

(5), and 0.332 (6) Å for N(3), N(13), N(1), N(15), and N(8), respectively. N(3) and N(13) have the least contribution of sp^2 character and thus the longest N-C bonds while N(8) has the shortest N-C bonds due to increased sp^2 character. The average N-C length for the secondary N(6) and N(10) atoms is 1.496 ± 0.011 Å.

Two perchlorate anions are assumed to be rotationally disordered about the Cl(A)-O(1) and Cl(B)-O(5) bonds. The average angles of rotation are about 48 and 38° for perchlorate A and B, respectively. Two anions are located above and below the coordination plane. The Ni-Cl(A) and Ni-Cl(B) distances are 4.338 (1) and 3.299 (1) Å, respectively.

There are five six-membered and two five-membered rings in the cation. The two six-membered rings in the bicyclononane ring assume a stable chair conformation with average intracyclic torsion angles of 59 ± 5 and $58 \pm 4^\circ$. The two six-membered chelate rings formed between the bicyclononane ring and the nickel ion also assume a chair conformation. However, the six-membered ring formed by Ni, N(6), C(7), N(8), C(9), and N(10) assumes a conformation intermediate between the normal and the half-chair conformations, with C(7)-N(6)-Ni-N(10) and C(9)-N(10)-Ni-N(6) torsion angles of 30.9 (4) and -29.5 (4)°, respectively. The two five-membered chelate rings formed by the ethylenediamine moieties assume an unsymmetrical gauche (or an envelope) conformation. C(4) and C(12) are 0.136 (7) and 0.093 (6) Å below the coordination plane, while C(5) and C(11) are 0.569 (7) and 0.572 (7) Å above this plane, respectively. The N(3)-C(4)-C(5)-N(6) and N(13)-C(12)-C(11)-N(10) torsion angles are -50.9 (5) and 51.2 (5)°, respectively.

The N-Ni-N bite angle in each of the five-membered chelate rings is 87.7 (2)° and the N-N bite distances are 2.654 (6) and 2.660 (6) Å, which are normally observed values in the five-membered rings of the Ni(II) macrocyclic complexes.^{33,36,37,46} The N(6)-Ni-N(10) bite angle of 95.4 (2)° and the N(6)-N(10) distance of 2.836 (6) Å are also the normal values for the six-membered rings.^{33,36,37} However, the N(3)-Ni-N(13) bite angle of 89.1 (2)° and the N(3)-N(13) bite distance of 2.691 (6) Å involving the bicyclononane ring are smaller than those for the

six-membered ring but comparable to the values for the five-membered ring. The same trend is also observed in $[\text{Ni}(\text{C}_9\text{H}_{22}\text{N}_6)](\text{ClO}_4)_2$. The intracyclic valence angles at N(1), N(15), C(2), C(18), C(17), and C(14) are important for determining the N-N separation in the tetraazabicyclononane ring. There seems to be no chance for lengthening of this bite distance because these angles, ranging from 112.2 to 114.5° , are already larger than the normal values of 107° for N(sp^3) and 109.5° for C(sp^3).

The present study shows that the overall structural properties of the tetraazabicyclononane ring are similar to those of the five-membered ring in the coordination sphere. Therefore, the macrocyclic ligand in this study is more similar to a [13]aneN₄, which contains three five-membered rings and a six-membered ring, than to a [14]aneN₄, in which the five-membered and the six-membered rings are alternating. Then the properties of a ligand containing two bicyclononane rings symmetrically would resemble those of the [12]aneN₄ rather than those of the [14]aneN₄. In general, the stability of the square-planar Ni(II) macrocyclic complexes depends on the ring size of the ligand in the order $[\text{12}]aneN_4 < [\text{13}]aneN_4 < [\text{14}]aneN_4 > [\text{15}]aneN_4 > [\text{16}]aneN_4$.⁴⁷⁻⁵⁰ Therefore, the failure in synthesizing the Ni(II) complex of VII, in which two bicyclononane rings are linked by the ethylenediamine moieties, may be explained by assuming its resemblance to the complex of a [12]aneN₄ having lower stability.

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates of the hydrogen atoms, bond lengths and angles involving the hydrogen atoms and the perchlorate ions, least-squares planes, and torsion angles for $[\text{Ni}(\text{C}_{12}\text{H}_{27}\text{N}_7)](\text{ClO}_4)_2$ (6 pages); tables of final observed and calculated structure factors for the two complexes (14 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Chemical Sciences,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Organosulfide Group Transfer Reactions of Transition-Metal Carbonyl Radicals: Electronic and Steric Effects¹

