

literature may be consulted.²⁶ The delocalization of the two remaining s-like electrons, now in the σ_s orbital, should reduce the closed-shell repulsion with the ethylene π orbital, if the ethylene molecule binds to one end of Fe_2 . Another possible orientation is di- σ , as occurs on the Pt(111) surface.²⁷ Two isomers of the ethylene monomer and dimer have been observed.⁴

(26) Anderson, A. B. *J. Chem. Phys.* 1977, 66, 108.

(27) Kang, D. B.; Anderson, A. B. *Surf. Sci.* 1985, 155 639.

The methyliron and ethynyliron hydrides can be photolytically converted back to methane and ethylene plus iron atoms, suggesting an interesting topic for future theoretical analysis.

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Cobalt Carbonyl and Phase Transfer Catalyzed Carbonylation of Thiiranes

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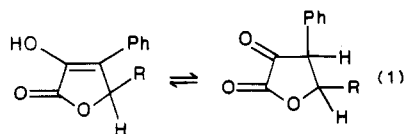
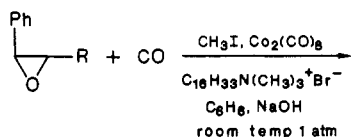
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Cobalt carbonyl catalyzes the carbonylation of thiiranes to β -mercapto acids using methyl iodide or a benzylic bromide, 3 N potassium hydroxide, benzene as the organic phase, and polyethylene glycol (PEG-400) as the phase-transfer agent. An acylcobalt carbonyl and a thietan-2-one are possible intermediates in this reaction.

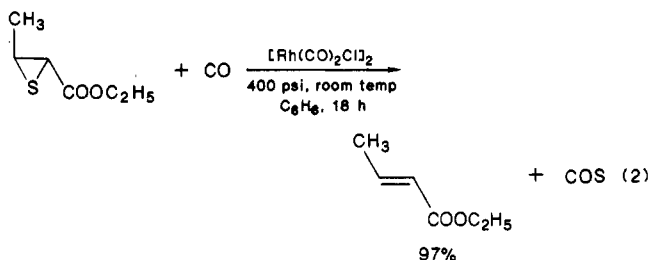
Phase-transfer catalysis is a useful method for effecting a variety of carbonylation reactions under remarkably mild conditions.² Of particular note are reactions involving halides and epoxides as substrates. For example, cyanonickel(II) complexes are active catalysts for the phase-transfer-catalyzed carbonylation of allyl halides to acids,³ and cobalt carbonyl can catalyze the conversion of benzylic halides, and methyl iodide, to acids in the fine yields.^{4,5} The key intermediate in the latter reaction is believed to be an acylcobalt tetracarbonyl complex. Such a complex can be intercepted by effecting the phase-transfer process in the presence of suitable unsaturated substrates [e.g. alkynes, dienes]² or haloarenes.⁶

A fascinating double carbonylation is observed when a styrene oxide is employed as the reactant, together with methyl iodide, carbon monoxide, benzene as the organic phase, aqueous sodium hydroxide, and cetyltrimethylammonium bromide as the phase-transfer agent (eq 1).⁷



In contrast to the reaction involving haloarene or unsaturated reactants, the methyl group of the iodide is not incorporated in the product, although the α -keto lactone is not formed in the absence of methyl iodide.

Little is known concerning metal-catalyzed reactions of thiiranes, which are sulfur analogues of epoxides. Recently, it was shown that chlorodicarbonylrhodium(I) dimer can catalyze the homogeneous desulfurization of thiiranes to olefins.⁸ This stereospecific reaction proceeds for thiiranes bearing aliphatic, aromatic, ether, and ester substituent groups (eq 2). We now wish to report that one can achieve the carbonylation of thiiranes to β -mercapto acids by cobalt carbonyl and phase-transfer catalysis.



