peroxide) in the system and did not occur in the presence of only dioxygen.

We have also attempted the oxidation of methane to formic acid using the same catalytic system. The number of turnovers corresponding to formic acid formation was in the range of 80–160. The major problem was that formic acid was less stable than acetic acid and was more prone to decomposition (to carbon monoxide and water) and overoxidation (to carbon dioxide and water).

As shown in Table I, Pt on carbon was also an active catalyst although less effective than Pd on carbon. The difference appears to be due to the greater tendency of the former to decompose hydrogen peroxide. For example, under comparable conditions (20 mg of 5% Pt/C versus 10 mg of 5% Pd/C; H<sub>2</sub>O, 5 mL; HCl, 0.1 M; H<sub>2</sub>, 150 psi; O<sub>2</sub>, 300 psi; temperature, 25 °C; time, 6 h) the concentrations of hydrogen peroxide formed were 0.024 and 1.4 M, respectively, even though the extent of the reaction of dihydrogen with dioxygen as judged by pressure drop was comparable.

In conclusion, we have discovered a highly catalytic system for the direct oxidation of ethane and methane by dioxygen under unusually mild conditions. While the detailed mechanism must await further studies, the overall transformation appears to involve three catalytic reactions in tandem.<sup>8</sup> The requirement of a coreductant makes the overall reaction formally analogous to the reaction of monooxygenases<sup>9</sup> in which only one of the two oxygen atoms in the dioxygen molecule is used for substrate oxidation. A very curious feature of the reaction is that dioxygen alone is ineffective,<sup>4</sup> thereby indicating that the active surface metal species that was generated using hydrogen peroxide *must* be different from any that may form through the reaction with dioxygen. Note that

since free alkyl radicals do not appear to be intermediates (due to the absence of products derived from trapping by carbon monoxide), the role of the metal cannot simply be to initiate Fenton-type<sup>10</sup> chemistry through O–O bond cleavage of hydrogen peroxide. However, rapid radical recombinations that may occur at or near the metal surface cannot be ruled out at this point.

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**Registry No.** CH<sub>3</sub>CH<sub>3</sub>, 74-84-0; CH<sub>3</sub>CO<sub>2</sub>H, 64-19-7; HCO<sub>2</sub>H, 64-18-6; CH<sub>3</sub>CH<sub>2</sub>OH, 64-17-5; O<sub>2</sub>, 7782-44-7; H<sub>2</sub>, 1333-74-0; Pd, 7440-05-3; Pt, 7440-06-4; CH<sub>4</sub>, 74-82-8; CO, 630-08-0; H<sub>2</sub>O, 7732-18-5; H<sub>2</sub>O<sub>2</sub>, 7722-84-1.

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### A Chelation Approach toward Activation of C<sub>sp</sub>–S Bonds. Nickel-Catalyzed Selective Cross Coupling of Bisdithioacetals with Grignard Reagents<sup>1a</sup>

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Although the use of the transition metal-catalyzed cross-coupling reactions is widespread,<sup>2</sup> the corresponding reactions involving the replacement of the aliphatic C–X bond are rare.<sup>3</sup> Only neopentyl iodides undergo coupling reactions with aromatic Grignard reagents in the presence of a palladium catalyst.<sup>3c</sup> The major impediment is due to the low reactivity of the C<sub>sp</sub>–X bond toward oxidative addition with transition metals. Side reactions such as reduction, β-elimination, and/or homocoupling frequently become predominant.<sup>3b–d</sup> Our recent discovery of the nickel-catalyzed cross-coupling reactions of benzylic or allylic dithioacetals with Grignard reagents<sup>4</sup> has prompted us to investigate the simple aliphatic substrates. As expected, these compounds are unreactive even under refluxing benzene conditions.<sup>4,5</sup> The low reactivity of these carbon–sulfur bonds may arise from the weak coordination ability of the sulfur moiety toward the nickel catalyst. Polythioethers are known to form chelation complexes with transition metals.<sup>6</sup> It is envisaged that such complexation may enhance the reactivity of the carbon–sulfur bond in the cross-coupling reactions. Scheme I illustrates the strategy of this approach. The two dithioacetal moieties in **1**, located in a close proximity, may form a chelation complex **2** with the nickel catalyst. As such, the carbon–sulfur bond is activated, and olefination of one of the dithioacetal moieties may occur. The remaining di-

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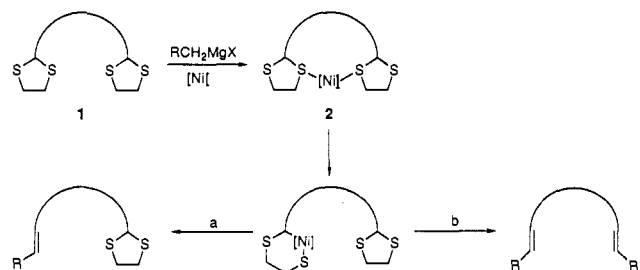
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Scheme I