Kang-Wook Lee and Theodore L. Brown*

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Photochemical reactions of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn, Re}$) with RSSR ($\text{R} = \text{Me, Ph}$) or MeSSiMe_3 in hexane at ambient temperature yield $(\mu\text{-SR})_2\text{M}_2(\text{CO})_8$ (70-85%) and $[\text{M}(\text{CO})_5\text{SR}]_4$ (0-15%). The corresponding reaction of $\text{Re}_2(\text{CO})_8\text{L}_2$ almost quantitatively yields $(\mu\text{-SR})_2\text{Re}_2(\text{CO})_8\text{L}_2$, and the reaction of $\text{Re}_2(\text{CO})_{10}$ and $[\text{Me}_2\text{NC}(\text{S})\text{S}]_2$ gives $(\eta^2\text{-S}_2\text{CNMe}_2)\text{Re}(\text{CO})_4$. The initial product for each reaction is $\text{RSM}(\text{CO})_4\text{L}$ ($\text{L} = \text{CO, PR}_3$), formed by RS group transfer from RSSR to the $^*\text{M}(\text{CO})_4\text{L}$ radical generated by photolysis. $(\mu\text{-SR})_2\text{M}_2(\text{CO})_8$ is in equilibrium with the 16-electron species $\text{RSM}(\text{CO})_4$ under photochemical conditions. Laser flash photolysis kinetics studies reveal the electronic and steric effects of L ligands in the $\text{Re}(\text{CO})_4\text{L}^*$ radical and the steric effect of the R group in RSSR on the group transfer rate constant. The relative rate constants for reactions of $\text{Re}(\text{CO})_4\text{PMe}_3^*$ with various dialkyl disulfides decrease in the order methyl > *n*-butyl > *sec*-butyl > *tert*-butyl (630:280:36:1). The rate constants for group transfer for a series of $\text{Re}(\text{CO})_4\text{L}^*$ radicals fit a two-parameter free energy relationship wherein the electronic and the steric parameters of L are represented. The reaction is accelerated by increased electron donor capability of L and retarded by increased size of L.

Introduction

There has recently been extensive interest in the reactions of photogenerated metal carbonyl species.² 17-electron transi-

tion-metal carbonyl radicals, formed by photolysis of metal-metal single-bonded dimers, undergo various reactions such as recom-

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bination,³ substitution,⁴ electron transfer,^{2b,5} and atom transfer.^{3d,4a,5-7} Abrahamson and Freeman⁸ have reported that the reaction of CpW(CO)₃^{*} radical with RSSR gives RSW(CO)₃Cp. This reaction can be termed a *group transfer*. The RS group is transferred from RSSR to the 17-electron metal-centered radical to form the metal-sulfur bond, in analogy with atom transfer processes. In this work we have observed that photogenerated ^{*}M(CO)₄L (M = Mn, Re; L = CO, PR₃) radicals also react with RSSR (R = Ph, Me, *n*-Bu, *sec*-Bu, *t*-Bu) or MeSSiMe₃, presumably to yield the unstable compound RSM(CO)₄L, which subsequently gives (μ-SR)₂M₂(CO)₆L₂. Continuous photolysis of Re₂(CO)₁₀ with [Me₂NC(S)S]₂ yields only the monorhenium compound (η²-S₂CNMe₂)Re(CO)₄. By employing laser flash photolysis techniques, we have measured various rate constants for these reactions.

We have reported the electronic and steric effects of L ligands on the rate constants for halogen atom transfer to Re(CO)₄L.⁷ The rate constants can be related in terms of the two-parameter free energy relationship eq 1, wherein electronic (δ) and steric

$$\ln k = a\delta + b\theta + c \quad (1)$$

(θ) parameters are represented. The constants *a* and *b* express the sensitivity of the rate constant in the particular reaction under study to electronic and steric factors, respectively. When the reaction rates are enhanced by increased electron donation and smaller steric requirement of L, the *a* value is positive and the *b* value is negative.

In this work we have extended the determination of the free energy parameters for atom and electron transfer reactions to the SR group transfer reactions of ^{*}Re(CO)₄L.

Experiments

General Methods. All reactions were carried out under an argon or nitrogen atmosphere. Continuous photochemical reactions were performed by irradiation with a General Electric 275-W sunlamp with Pyrex Schlenk vessels. Hexane was treated with H₂SO₄, washed with H₂O and aqueous NaHCO₃, and then dried over MgSO₄, followed by distillation from CaH₂. All disulfide compounds were purchased from Aldrich. The preparation of Re₂(CO)₈L₂ has been described previously.⁷

Infrared spectra were obtained on a Beckman IR-4240 spectrophotometer. Field desorption mass spectra (FDMS) and electron impact mass spectra (EIMS) were obtained with Finnigan-MAT 731 and CH-5 mass spectrometers, respectively, in the Mass Spectrometry Laboratory of the School of Chemical Sciences, University of Illinois. The ¹H and ¹³C NMR spectra were obtained with a Nicolet NIC-360 or a General Electric QE-300 instrument. Chemical shifts are referred to tetramethylsilane at δ 0. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

Kinetics Techniques. The laser flash photolysis apparatus and its use have been described previously.⁷

Photochemical Reaction of Re₂(CO)₈L₂ with RSSR or MeSSiMe₃ (Typical Procedure). Re₂(CO)₁₀ (0.150 g, 0.230 mmol) was added into a 50-mL Schlenk flask containing hexane (20 mL) and MeSSMe (0.087

g, 0.920 mmol). The solution was degassed by three consecutive freeze-pump-thaw cycles followed by irradiation at ambient temperature for 3 h. (μ-SMe)₂Re₂(CO)₈ was formed and isolated as a pale yellow solid. The isolated yield was 85%. The corresponding reaction of MeSSiMe₃ (0.110 g, 0.900 mmol) gives the same product. Anal. Calcd for C₁₀H₆O₈S₂Re₂: C, 17.39; H, 0.88; S, 9.28. Found: C, 17.46; H, 0.83; S, 9.44. IR (hexane): ν_{CO} 2109 (vw), 2092 (w), 2012 (s), 1997 (m), 1980 (w), 1960 (s), 1925 (vw) cm⁻¹. ¹H NMR (CDCl₃): δ 2.70 (s). EIMS (70 eV): *m/e* 692 (M⁺ where Re = 187) and successive CO loss peaks.

