atoms, away from the other rhodium atom.[19] It is stable in aqueous solution but does react readily with H_2SO_4 and H_3PO_4 to give sulfate- and dihydrogen phosphate-bridged complexes, respectively.[20,21] The Rh–Rh distance in the dihydrogen phosphate is 2.485 (1) Å, longer than in **1**, and identical to the Pt–Pt distance in **3**.[22]

Acknowledgment. We thank the Australian Research Council for financial support.

Supplementary Material Available: Preparative details, tables of atomic coordinates, thermal parameters, bond distances and angles (6 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(19) Calculated from data in ref 1.

(20) Baranovskii, I. B.; Chalisova, N. N.; Mazo, G. Ya *Zh. Neorg. Khim.* **1979**, *24*, 3395–3396.

(21) Baranovskii, I. B.; Abdullaev, S. S.; Shchelokov, R. N. *Zh. Neorg. Khim.* **1979**, *24*, 3149.

(22) Dikaneva, L. M.; Sadikov, G. G.; Porai-Koshits, M. A.; Baranovskii, I. B.; Abdullaev, S. S. *Zh. Neorg. Khim.* **1980**, *25*, 875.

A Highly Catalytic System for the Direct Oxidation of Lower Alkanes by Dioxygen in Aqueous Medium. A Formal Heterogeneous Analog of Alkane Monooxygenases

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Methane is the most abundant and the least reactive member of the hydrocarbon family (C–H bond energy: 104 kcal/mol). Ethane comes second in both categories. Hence, C–H activation leading to catalytic oxidation of these hydrocarbons is one of the most challenging chemical problems, in addition to being of great practical importance. In terms of oxidants, dioxygen (O_2) is clearly the most desirable oxidant due to its ready availability and high reduction potential. However, we are unaware of *any* report of a highly catalytic system for the direct oxidation of these two alkanes by dioxygen at low to moderate temperatures ($\leq$100 °C).[1] Herein, we describe a system that achieves this goal in aqueous medium. *For example, starting with ethane, it is possible to form acetic acid whose concentration exceeds 0.5 M!* The system involves a metal catalyst (palladium) and a coreductant (carbon monoxide). The metal serves as the catalyst for *three* reactions in tandem resulting eventually in the oxidation of the alkane and the coreductant and the reduction of dioxygen (Scheme I).

Scheme I

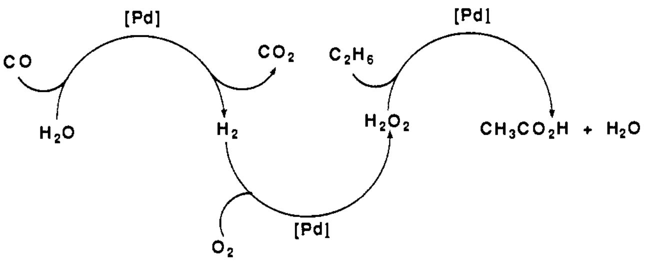

Table I. Oxidation of Ethane[a]

temp, °C	yield,[b] mmol (turnover = mmol of product/mmol of surface metal atoms[c])		
	CH_3CO_2H	HCO_2H	CH_3CH_2OH
70	0.53 (221)	0.12 (50)	0.035 (15)
85	2.55 (1063)	1.43 (596)	
100	2.73 (1138)	0.24 (100)	
110	0.88 (367)	0.16 (67)	
100[d]	<0.001		
100[e]	0.006		
95[f]	0.30	0.30	
95[g]	0.40 (88)	0.11 (24)	
95[h]	0.13		

[a] Typical conditions: 40 mg of 5% palladium on carbon (60 μmol of surface Pd atoms/g of catalyst); 5 mL of 0.1 M DCl in D_2O; CH_3CH_3, 500 psi; CO, 100 psi; O_2, 100 psi; time, 20–24 h. The reactions were run in 140-mL stainless steel bombs equipped with glass liners. Approximately 180 mmol of CH_3CH_3 was present in the initial gas mixture. [b] Yields determined independently by ^1H NMR and GC. [c] Amount of surface metal atoms in catalyst sample determined from dihydrogen chemisorption studies. [d] CO was not added. [e] DCl was not added. [f] 10.6 mg of palladium black was used. [g] 40 mg of 5% palladium on alumina (114 μmol of surface Pd atoms/g of catalyst) was used. [h] 50 mg of 5% platinum on carbon was used.