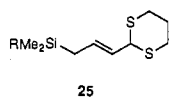


thioacetal group may either remain intact (route a) or undergo a further coupling process (route b). The selectivity of these routes depends on the relative position of this sulfur moiety to the first double bond thus produced. In other words, when the olefin moiety is formed in a relatively "remote" position, no "interaction" between this double bond and the sulfur group would occur. The reaction would stop at this stage to give an olefin-dithioacetal (route a). On the other hand, when an allylic dithioacetal or the like is formed in situ, a tandem coupling reaction<sup>5c</sup> via route b will occur readily to give a conjugated diene. Herein we report an unprecedented approach in the nickel-catalyzed cross-coupling reactions of aliphatic bisdithioacetals with Grignard reagents.

Treatment of bisdithioacetals 3–10 with excess MeMgI in the presence of the nickel(II) catalyst afforded the corresponding olefin-dithioacetals 13–20 in good yields (entries 1–8, Table I).<sup>7</sup> Only one of the dithioacetal groups of these substrates proceeded to the olefination reaction under these conditions. The formation of the double bond, in general, is regioselective; the endocyclic double bond was formed predominantly, if not exclusively, when the relatively unstrained five-membered-ring substrates were employed (entries 1, 5, and 8). On the other hand, the exocyclic methylenenorbornane derivative 14 was isolated as the sole product from the reaction of 4. Bicyclo[2.2.2]octane derivative 9, however, was less selective: a 1:1 ratio of 19a and 19b was obtained (entry 7).

When a bisdithioacetal contained both a dithiolane group derived from an aldehyde and a dithiolane moiety derived from a ketone, the less sterically hindered one was converted into the olefinic group (entry 3). However, the ring size of the sulfur heterocycle appeared to be more important in determining the reactivity. Thus, only the dithiolane group was transformed into the olefinic product when the starting bisdithioacetal contained both a dithiolane moiety and a dithiane group (entry 8).

Upon treatment with RMe<sub>2</sub>SiCH<sub>2</sub>MgCl (R = Me and Ph) under similar conditions, 1,3-bisdithioacetal 22 proceeded via route b (Scheme I) to afford the corresponding silyl-substituted dienes 23 and 24, respectively, in good yields (entries 11 and 12). The reaction may involve an allylic dithioacetal intermediate 25, which will further couple with the Grignard reagent leading to 23 or 24.



As shown in Scheme I, the general criterion for the success of these transformations depends on the ability of the two sulfur moieties coordinating simultaneously to the nickel catalyst (cf. 2). Poor chelation resulted in the recovery of a significant amount of the starting materials (entries 9 and 10).

(7) General procedure: Under N<sub>2</sub>, the Grignard reagent (4–6 equiv) in ether was evacuated to remove the ether. The bisdithioacetal (1 equiv) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol %) in benzene (15 mL) were added, and the mixture was refluxed for 5–20 h. After being cooled to room temperature, the mixture was quenched with saturated NH<sub>4</sub>Cl and extracted with ether. The organic solution was washed with NaOH (10%) and brine. The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated to give a residue, which was purified by chromatography. Isomers were separated by HPLC. Experimental details and spectroscopic data are summarized in the supplementary material.

Table I. NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-Catalyzed Reactions of Bisdithioacetals with MeMgI

entry	substrate	product	%yield
1			80
2			78
3			76
4			62
			16a (E/Z = 1/1) :16b = 11:1
5			72
			17a:17b = 8:1
6 <sup>a</sup>			72
			18a:18b = 5:1
7			68
			19a:19b = 1:1
8			82
			20a:20b = 6:1
9			0 <sup>b</sup>
10			18 <sup>c</sup>
			21a:21b = 3:2
11 <sup>d</sup>			76
			E/Z = 9/1
12 <sup>e</sup>			84
			E/Z = 10/1

<sup>a</sup> NiCl<sub>2</sub>(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene) was used as the catalyst. <sup>b</sup> 11 was recovered in 91% yield. <sup>c</sup> 12 was recovered in 75% yield. <sup>d</sup> Me<sub>2</sub>SiCH<sub>2</sub>MgCl was employed. <sup>e</sup> PhMe<sub>2</sub>SiCH<sub>2</sub>MgCl was employed.

In summary, we have demonstrated an unprecedented approach to activate the C<sub>sp</sub>-S bond in nickel-catalyzed cross-coupling reactions. Our theme was based on the formation of a chelation

complex which results in the enhancement of the reactivity of the aliphatic carbon-sulfur bonds. Selective coupling of one dithioacetal group of bisdithioacetals can thus be achieved conveniently. This discovery has led to further investigation on the activation of thioethers as well as other C-X bonds.