The corresponding reaction of Re₂(CO)₁₀ (0.105 g, 0.160 mmol) with PhSSPh (0.230 g, 1.05 mmol) yields (μ-SPh)₂Re₂(CO)₈ (0.117 g, 0.144 mmol). IR (hexane): ν_{CO} 2109 (vw), 2097 (w), 2019 (s), 1993 (m), 1960 (s) 1925 (vw) cm⁻¹ (lit.⁹ 2100-(m), 2022 (vs), 1995 (m), 1962 (s) cm⁻¹). ¹H NMR (CDCl₃): δ 7.47 (d, 4 H, *J* = 8.1 Hz), 7.35 (t, 4 H, *J* = 7.7 Hz), 7.19 (t, 2 H, *J* = 7.3 Hz). EIMS: *m/e* 816 (M⁺ where Re = 187), 788, 760, 732, 704, 676, 648, 620, 592, 295.

Photochemical reaction of 1,2-*diag*-Re₂(CO)₈(PMe₃)₂ with MeSSMe quantitatively yields (μ-SMe)₂Re₂(CO)₆(PMe₃)₂. IR (CH₂Cl₂): ν_{CO} 2022 (m), 2009 (s), 1959 (m), 1933 (s), 1905 (sh), 1893 (s) cm⁻¹. FDMS: *m/e* 788 (Re = 187).

Photochemical Reaction of Mn₂(CO)₁₀ with RSSR (R = Me, Ph). Mn₂(CO)₁₀ (0.175 g, 0.449 mmol), MeSSMe (0.209 g, 2.221 mmol), and hexane (20 mL) were added into a 50-mL Schlenk flask. The solution was degassed by three consecutive freeze-pump-thaw cycles. The solution was then irradiated with a GE sunlamp for 1 h, and the orange solid was precipitated. The solid, which was collected and washed with hexane, was identified as a mixture of (μ-SMe)₂Mn₂(CO)₈ (~70%) and [Mn(CO)₃SMe]₄ (~15%). The yields were estimated from the isolated amounts and from peak intensities in the ¹H NMR spectrum of the mixture. The tetramer could not be isolated; (μ-SMe)₂Mn₂(CO)₈ was isolated in reasonable purity. IR (hexane): ν_{CO} 2093 (w), 2071 (m), 2012 (s), 1999 (s), 1982 (w), 1968 (s), 1932 (vw) cm⁻¹ (lit.¹⁰ (C₆H₁₂)₂ 2095 (w), 2074 (s), 2016 (vs), 2002 (vs), 1985 (m), 1969 (s), 1937 (w) cm⁻¹). ¹H NMR (CDCl₂): δ 2.02 (s). FDMS: *m/e* 428.

The corresponding reaction of PhSSPh was carried out as for the methyl compound. (μ-SPh)₂Mn₂(CO)₈ was isolated as an orange solid (0.198 g, 0.359 mmol, 80% yield). Anal. Calcd for C₂₀H₁₀S₂O₈Mn₂: C, 43.49; H, 1.83; S, 11.61. Found: C, 44.32; H, 1.77; S, 10.79. FDMS: *m/e* 552. IR (hexane): ν_{CO} 2095 (vw), 2079 (m), 2021 (s), 2004 (m), 1997 (w, sh), 1971 (s), 1938 (vw) cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.26-7.62 (m).

Photochemical Reaction of Re₂(CO)₁₀ with Tetramethylthiuram Disulfide, [Me₂NC(S)S]₂. The reaction, complete in 3 h, was carried out as described above. The product was isolated by using preparative silica gel column chromatography with a mixture of hexane and CH₂Cl₂ (3:1) and recrystallized with the same solvent system. The white solid (~85% yield) was assigned as (η²-S₂CNMe₂)Re(CO)₄. Anal. Calcd for C₇H₆O₄NS₂Re: C, 20.09; H, 1.45; N, 3.35; S, 15.32. Found: C, 20.21; H, 1.41; N, 3.41; S, 15.20. IR (toluene): ν_{CO} 2099 (w), 2000 (s), 1982 (s), 1938 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 3.23 (s). ¹³C{¹H} NMR (CDCl₃): δ 213.3 (s), 186.4 (s), 185.2 (s), 38.9 (s). EIMS: *m/e* 419 (M⁺ where Re = 187), 391, 363, 335, 307, 297, 251, 88. FDMS: *m/e* 419.