Our results on the oxidation of ethane are summarized in Table I. Both carbon monoxide and an acidic solution were clearly necessary since little or no oxidation of ethane occurred in their absence. Although Pd on carbon was the most active catalyst examined, other forms of metallic Pd, as well as metallic Pt, were also effective. The following pieces of evidence support the mechanism shown in Scheme I. The use of ^{13}CO resulted in the formation of $^{13}CO_2$ as the *only* ^{13}C-containing product (as determined by ^{13}C NMR). Water was also necessary since no oxidation was observed in a dry CH_3NO_2/CF_3CO_2H mixture (however, vide infra). The above observations were consistent with a metal-catalyzed water gas shift reaction.[2] It was possible to bypass this first catalytic reaction by replacing carbon monoxide with dihydrogen (H_2). In the latter instance it was possible to run the reaction in a nonaqueous medium as shown in eq 1.

$$CH_3CH_3\ (350\ psi) + H_2\ (100\ psi) + O_2\ (100\ psi) \xrightarrow[CH_3NO_2\ (3\ mL)/CF_3CO_2H\ (0.08\ mL),\ 85\ ^\circ C,\ 12\ h]{5\%\ Pd/C\ (50\ mg)} CH_3CO_2H\ (0.46\ mmol) + HCO_2H\ (0.26\ mmol) \quad (1)$$

The second catalytic reaction involved the formation of hydrogen peroxide from dihydrogen and dioxygen and has been reported previously in a patent.[3] This reaction occurred only under acidic conditions. That hydrogen peroxide was formed in our system starting with carbon monoxide and dioxygen in the presence of water was verified by running the reaction in the absence of alkane. Titration of the resultant solution with a standard solution of $KMnO_4$ indicated a hydrogen peroxide concentration of 0.002 M. In an independent experiment we observed the slow Pd-catalyzed oxidation of ethane to ethanol, acetic acid, and formic acid by hydrogen peroxide at 30 °C. A lower reaction temperature was chosen in order to avoid the observed metal-catalyzed decomposition of hydrogen peroxide to water and dioxygen. It was this latter undesirable reaction that made carbon monoxide a more effective coreductant than dihydrogen. Starting with carbon

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(1) Examples of high-temperature oxidations and/or oxidations with significantly lower turnovers: (a) Baerns, M.; van der Wiele, K.; Ross, J. R. H. *Catal. Today* **1989**, *4*, 471. (b) Pitchai, R.; Klier, K. *Catal. Rev.—Sci. Eng.* **1986**, *28*, 13. (c) Kung, H. H. *Stud. Surf. Sci. Catal.* **1989**, *45*, 200. (d) Hunter, N. R.; Gesser, H. D.; Morton, L. A.; Yarlagadda, P. S.; Fung, D. P. C. *Appl. Catal.* **1990**, *57*, 45. (e) Burch, R. B.; Squire, G. D.; Tsang, S. C. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3561. (f) Kowalak, S.; Moffat, J. B. *Appl. Catal.* **1988**, *36*, 139. (g) Stolarov, I. P.; Vargaftik, M. N.; Sishkin, D. I.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1991**, 938. (h) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049. (i) Herron, N. *New J. Chem.* **1989**, *13*, 761. (j) Lyons, J. E.; Ellis, P. E.; Durante, V. A. *Stud. Surf. Sci. Catal.* **1991**, *68*, 99. The reaction conditions and rates described in the last paper come closest to our system.

(2) Reviews: (a) Thomas, C. L. *Catalytic Processes and Proven Catalysts*; Academic: New York, 1970; p 104. (b) Happel, J. *Catal. Rev.* **1972**, *6*, 221. (c) Laine, R. M.; Wilson, R. B. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, 1984; p 217. (d) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

(3) Gosser, L. W. U.S. Patent, 4,681,751, 1987.

