Ligand-Centered Oxidations of Organometallic Thiolates Using Dimethyldioxirane[1]

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Introduction

Oxygen transfer reactions involving organo-transition metal compounds pose a synthetic challenge as the usually electron-rich metal center will be the preferred site of attack by the oxidant. A notable exception is the oxidation of coordinated ligands by strongly nucleophilic reagents such as trimethylamine oxide, a reagent which is being used with great advantage for the oxidative removal of carbon monoxide ligands.[3] Such a methodology, however, is limited to cases where the functionality to be oxidized is sufficiently electrophilic.

Recently, dimethyldioxirane (**1**) has been shown to be a highly reactive, yet surprisingly selective oxygen transfer reagent.[4] It is readily available in solution in sufficient quantities[5] and operates very cleanly, since acetone, the precursor and solvent for **1**, is the only byproduct after complete oxygen atom transfer. Furthermore, **1** functions as an ambiphilic reagent in that its electrophilic nature is established through the epoxidation of a wide range of electron-rich alkenes[6] and through the selective oxidation of thioethers to sulfoxides;[7] on the other hand its nucleophilic character is exhibited by the epoxidation of electron-poor alkenes[8] and by the pronounced selectivity for attack at the sulfoxide group of thianthrene 9-oxide.[9] In all, the high reactivity of dimethyldioxirane and the apparent absence of radical pathways[4] make this compound the reagent of choice to perform selective oxidations on organo-transition metal complexes.[10]

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standards methods. Solutions of **1** in acetone (approximately 0.1 M) were obtained as described previously,[5] their content was estimated by addition of a known excess of methyl phenyl sulfide and NMR analysis of the sulfide/sulfoxide mixture obtained. $Na[CpW(CO)_3]$[11] was synthesized following published procedures; ruthenium thiolates $[CpRuL_2(SR)]$ were obtained from the corresponding chlorides and NaSR.[12] Infrared spectra were recorded with a Bruker IFS 25 spectrometer; NMR spectra were obtained using Bruker AMX 400 (^1H, ^{13}C) and Jeol FX 90 Q (^{31}P) instruments.

Preparation of $[CpRuL_2(SO_2R)]$ (3a–g). To a cooled (−40 °C) solution of $[CpRuL_2(SR)]$ (0.20 mmol) in dichloromethane (3 mL) is added a solution of **1** (0.60 mmol) in acetone. After 10 min all volatiles are removed under vacuum and the yellow residue chromatographed over a short (5 cm) silica column using 2:1 dichloromethane/acetone. Crystallization from dichloromethane/hexane gives the sulfinates **3a–g** in about 90% yield as light yellow crystals. **3a**, **3e**, and **3g** have been obtained previously by SO_2 insertion into the ruthenium–carbon bond.[13]

3a. Anal. Calcd for $C_{42}H_{38}O_2P_2RuS$: C, 65.53; H, 4.98. Found: C, 64.98; H, 5.19. IR (Nujol, cm^{-1}): 1144 (s, $\nu_{asym}(SO)$), 1024 (s, $\nu_{sym}(SO)$). ^1H NMR ($CDCl_3$): δ 2.32 (s, SO_2CH_3), 4.44 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 58.9 (s, SO_2CH_3), 86.3 (s, C_5H_5). ^{31}P NMR ($CDCl_3$): δ 39.5 (s).

3b. Anal. Calcd for $C_{32}H_{32}O_2P_2RuS$: C, 59.71; H, 5.01. Found: C, 59.91; H, 5.28. IR (Nujol, cm^{-1}): 1140 (s, $\nu_{asym}(SO)$), 1024 (s, $\nu_{sym}(SO)$). ^1H NMR ($CDCl_3$): δ 1.91 (s, SO_2CH_3), 2.20 (m, dppe), 3.20 (m, dppe), 4.84 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 27.1 (vt, N = 45 Hz, dppe), 59.2 (s, SO_2CH_3), 85.4 (s, C_5H_5). ^{31}P NMR ($CDCl_3$): δ 83.9 (s).