Continuous Photolysis of a 1:1 Mixture of (μ-SMe)₂Re₂(CO)₈ (1a) and (μ-SPh)₂Re₂(CO)₈ (1b). 1a (0.042 g, 0.061 mmol), 1b (0.050 g, 0.061 mmol), and hexane (20 mL) were added into a 50-mL Schlenk flask. The solution was degassed by freeze-pump-thaw cycles three times, followed by irradiation with a GE 275-W sunlamp for 2 h. The reaction mixture in CH₂Cl₂ and hexane (1:1) was filtered through a silica gel column and recrystallized with the same solvent system. EIMS and FDMS showed the molecular ion peaks (*m/e* 692, 754, and 816) due to 1a, 1b, and (μ-SMe)(μ-SPh)Re₂(CO)₈ (1c), respectively. The IR spectrum of the product mixture is similar to that of the mixture of the reactants. The components could not be readily isolated from the mixture. The ¹H NMR spectrum of the mixture in CD₂Cl₂ shows two singlets at 2.78 (s) and 2.73 (s) ppm. The peak at 2.73 ppm corresponds to 1a. Thus, the peak at 2.77 ppm probably corresponds to the methyl group of 1c. Integration revealed that approximately equal amounts of 1a, 1b, and 1c are present.

Continuous Photolysis of a 1:1 Mixture of (μ-SMe)₂Mn₂(CO)₈ (2a) and (μ-SPh)₂Mn₂(CO)₈ (2b). The reaction was carried out as described above. The yellow solid was isolated. ¹H NMR (CD₂Cl₂): δ 7.20-8.30 (m), 2.46 (s, br), 2.29 (s, br), 2.02 (s, br). FDMS yielded eight peaks that appeared to correspond to molecular ions: *m/e* 428, 490, 552, 744, 806, 868, 930, 992. These eight molecular ion peaks probably correspond to 2a, 2b, (μ-SMe)(μ-SPh)Mn₂(CO)₈, Mn₄(CO)₁₂(SMe)₄, Mn₄(CO)₁₂-

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Table I. Group Transfer Rate Constants for Reactions of $\text{Re}(\text{CO})_4\text{L}^*$ with $n\text{-BuSS}(n\text{-Bu})$ or MeSSiMe_3 in Hexane

L	δ_{CO}^a	θ , deg ^b	$n\text{-BuSS}(n\text{-Bu})$		MeSSiMe_3	
			$[n\text{-BuSS}(n\text{-Bu})]$, M	$10^{-6}k$, $\text{M}^{-1} \text{s}^{-1}$	$[\text{MeSSiMe}_3]$, M	$10^{-6}k$, $\text{M}^{-1} \text{s}^{-1}$
CO	0.00	95	0.42	14 ± 1	1.5	0.60 ± 0.02
PMe_3	5.05	118	0.021	370 ± 20	0.3	9.3 ± 0.2
$\text{P}(\text{OMe})_3$	3.18	107	0.13	27 ± 1	1.0	0.95 ± 0.07
$\text{P}(\text{O-}i\text{-Pr})_3$	3.90	130	0.32	7.8 ± 0.3	0.5	0.47 ± 0.01
$\text{P}(n\text{-Bu})_3$	5.69	132	0.10	82 ± 2	1.5	1.7 ± 0.2
$\text{P}(i\text{-Bu})_3$	5.40	143	0.79	4.7 ± 0.2	0.5	0.22 ± 0.01
$\text{P}(i\text{-Pr})_3$	6.20	160	1.2	1.6 ± 0.1	1.5	0.10 ± 0.01
PCy_3	6.32	170	1.3	1.2 ± 0.1	1.0	0.071 ± 0.00
AsEt_3	5.33	128	0.063	140 ± 10	1.0	3.8 ± 0.1

^a δ_{CO} is the ¹³C chemical shift for $\text{Ni}(\text{CO})_3\text{L}$, reported downfield from $\text{Ni}(\text{CO})_4$.¹⁴ ^b Phosphine cone angle from ref 13.

$(\text{SMe})_3(\text{SPh})$, $\text{Mn}_4(\text{CO})_{12}(\text{SMe})_2(\text{SPh})_2$, $\text{Mn}_4(\text{CO})_{12}(\text{SMe})(\text{SPh})_3$, and $\text{Mn}_4(\text{CO})_{12}(\text{SPh})_4$. The relative amounts of the eight products could not be determined with useful accuracy.