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**Supplementary Material Available:** Experimental procedures and spectroscopic data (IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and HRMS) for compounds 13-20, (1*E*,3*E*)-23, and (1*E*,3*E*)-24 (3 pages). Ordering information is given on any current masthead page.

### *cis*-Dioxobis(benzenedithiolato)tungsten(VI) and the Related Monooxotungsten(V) and -(IV) Complexes. Models of Tungsten Oxidoreductases

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Recently a variety of tungsten-containing enzymes have been found, e.g., formate dehydrogenase, carboxylic acid reductase (aldehyde oxidase), and aldehyde oxidoreductase (aldehyde ferredoxin oxidoreductase).<sup>1-6</sup> The EXAFS spectroscopic analysis of aldehyde oxidoreductase from *Pyrococcus furiosus* has suggested the presence of octahedral dioxotungsten(VI) species.<sup>5,6</sup> The metal center is considered to be surrounded by many thiolate ligands that include molybdopterin as those in the metal centers of molybdooxidases.<sup>4,7-12</sup> The molybdopterin is a dithiolene ligand connecting phosphate and perin derivatives. The resonance Raman study on dimethyl sulfoxide reductase has suggested the chelating coordination of the dithiolate to a Mo(VI) center.<sup>13</sup> Similar coordination seems to be involved in the metal center of W-containing oxidoreductases.

Our successful synthesis of model oxotungsten complexes having a dithiolene-like skeleton is based on a novel method utilizing the low solubility of monooxotungsten(V) benzenedithiolate complex  $(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{bdt})_2]$  (1),<sup>14</sup> excluding the preferred formation of  $[\text{W}^{\text{V}}(\text{bdt})_3]^-$  in the ligand-exchange reaction between

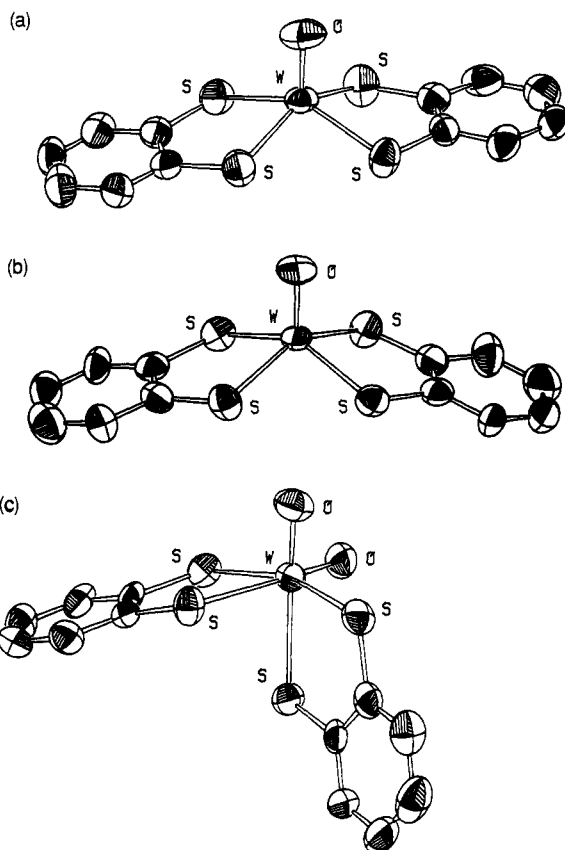


Figure 1. The ORTEP drawings of (a)  $(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{bdt})_2]$  (1), (b)  $(\text{NET}_4)_2[\text{W}^{\text{IV}}\text{O}(\text{bdt})_2]$  (2b), and (c)  $(\text{PPh}_4)_2[\text{W}^{\text{VI}}\text{O}_2(\text{bdt})_2]$  (3a).