3c. Anal. Calcd for $C_{47}H_{40}O_2P_2RuS$: C, 67.86; H, 4.85. Found: C, 67.70; H, 5.07. IR (Nujol, cm^{-1}): 1160, 1148 (s, $\nu_{asym}(SO)$), 1030, 1020 (s, $\nu_{sym}(SO)$). ^1H NMR (CD_2Cl_2): δ 4.04 (s, C_5H_5). ^{13}C NMR (CD_2Cl_2): δ 86.2 (s, C_5H_5). ^{31}P NMR (C_6D_6): δ 39.2.

3d. Anal. Calcd for $C_{37}H_{34}O_2P_2RuS$: C, 62.97; H, 4.86. Found: C, 63.25; H, 5.05. IR (Nujol, cm^{-1}): 1156 (s, $\nu_{asym}(SO)$), 1028, 1018 (s, $\nu_{sym}(SO)$). ^1H NMR ($CDCl_3$): δ 2.50 (m, dppe), 3.42 (m, dppe), 4.90 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 27.1 (vt, N = 45 Hz, dppe). ^{31}P NMR (C_6D_6): δ 84.2 (s).

3e. Anal. Calcd for $C_{48}H_{42}O_2P_2RuS$: C, 68.15; H, 5.00. Found: C, 67.81; H, 5.13. IR (Nujol, cm^{-1}): 1154 (s, $\nu_{asym}(SO)$), 1030 (s, $\nu_{sym}(SO)$). ^1H NMR ($CDCl_3$): δ 3.67 (s, SO_2CH_2), 4.52 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 74.6 (s, SO_2CH_2), 86.2 (s, C_5H_5). ^{31}P NMR (C_6D_6): δ 39.6 (s).

3f. Anal. Calcd for $C_{38}H_{36}O_2P_2RuS$: C, 63.41; H, 5.04. Found: C, 63.61; H, 5.00. IR (Nujol, cm^{-1}): 1167 (s, $\nu_{asym}(SO)$), 1034 (s, $\nu_{sym}(SO)$). ^1H NMR (C_6D_6): δ 2.01 (m, dppe), 3.25 (m, dppe), 3.37 (s, SO_2CH_2), 4.71 (s, C_5H_5). ^{13}C NMR (C_6D_6): δ 27.1 (vt, N = 44 Hz, dppe), 74.5 (s, SO_2CH_2), 84.9 (s, C_5H_5). ^{31}P NMR (C_6D_6): δ 83.3 (s).

3g. Anal. Calcd for $C_{31}H_{27}O_3PRuS$: C, 60.87; H, 4.45. Found: C, 60.84; H, 4.73. IR (Nujol, cm^{-1}): 1962 (vs, $\nu(CO)$), 1174 (s, $\nu_{asym}(SO)$), 1040 (s, $\nu_{sym}(SO)$). ^{13}C NMR (C_6D_6): δ 77.8 (s, SO_2CH_2), 88.3 (s, C_5H_5), 203.3 (s, CO). ^{31}P NMR ($CDCl_3$): δ 47.3 (s).