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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.[4,5] 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 ^{13}CO, $CH_3{}^{13}CO_2H$ was not observed as a product. Note that carbon monoxide was an efficient trapping agent for methyl radical (rate constant in water:[6] 2×10^6 L mol^{-1} s^{-1} 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.[7] 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_2O, 5 mL; HCl, 0.1 M; H_2, 150 psi; O_2, 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.[8] The requirement of a coreductant makes the overall reaction formally analogous to the reaction of monooxygenases[9] 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,[4] 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[10] 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_3CH_3, 74-84-0; CH_3CO_2H, 64-19-7; HCO_2H, 64-18-6; CH_3CH_2OH, 64-17-5; O_2, 7782-44-7; H_2, 1333-74-0; Pd, 7440-05-3; Pt, 7440-06-4; CH_4, 74-82-8; CO, 630-08-0; H_2O, 7732-18-5; H_2O_2, 7722-84-1.

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(4) (a) Sen, A.; Lin, M. *J. Chem. Soc., Chem. Commun.* **1992**, 508. (b) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

(5) Nicoletti, J. W.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 759.

(6) Bakac, A.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1497.

(7) Lin, M.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1992**, 892.

(8) An analogous mechanistic pathway may also operate in the recently reported aromatic oxidations by the Pd metal/Cu^{II}/H_2/O_2 system: (a) Kunai, A.; Wani, T.; Uehara, Y.; Iwasaki, F.; Kuroda, Y.; Ito, S.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2613. (b) Kuroda, Y.; Kunai, A.; Hamada, M.; Kitano, T.; Ito, S.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3089.

(9) Reviews: (a) Groh, S. E.; Nelson, M. J. In *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990; p 207. (b) Ortiz de Montellano, P. R. In *Cytochrome P-450*: *Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; p 217. (c) Guegerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9. (d) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928.

(10) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

A Chelation Approach toward Activation of C_{sp^3}–S Bonds. Nickel-Catalyzed Selective Cross Coupling of Bisdithioacetals with Grignard Reagents[1a]

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Although the use of the transition metal-catalyzed cross-coupling reactions is widespread,[2] the corresponding reactions involving the replacement of the aliphatic C–X bond are rare.[3] Only neopentyl iodides undergo coupling reactions with aromatic Grignard reagents in the presence of a palladium catalyst.[3c] The major impediment is due to the low reactivity of the C_{sp^3}–X bond toward oxidative addition with transition metals. Side reactions such as reduction, β-elimination, and/or homocoupling frequently become predominant.[3b–d] Our recent discovery of the nickel-catalyzed cross-coupling reactions of benzylic or allylic dithioacetals with Grignard reagents[4] has prompted us to investigate the simple aliphatic substrates. As expected, these compounds are unreactive even under refluxing benzene conditions.[4,5] 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.[6] 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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(1) (a) Presented at the 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992; ORGN 300. (b) Recipient of Li-Ching Foundation Scholarship, 1991–1992.

(2) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

(3) (a) Castle, P. L.; Widdowson, D. A. *Tetrahedron Lett.* **1986**, *27*, 6013. (b) Yuan, K.; Scott, W. J. *Tetrahedron Lett.* **1989**, *30*, 4779. (c) Yuan, K.; Scott, W. J. *J. Org. Chem.* **1990**, *55*, 6188. (d) Yuan, K.; Scott, W. J. *Tetrahedron Lett.* **1991**, *32*, 189. (e) Recently, Scott showed that the anomeric carbon mesylate in protected monosaccharides undergoes palladium-catalyzed oxidative addition across the C–O bond followed by β-hydride elimination, but no coupling reaction is observed. Cf. Jones, G. S.; Scott, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1491.

(4) For a review, see: Luh, T.-Y. *Acc. Chem. Res.* **1991**, *24*, 257.

(5) (a) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1515. (b) Ni, Z.-J.; Mei, N.-W.; Shi, X.; Wang, M. C.; Tzeng, Y.-L.; Luh, T.-Y. *J. Org. Chem.* **1991**, *56*, 4035. (c) Wong, K.-T.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1992**, 564.

(6) For leading references, see: (a) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141. (b) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.