Results and Discussion

Synthesis. Photochemical reactions (irradiation wavelength >300 nm) of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$) with RSSR ($\text{R} = \text{Me}, \text{Ph}$) or MeSSiMe_3 in hexane at ambient temperature yield $(\mu\text{-SR})_2\text{M}_2(\text{CO})_8$ [**1a** ($\text{M} = \text{Re}; \text{R} = \text{Me}$), **1b** ($\text{M} = \text{Re}; \text{R} = \text{Ph}$), **2a** ($\text{M} = \text{Mn}; \text{R} = \text{Me}$), **2b** ($\text{M} = \text{Mn}; \text{R} = \text{Ph}$)] (70–85% yield) and $[\text{M}(\text{CO})_3\text{SR}]_4$ (0–15% yield). The corresponding reaction of $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ yields only the dinuclear product $(\mu\text{-SR})_2\text{Re}_2(\text{CO})_6(\text{PMe}_3)_2$ (**3**). Treichel et al.¹⁰ reported that the thermal reaction of $\text{HMn}(\text{CO})_5$ and MeSSMe at room temperature yields $(\mu\text{-SMe})_2\text{Mn}_2(\text{CO})_8$. Osborne and Stone⁹ have also reported that the thermal reaction of $\text{HRe}(\text{CO})_5$ and PhSH in benzene at 20 °C gives $(\mu\text{-SPh})_2\text{Re}_2(\text{CO})_8$, whereas the corresponding reaction of $\text{C}_6\text{F}_5\text{SH}$ yields only $\text{C}_6\text{F}_5\text{SRe}(\text{CO})_5$. The former compound is probably formed by dimerization of $\text{PhSRe}(\text{CO})_5$, which is believed to be the initial product. Presumably, $\text{C}_6\text{F}_5\text{SRe}(\text{CO})_5$ is not dimerized because the electron-withdrawing capability of the C_6F_5 group retards the substitution reaction. Dinuclear products dominate in the photochemical reactions because the initial product, $\text{RSRe}(\text{CO})_4\text{L}$, probably formed by group transfer from RSSR to the $^*\text{Re}(\text{CO})_4\text{L}$ radical, would be even more likely to lose CO and to form $(\mu\text{-SR})_2\text{Re}_2(\text{CO})_6\text{L}_2$ under photochemical than under thermal conditions. Photolysis of $\text{Re}_2(\text{CO})_{10}$ and tetramethylthiuram disulfide in hexane gives $(\text{OC})_4\text{Re}(\eta^2\text{-S}_2\text{CNMe}_2)$ (**4**), identified by elemental analysis and IR, ¹H NMR, ¹³C NMR, and mass spectra. The electron-impact (70-eV) mass spectrum (EIMS) shows the molecular ion peak (m/e 419 where $\text{Re} = 187$), peaks due to successive loss of up to four CO's, and the $\text{C}(\text{S})\text{NMe}_2$ ion peak. The field desorption mass spectrum (FDMS) also shows M^+ (m/e 419). The ¹³C NMR spectrum shows two singlet carbonyl peaks of equal intensity (δ 186.4 (s) and 185.2 (s)). The ¹H NMR spectrum in CDCl_3 shows one singlet that corresponds in intensity to two methyl groups. The NMR data exclude the possible isomer $\eta^2\text{-SC}(\text{S})\text{NMe}_2\text{Re}(\text{CO})_4$, involving nitrogen coordination to Re. The initial product, $\text{Me}_2\text{NC}(\text{S})\text{S-Re}(\text{CO})_5$, formed by group transfer, is presumably transformed into **4** due to chelation of $\eta^2\text{-S}_2\text{CNMe}_2$ upon CO loss.

Flash photolysis experiments provide direct evidence for reaction of the metal-centered radicals with RSSR. Nitrogen laser (337 nm) flash photolysis of $\text{Re}_2(\text{CO})_{10}$ is known to give two primary photoproducts, $\text{Re}_2(\text{CO})_9$ ($\lambda_{\text{max}} \sim 380$ nm) and $^*\text{Re}(\text{CO})_5$ ($\lambda_{\text{max}} = 540$ nm).^{2b} The disappearance of $\text{Re}(\text{CO})_5^*$ in the presence of RSSR ($t_{1/2} = 50$ ns where $[\text{BuSSBu}] = 0.42$ M) is much faster than in the absence of RSSR ($t_{1/2} \sim 7\text{--}10$ μs). The rate of disappearance of $\text{Re}_2(\text{CO})_9$ in the presence of RSSR is slow even on the millisecond time scale, indicating that reaction of $^*\text{Re}(\text{CO})_5$ with RSSR is much faster than that of $\text{Re}_2(\text{CO})_9$, if the latter occurs at all. Nitrogen laser flash photolysis of $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ in hexane yields almost exclusively the metal-centered radical as a primary photoproduct.¹¹ The reaction of $\text{Re}(\text{CO})_4(\text{PMe}_3)^*$

with RSSR is 26 times faster than that of $^*\text{Re}(\text{CO})_5$. Correspondingly, reaction of $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ with RSSR under continuous photolysis occurs faster than that of $\text{Re}_2(\text{CO})_{10}$ to yield $(\mu\text{-SR})_2\text{Re}_2(\text{CO})_6\text{L}_2$ ($\text{L} = \text{PMe}_3, \text{CO}$). These results indicate that the 17-electron rhenium-centered radical reacts with RSSR to give $\text{RS-Re}(\text{CO})_4\text{L}$, which immediately forms $(\mu\text{-SR})_2\text{Re}_2(\text{CO})_6\text{L}_2$ by RS group substitution for CO.

Photochemical Disproportionation of the Bridging Sulfido Ligand of $(\mu\text{-SR})_2\text{M}_2(\text{CO})_8$ ($\text{M} = \text{Re}, \text{Mn}; \text{R} = \text{Me}, \text{Ph}$). Photolysis of a 1:1 mixture of **1a** and **1b** in hexane for 2 h yields **1a**, **1b**, and $(\mu\text{-SMe})(\mu\text{-SPh})\text{Re}_2(\text{CO})_8$ (**1c**) in almost equal amounts. The corresponding reaction of the 1:1 mixture of **2a** and **2b** for 1 h yields **2a**, **2b**, $(\mu\text{-SMe})(\mu\text{-SPh})\text{Mn}_2(\text{CO})_8$ (**2c**), and tetramers, $\text{Mn}_4(\text{CO})_{12}(\text{SMe})_4\text{-}n(\text{SPh})_n$ on the basis of FDMS. The ¹H NMR spectrum of the reaction mixture in CD_2Cl_2 shows three significant broad methyl proton peaks at δ 2.02 (s), 2.29 (s), and 2.46 (s). More peaks seem to exist underneath these three broad peaks. The peak at δ 2.02 corresponds to **2a**, but we were unable to assign the others.