Preparation of $[CpW(CO)_3(CH_2SMe)]$ (4). The procedure given here is similar to those published for $[CpMo(CO)_3(CH_2SMe)]$[14] and $[CpW(CO)_3CH_2SPh]$.[15] To a solution of $Na[CpW(CO)_3]\cdot 2$diglyme (0.63 g, 1.00 mmol) in THF (10 mL) is added $ClCH_2SCH_3$ (0.15 mL, 1.38 mmol) with stirring. After 2 h, the mixture is taken to dryness, and the residue is extracted with dichloromethane and chromatographed over a short (10 cm) alumina column. The yellow solution is concentrated to 5 mL, pentane (10 mL) is added, and the product is allowed to crystallize at −20 °C; yield 0.35 g (89%). Anal. Calcd for $C_{10}H_{10}O_3SW$: C, 30.48; H, 2.56. Found: C, 30.34; H, 2.54. IR (CH_2Cl_2, cm^{-1}): 2020, 1928 (vs, $\nu(CO)$). ^1H NMR ($CDCl_3$): δ 2.09 (s, CH_3), 2.46 (s, CH_2), 5.47 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ −9.9 (s, $^1J_{W-C}$ = 37 Hz, CH_2), 26.0 (s, CH_3), 91.7 (s, C_5H_5), 216.2 (s, $^1J_{W-C}$ = 157 Hz, CO), 229.0 (s, $^1J_{W-C}$ = 124 Hz, CO).

Preparation of $[CpW(CO)_3(CH_2S(O)Me)]$ (5). To a solution of **4** (0.10 g, 0.25 mmol) in dichloromethane (3 mL) is added an equimolar amount of **1** in acetone at −65 °C. After 10 min all volatiles are removed under vacuum, and the residue is dissolved in dichloromethane and filtered over alumina. The filtrate is concentrated and the product is precipitated by adding hexane; yield 0.09 g (88%) of yellow solid. Anal. Calcd for $C_{10}H_{10}O_4SW$: C, 29.29; H, 2.46. Found: C, 29.20; H, 2.45. IR (CH_2Cl_2, cm^{-1}): 2026, 1928 (vs, $\nu(CO)$), 1017 (s, $\nu(SO)$). ^1H NMR ($CDCl_3$): δ 2.61 (s, CH_3), 2.58, 2.62 (AB system, $^2J_{H-H}$ = 12 Hz, CH_2), 5.67 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 11.9 (s, $^1J_{W-C}$ = 46 Hz, CH_2), 45.6 (s, CH_3), 91.2 (s, C_5H_5), 216.3 (s, $^1J_{W-C}$ = 153 Hz, CO), 226.8 (s, $^1J_{W-C}$ = 122 Hz, CO).

Preparation of $[CpW(CO)_3(CH_2S(O)_2Me)]$ (6). The synthesis is carried out as described for **5** but using the double amount of **1**. **6** was thus obtained as a light-yellow solid in 70% yield. Anal. Calcd for $C_{10}H_{10}O_5SW$: C, 28.19; H, 2.37. Found: C, 28.01; H, 2.36. IR (CH_2Cl_2, cm^{-1}): 2033, 1937 (vs, $\nu(CO)$), 1288 (s, $\nu_{asym}(SO)$), 1128 (s, $\nu_{sym}(SO)$). ^1H NMR ($CDCl_3$): δ 2.95 (s, CH_2), 3.04 (s, CH_3), 5.75 (s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 11.2 (s, $^1J_{W-C}$ = 49 Hz, CH_2), 45.1 (s,

(1) Sulfur(IV) Compounds as Ligands. 15. Part 14: Schenk, W. A.; Urban, P. *J. Organomet. Chem.* **1991**, *411*, C 27.
(2) (a) Institute of Inorganic Chemistry. (b) Institute of Organic Chemistry.
(3) (a) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. (b) Luh, T. Y. *Coord. Chem. Rev.* **1984**, *60*, 225.
(4) (a) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205. (b) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.
(5) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.
(6) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437.
(7) Murray, R. W.; Jeyaraman, R.; Pillay, M. K. *J. Org. Chem.* **1987**, *52*, 746.
(8) Adam, W.; Hadjiarapoglou, L.; Smerz, A. *Chem. Ber.* **1991**, *124*, 227.
(9) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.
(10) Very recently, **1** has been successfully used for the complete oxidative decarbonylation of both a fairly electron-poor ($Cp^*Re(CO)_3$) metal carbonyl and a very electron-rich ($TpMo(CO)_3^-$) metal carbonyl: Wolowiec, S.; Kochi, J. K. *Inorg. Chem.* **1991**, *30*, 1215.
(11) Behrens, U.; Edelmann, F. *J. Organomet. Chem.* **1984**, *263*, 179.
(12) Schenk, W. A.; Stur, T. *Z. Naturforsch., B* **1990**, *45*, 1495.
(13) Joseph, M. F.; Baird, M. C. *Inorg. Chim. Acta* **1985**, *96*, 229.
(14) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486.
(15) Kneuper, H. J.; Zimmermann, C.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 1043.