$(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{SPh})_4]$ <sup>15</sup> and bdt- $\text{H}_2$ . Use of the above method allows extension to the synthesis of monooxotungsten(IV) thiolate complexes, which have been considered to be extremely unstable due to the negative W(IV)/W(V) redox potential in  $(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{SPh})_4]$ .<sup>15</sup> Thus,  $(\text{PPh}_4)_2[\text{W}^{\text{IV}}\text{O}(\text{bdt})_2]$  (2a) and  $(\text{NET}_4)_2[\text{W}^{\text{IV}}\text{O}(\text{bdt})_2]$  (2b) were synthesized by a simple borohydride reduction of 1 or  $(\text{NET}_4)_2[\text{W}^{\text{VO}}(\text{bdt})_2]$ .<sup>16</sup> 2a and 2b readily react with trimethylamine *N*-oxide to give dioxotungsten(VI) complexes,  $(\text{PPh}_4)_2[\text{W}^{\text{VI}}\text{O}_2(\text{bdt})_2]$  (3a) and  $(\text{NET}_4)_2[\text{W}^{\text{VI}}\text{O}_2(\text{bdt})_2]$  (3b), in ca. 70% yield.<sup>17</sup> The O-atom transfer to 2b by trimethylamine *N*-oxide is relatively fast ( $k_{\text{obsd}} = 5 \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ ) at room temperature, compared with that ( $k_{\text{obsd}} = 0.2 \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ ) to  $[\text{Mo}^{\text{IV}}\text{O}(\text{bdt})_2]^{2-}$  under stoichiometric conditions. The reduction gives only trimethylamine and  $(\text{NET}_4)_2[\text{W}^{\text{VI}}\text{O}_2(\text{bdt})_2]$  since the  $^1\text{H}$  NMR spectrum of a solution of trimethylamine *N*-oxide and  $[\text{Mo}^{\text{IV}}\text{O}(\text{bdt})_2]^{2-}$  indicates clean conversion during the reduction. 2a and 2b exhibit a negative redox potential of W(IV)/W(V) at  $-0.63 \text{ V}$  vs SCE in *N,N*-dimethylformamide (DMF), when compared with that ( $-0.35 \text{ V}$  vs SCE)<sup>18</sup> of Mo-

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(14)  $(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{SPh})_4]$  (250 mg, 0.26 mmol) prepared by the modification of a reported procedure<sup>28</sup> was suspended in 140 mL of 1,2-dimethoxyethane/diethyl ether (1/2, v/v). To the suspension was added bdt- $\text{H}_2$  (80 mg, 0.51 mmol) dropwise at room temperature. The mixture was stirred for 96 h, and the blue powder obtained was collected with filtration. Dark blue microcrystals formed by recrystallization from acetonitrile/diethyl ether/n-hexane in 48% yield. Anal. Calcd for  $\text{C}_{36}\text{H}_{28}\text{OPWS}_4$ : C, 59.07; H, 4.13. Found: C, 58.77; H, 4.13. UV-visible absorption: 353 (sh,  $3600 \text{ M}^{-1} \text{ cm}^{-1}$ ), 462 (1200), 618 nm (3100). ESR:  $g_{\text{av}} = 1.960$ ,  $A_{\text{av}} = 50 \times 10^{-4} \text{ cm}^{-1}$ .

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(16) To an acetonitrile solution (200 mL) of  $(\text{PPh}_4)[\text{W}^{\text{VO}}(\text{bdt})_2]$  (1) (680 mg, 0.83 mmol) was added  $\text{PPh}_4\text{BH}_4$  (1.2 g, 6.6 mmol). The solution was kept at  $-20^\circ\text{C}$  for 2 days. Precipitating red plate crystals of 2a were collected by filtration, washed with acetonitrile, and dried under vacuum. Yield: 680 mg (71%). Anal. Calcd for  $\text{C}_{60}\text{H}_{48}\text{OP}_2\text{WS}_4$ : C, 62.17; H, 4.17. Found: C, 59.60; H, 4.14. 2b was obtained by the  $\text{NET}_4\text{BH}_4$  reduction of  $(\text{NET}_4)[\text{W}^{\text{VO}}(\text{bdt})_2]$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{48}\text{ON}_2\text{WS}_4$ : C, 45.40; H, 6.53; N, 3.78. Found: C, 45.32; H, 6.56; N, 3.88.  $^1\text{H}$  NMR (DMF- $d_7$ ):  $\delta$  7.73 (q, 4 H,  $J = 5.4, 3.2 \text{ Hz}$ ), 6.68 (q, 4 H,  $J = 5.4, 3.2 \text{ Hz}$ ).

(17) To a DMF solution (70 mL) of 2a (680 nm, 0.59 mmol) was added  $\text{Me}_3\text{NO}$  (90 mg, 1.2 mmol) at room temperature. The red solution turned yellow in 5 min. Diethyl ether (20 mL) was added dropwise after 2 h. Yellow needles obtained were collected by filtration and dried under vacuum. Yield: 490 mg (70%). Anal. Calcd for  $\text{C}_{60}\text{H}_{48}\text{O}_2\text{P}_2\text{WS}_4$ : C, 61.33; H, 4.10. Found: C, 61.50; H, 4.14. 3b was synthesized by the same procedure. Anal. Calcd for  $\text{C}_{28}\text{H}_{48}\text{ONWS}_4$ : C, 44.44; H, 6.39; N, 3.70. Found: C, 44.21; H, 6.33; N, 3.74.  $^1\text{H}$  NMR (DMF- $d_7$ ):  $\delta$  7.73 (q, 4 H,  $J = 5.4, 3.2 \text{ Hz}$ ), 6.68 (q, 4 H,  $J = 5.4, 3.2 \text{ Hz}$ ).