We have not further studied the mechanism for disproportionation and tetramer formation. Possibly the metal-sulfur bond is photochemically cleaved to give the 16-electron monomeric intermediates $\text{MeSM}(\text{CO})_4$ and $\text{PhSM}(\text{CO})_4$, which subsequently form $(\mu\text{-SMe})_2\text{M}_2(\text{CO})_8$, $(\mu\text{-SPh})_2\text{M}_2(\text{CO})_8$, and $(\mu\text{-SMe})(\mu\text{-SPh})\text{M}_2(\text{CO})_8$ or lose a CO and then combine to form five isomeric tetranuclear compounds.

Flash Photolysis Kinetics. We have measured the rates of reaction of the rhenium-centered radicals with various SR donors. Each experiment was designed so that reaction with the donor was fast with respect to recombination of the $\text{Re}(\text{CO})_4\text{L}^*$ radicals. The concentration of RSSR or MeSSiMe_3 was much greater than that of $\text{Re}(\text{CO})_4\text{L}^*$ to ensure pseudo-first-order conditions. Examples of the transient decay due to $\text{Re}(\text{CO})_4\text{L}^*$ and the linear relationship between $\log(\text{absorbance})$ due to $\text{Re}(\text{CO})_4\text{L}^*$ and time have been shown elsewhere.⁷ The pseudo-first-order rate constants in the reactions of $\text{Re}(\text{CO})_4(\text{PMe}_3)^*$ with di-*n*-butyl disulfide were measured for various concentrations of di-*n*-butyl disulfide. A plot of k_{obsd} values vs. the di-*n*-butyl disulfide concentration is linear, with zero intercept within the error limits, as shown in Figure 1. Thus, the reaction is first order in di-*n*-butyl disulfide. The bimolecular rate constant, calculated from the slope of the line in Figure 1, has the value of $3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The reactions of other $^*\text{Re}(\text{CO})_4\text{L}$ radicals with RSSR or MeSSiMe_3 are assumed to follow the same rate law; the corresponding rate constants are compiled in Table I.

We have reported that the atom transfer rate constants for a series of $\text{Re}(\text{CO})_4\text{L}^*$ radicals with a given donor fit a two-parameter free energy relationship, eq 1.⁷ The steric parameter (θ) is defined in terms of the cone angle;¹³ the electronic parameter (δ) is represented by the carbonyl downfield ¹³C NMR chemical shift value for $\text{Ni}(\text{CO})_3\text{L}$ complexes in relation to $\text{Ni}(\text{CO})_4$.¹⁴ As for atom transfer, the rate constants for group transfer are in-

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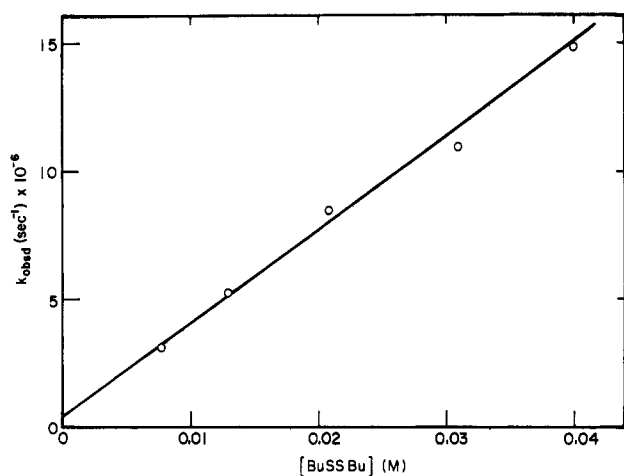


Figure 1. Pseudo-first-order rate constant k_{obsd} for reaction of $\text{Re}(\text{CO})_4\text{PMe}_3^*$ with di-*n*-butyl disulfide as a function of sulfide concentration.

Table II. a , b , and c Values from the Reactions of $\text{Re}(\text{CO})_4\text{L}^*$ with Atom Donors or Group Donors in Hexane

atom or group donor	a	b	c	$-a/b$	ref
(<i>n</i> -BuS) ₂	1.36	-0.156	30.9	8.7	this work
MeSSiMe ₃	1.07	-0.124	24.8	8.6	this work
CH ₂ Br ₂	1.32	-0.140	30.7	9.4	7a
CCl ₄	1.22	-0.108	27.9	11.3	7a
CHCl ₃	1.29	-0.121	24.2	10.7	7a