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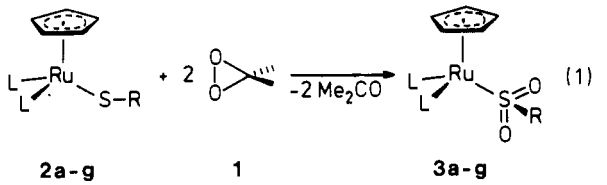
CH_3), 91.2 (s, C_5H_5), 215.7 (s, $^1J_{W-C}$ = 152 Hz, CO), 227.4 (s, $^1J_{W-C}$ = 119 Hz, CO).

Results

Treatment of ruthenium thiolate complexes **2a–g** at −40 °C with an excess of dimethyldioxirane (**1**) gives the sulfinato complexes **3a–g** in excellent yields (eq 1). If **1** is used in stoi-



(1)

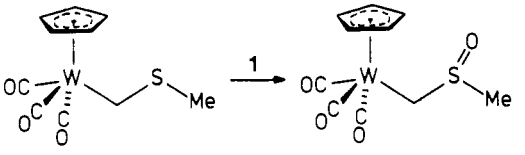
2a-g **1** **3a-g**

L_2 \ R	Me	Ph	CH_2Ph
$(PPh_3)_2$	a	c	e
dppe	b	d	f
CO/PPh_3			g

chiometric quantities, one obtains 1:1 mixtures of sulfinato complexes **3** and starting materials **2**. Treatment of an equimolar mixture of **2f** and dibenzyl sulfide (0.2 mmol each) with only a small quantity of **1** (0.05 mol) again gave sulfinate **3f** as the only detectable oxidation product.

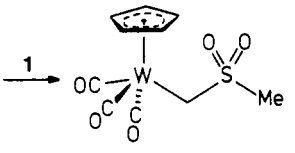
The identification of sulfinato complexes **3** is straightforward. Two intense SO stretching absorptions are found in the expected range,[14,16,17] the CO stretching frequency of **3g** is 26 cm^{-1} higher compared to **2g**,[12] and the ^{13}C resonances of the α carbons of the organic groups on sulfur experience the expected downfield shift upon oxidation.[18] Careful monitoring of the reaction by ^1H and ^{13}C NMR did not reveal even a trace of the expected intermediates, the sulfenato complexes $[CpRuL_2(S(O)R)]$.

Treatment of the α-metalated thioether **4** with a stoichiometric amount of **1** gives the corresponding sulfoxide **5** in very good yield. Further oxidation converts **5** into the sulfone **6** (eq 2).



4 **5**

(2)



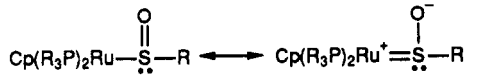
6

Both **5** and **6** exhibit SO stretching frequencies which are considerably lower than those of organic sulfoxides and sulfones, respectively. On the other hand removal of electron density from the metal on going from **4** via **5** to **6** leads to an increase of the CO stretching frequencies of the $W(CO)_3$ unit. As expected the first oxygen transfer results in a 20 ppm downfield shift of the carbon atoms adjacent to sulfur whereas the second O-transfer step leaves these resonances virtually unchanged.[18]

Discussion

Transition metal thiolates L_nM–S–R are far better nucleophiles than thioethers R–S–R. This is due to an antibonding interaction between the p orbitals on sulfur and the occupied metal t_{2g} set, which raises the energy of the sulfur-centered HOMO.[19] Thus it is not unexpected that thiolate complexes of the type investigated here are more rapidly oxidized than dibenzyl sulfide. What is surprising, however, is the fact that no intermediate monooxidation products could be observed. Since there is no reason to assume that the sulfenates $[CpRu(PR_3)_2(S(O)R)]$ would be unstable and would disproportionate to **2** and **3**—a few examples of stable transition metal sulfenates $[L_nM(S(O)R)]$ are known in fact[20,21]—we are left to conclude that the intermediates are even more rapidly oxidized than the starting thiolates. This is unexpected in view of the fact that a number of cationic cobalt complexes $[en_2Co(SR)]^{n+}$ have been selectively oxidized with H_2O_2/H^+ to the corresponding sulfenates.[20] This "normal" order of attack by electrophilic oxidants, i.e., L_nM–SR > L_nM–S(O)R, which parallels that of simple thioethers and sulfoxides,[22] appears to be reversed if L_nM is an electron-rich, low-valent metal fragment. Previous experience with tungsten[23] and nickel[24] thiolates seems to indicate that this is a general phenomenon and not limited to oxidations by **1**.

It has been suggested recently that the primary attack on sulfoxides by dimethyldioxirane—and possibly by electrophilic oxidants in general—occurs at oxygen rather than at sulfur.[4b,7] Indeed transition metal sulfenates may be expected to be very good nucleophiles if the excellent π-donor ability of low-valent transition metal fragments is taken into account (cf. mesomeric structures below).



Clearly, this type of resonance would be much less important for positively charged sulfenate complexes and would be unavailable to normal sulfoxides. Support for this view comes from the observation that the SO stretching frequencies of sulfenate complexes (e.g. $[IrCl_2(CO)(PPh_3)_2(S(O)Me)]$: 1013 cm^{-1})[21a] are much lower than those of organic sulfoxides (Me_2SO: 1060 cm^{-1}).

The compatibility of this oxidation method with metal–carbon σ bonds is demonstrated by the clean and selective conversion of metalated thioether **4** to the corresponding sulfoxide and sulfone, respectively (eq 2). In these reactions the superiority of **1** over more conventional oxidants becomes obvious. Boche et al. reported that a closely related compound, $[CpW(CO)_3(CH_2S(O)_2Ph)]$, could only be obtained in trace quantities from the corresponding sulfoxide and mCPBA; stronger oxidants such as H_2O_2/HOAc led to complete degradation.[15]

(16) Vitzthum, G.; Lindner, E. *Angew. Chem.* **1971**, *83*, 315; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 315.
(17) Fujihara, H.; Furukawa, N. *The Chemistry of Sulfinic Acids, Esters, and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1990; p 279.
(18) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; G. Thieme: Stuttgart, Germany, 1984.
(19) Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297.
(20) (a) Jackson, W. G.; Sargeson, A. M.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1976**, 934. (b) Herting, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Inorg. Chem.* **1978**, *17*, 1649. (c) Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.
(21) (a) George, T. A.; Watkins, D. D. *Inorg. Chem.* **1973**, *12*, 398. (b) Markham, S. J.; Chung, Y. L.; Branum, G. D.; Blake, D. M. *J. Organomet. Chem.* **1976**, 107, 121.
(22) Hoyle, J. *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988; p 969.
(23) Weinmann, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 3034.
(24) (a) Kumar, M.; Colpas, G. J.; Day, R. O.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, 111, 8323. (b) Schrauzer, G. N.; Zhang, C.; Chadha, R. *Inorg. Chem.* **1990**, *29*, 4104. (c) Darensbourg, M. Y. Personal communication.

Further work will be essential to provide a deeper insight into the mechanism of the oxygen transfer in eq 1 as well as to evaluate the synthetic utility of dioxiranes in ligand-centered oxidations.

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