Table III. Rate Constants for the Reactions of $\text{Re}(\text{CO})_4\text{L}^*$ with Various Group Donors in Hexane

group donor	L = PMe ₃		L = P(<i>O</i> - <i>i</i> -Pr) ₃
	$10^{-7}k$, M ⁻¹ s ⁻¹	rel values	
PhSSPh	130 ± 10	1000	12 ± 0.2
MeSSMe	82 ± 15	630	3.6 ± 0.1
<i>n</i> -BuSS(<i>n</i> -Bu)	37 ± 2	280	0.78 ± 0.03
<i>sec</i> -BuSS(<i>sec</i> -Bu)	4.7 ± 0.2	36	0.10 ± 0.01
<i>t</i> -BuSS(<i>t</i> -Bu)	0.13 ± 0.01	1	<0.005
MeSSiMe ₃	0.93 ± 0.02	7	0.047 ± 0.001

fluenced by both electronic and steric properties of the rhenium substituent L. Linear regression analysis of the data in terms of employing eq 1 gives a , b , and c values, listed in Table II, with correlation coefficients of greater than 0.92 between experimental and calculated values of $\ln k$. A positive value for a indicates that electron donation from L to the metal center enhances the rate; negative values of b indicate that an increased steric requirement of L decreases the rate. The magnitudes of a and b for group transfer are similar to those for halogen atom transfer.⁷ The absolute value of the ratio a/b is smaller for SR group transfer than for halogen atom transfer, indicating that the relative contribution of the electronic parameter is smaller for group transfer. While a and b values are different for the group transfer reactions of di-*n*-butyl disulfide and trimethylsilyl methyl sulfide, the a/b ratios are almost the same. Thus, we observe the same pattern of scatter of points about the line of identity in a free energy relationship, as shown in Figure 2.

To study the steric effects of R groups on group transfer, various organic disulfides were employed. As shown in Table III, the relative rate constants are in the order Me > *n*-Bu > *sec*-Bu > *t*-Bu (630:280:36:1). Since the S-S bond energy is likely to be roughly constant in this series, the order of reactivity reflects the steric influence of the R group. A similar marked steric dependence has been noted in the reactions of Cr²⁺ with ROOR in water/methanol.¹⁵ The large rate constant for diphenyl disulfide (Table III) may be due to the low S-S bond energy (55 kcal/mol vs. 74 kcal/mol for MeSSMe)¹⁶ but can also be related to the

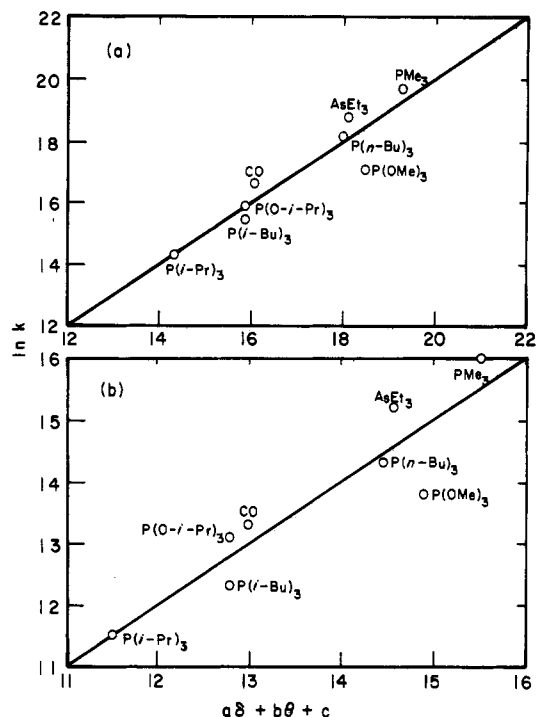
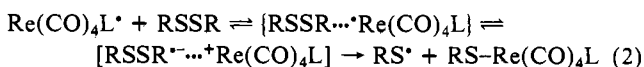


Figure 2. Correlation of atom transfer rate constant with ligand steric and electronic parameters for reactions of $\text{Re}(\text{CO})_4\text{L}^*$ radicals with *n*-BuSS(*n*-Bu) (a) and with MeSSiMe₃ (b).

electron-accepting capability of the phenyl group (discussed below).

Mechanism. Given the observation that an $\text{Re}(\text{CO})_5\text{SR}$ species is not seen, and given the demonstrated great lability of $\text{Re}(\text{CO})_5^*$ toward substitution by nucleophiles such as phosphine,^{4a} it is worth considering whether the first step in the reaction might not be substitution of CO by the disulfide, resulting in $\text{Re}(\text{CO})_4\text{S}_2\text{R}_2^*$, with a sulfur coordinated to Re. It is not entirely clear how the observed products would follow from this beginning. In any case, the flash photolysis data rule out this as the initial pathway, because the phosphine-substituted radicals react with RSSR in some cases more rapidly than $\text{Re}(\text{CO})_5^*$. This is the behavior to be expected for an atom (or group) transfer reaction, but just the opposite of what one expects for replacement of CO by a nucleophile. In general, phosphine-substituted radicals are considerably less labile than the parent unsubstituted radical.

Abrahamson and Freeman⁸ have postulated that the reaction of $\text{CpW}(\text{CO})_3^*$ radicals with RSSR proceeds via attack of the metal-centered radical on the organic disulfide to yield an intermediate that quickly loses RS^* to form $\text{RS}-\text{W}(\text{CO})_3\text{Cp}$. Whether or not a discrete intermediate exists is not clear. In any case, we propose a similar reaction pathway for the reactions of $\text{Re}(\text{CO})_4\text{L}^*$ radicals, one that parallels the atom-transfer process:



We have discussed elsewhere the extent to which the atom transfer process may be thought to proceed via electron transfer.¹⁷ It is noteworthy that diorganic disulfides form transient radical anions upon reaction with an electron or electron donor; the radical anions dissociate rapidly to form thiolate anions and thyl radicals.¹⁸ The proposed mechanism is consistent with the observed

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dependences of the rate constant on steric and electronic characteristics of R and L. Electron-releasing ligands L on the metal center should promote reaction when there is a net withdrawal of electrons from the metal center in the transition state. Increased steric requirement at either the metal or the group donor is expected to slow the reaction by impeding the effective approach of reactants. A higher electron affinity of the group donor molecule should speed up the reaction. Such an effect is observed for PhSSPh as compared to the alkyl disulfides (Table III). However, we noted above that the S-S bond energy in PhSSPh is only about 55 kcal/mol as compared with 74 kcal/mol for MeSSMe. This difference in bond energy also accounts for the faster reaction of the phenyl compound.

In summary, the reactions of transition-metal carbonyl radicals with RSSR provide an efficient synthetic pathway for forming thiolate-metal carbonyl complexes.¹⁹ The group transfer reaction rates are influenced by the electronic and steric characteristics of ligands on the metal in the same manner as observed for halogen atom transfer processes. The rate constants fit a two-parameter free energy relationship wherein the electronic and steric parameters are represented. Finally, the group transfer rate constants are observed to be very sensitive to the steric properties of the alkyl groups bound to sulfur.

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Contribution from the Department of Chemistry,
Mount Holyoke College, South Hadley, Massachusetts 01075

Unusual Oxidative Behavior of $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2$ (R = H, CH₃; M = Rh, Co) Complexes at Mercury and Platinum Electrodes[†]

Thomas Gennett,* Elizabeth Grzeszczyk, Anne Jefferson, and Kathy M. Sidur

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The electrochemical oxidative behavior of a series of cyclopentadienyl and pentamethylcyclopentadienyl carbonyl complexes of rhodium and cobalt is described. The voltammetric, polarographic, and coulometric data from the oxidations of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$, $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Co}(\text{CO})_2$, and $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$ are reported. The electrochemical experiments were conducted in methylene chloride at platinum and mercury electrodes. The cyclopentadienyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ exhibited oxidative behavior dependent on electrode material. At a platinum-bead electrode there was evidence that the organometallic solute adsorbs to the electrode surface, while at a hanging-mercury-drop electrode it was found that mercuric chloride formed at the surface of the electrode at potentials greater than 0.200 V vs. SCE. This HgCl₂ reacts with the solute to form an insoluble Lewis acid-base adduct, $[\text{Cl}_2\text{Hg}]\cdot[\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$, where M = Rh, Co. These adducts were also formed from the homogeneous oxidation of the organometallic solute with $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{PF}_6]$, but only when mercury was present in the solution. The pentamethylcyclopentadienyl complexes $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Co}(\text{CO})_2$ and $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$ were found to undergo chemically reversible one-electron oxidations to relatively stable cation radicals at both platinum and mercury electrodes. There was no evidence of either pentamethylcyclopentadienyl complex reacting with the mercuric chloride. Extended Hückel calculations were conducted on all four complexes. Correlations were seen between the experimental observations and Hückel predictions of adduct formation and radical stability.

Introduction

Among the cyclopentadienyl derivatives of organometallic complexes, monomeric carbonyl species with the general formula $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{n-x}(\text{L})_x$ are of particular interest because of their catalytic importance in a number of organic syntheses.¹⁻⁹ We report here the unusual oxidative behavior of a series of cyclopentadienyl and pentamethylcyclopentadienyl dicarbonyl derivatives of rhodium and cobalt: $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ (I), $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (II), $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Co}(\text{CO})_2$ (III), and $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$ (IV). (The $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5(\text{CH}_3)_5$ rings will be abbreviated as Cp and Cp', respectively.)

The main thrust of recent research on π -bonded polyolefin organometallic complexes has centered on the chemistry of their paramagnetic derivatives. These radical systems have been suggested as possible catalytic intermediates and/or transition states for important synthetic and industrial processes.^{3,4,7-10} The rate at which the metal center undergoes nucleophilic substitution has been shown to control catalytic efficiency.^{4,9-11} Therefore, investigations have been primarily concerned with developing processes that enhance the susceptibility of the metal center to nucleophilic substitution reactions. Kochi has reported that the rate of nucleophilic substitution at the metal center increases substantially for complexes with the general formula $\text{CpMn}(\text{CO})_{3-x}(\text{L})_x$, when the complexes are oxidized to their cation radicals.¹² Also of interest are the independent observations of Connelly¹³ and McKinney¹⁴ that $\text{CpRh}(\text{CO})(\text{PR}_3)$ complexes

undergo one-electron-oxidation reactions to cation radicals, which dimerize to form bimolecular fulvalene dications.⁶ Other important studies include the extended Hückel theoretical determinations by Hofmann on the plausibility of 16-electron organometallic intermediates being involved in catalytic processes¹⁵ and the work of Casey on the effect of substitution at the metal center on the η number of a π -bonded polyolefin ring.¹⁶ Finally,

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[†] This paper is dedicated to the memory of Dr. Dorothy Z. Gennett, an extremely remarkable scholar and colleague who will be missed by us all.