Results and Discussion

When 2-phenylthiirane (styrene sulfide), 1, was treated with carbon monoxide, methyl iodide, potassium hydroxide (3 N), benzene as the organic phase, a catalytic amount of cobalt carbonyl, and tetrabutylammonium bromide as the phase-transfer agent, at room temperature and one atmosphere, the β -mercapto acid 2 was isolated in 17% yield (no reaction occurs in the absence of the phase-

(1) John Simon Guggenheim Fellow, 1985-1986. Killam Research Fellow, 1986-1988.

(2) Alper, H. *Fundam. Res. Homogeneous Catal.* 1984, 4, 79.

(3) Joo, F.; Alper, H. *Organometallics* 1985, 4, 1775.

(4) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* 1977, 134, C11.

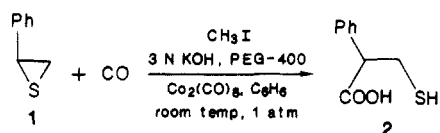
(5) Cassar, L.; Foa, M. *J. Organomet. Chem.* 1977, 134, C15.

(6) Miura, M.; Akase, F.; Nomura, M. *J. Chem. Soc., Chem. Commun.* 1986, 241.

(7) Alper, H. Arzoumanian, H.; Petrigani, J. F.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* 1985, 340.

(8) Calet, S.; Alper, H. *Tetrahedron Lett.* 1986, 27, 3573.

transfer catalyst). Cetyltrimethylammonium bromide



afforded 2 in higher yield (39%). Superior to the use of a quaternary ammonium salt as the phase-transfer agent was the utilization of polyethylene glycols (PEG) as the catalyst. Recent work has demonstrated that polyethylene glycols can promote metal-catalyzed processes such as oxidation and oxidative homologation.^{9,10} Substitution of PEG-400 for a quaternary ammonium salt in the reaction of 1 resulted in a doubling of the yield of the β -mercapto acid (to 78%).

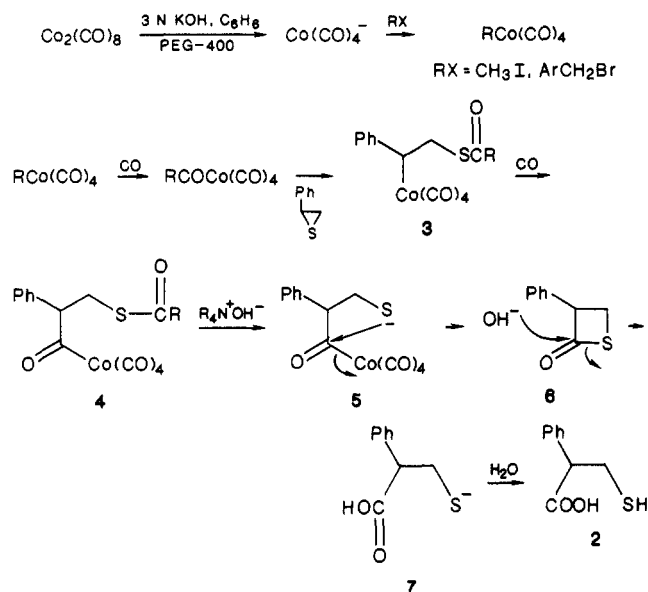
The conversion of 1 to 2 can also be realized, albeit in lower yield, by using benzyl bromide instead of methyl iodide. The presence of electron-attracting substituents (F, NO_2) at the para position of the benzene ring of benzyl bromide is not desirable, as 2 is isolated in lower yield (see Table I for data). Sodium hydroxide is inferior to potassium hydroxide for the reaction while no reaction takes place when triethylamine is used as the base. Only traces of β -mercapto acid were detected by using tetrakis(triphenylphosphine)palladium(0) as the catalyst while the dimer of cyclopentadienyltungsten tricarbonyl is inactive.

Carbonylation of a series of mono- and bicyclic thiiranes was effected with PEG-400 as the phase-transfer agent and methyl iodide or benzyl bromide as the halide, affording β -mercapto acids in fair to good yields (Table I). The reaction is regiospecific except for 2-hexylthiirane, with the acid function attached to the more substituted carbon (when there is a choice). Other noteworthy points about the reaction include the following: (a) the success of the process is sensitive to the concentration of thiirane in benzene, the optimum being 2 mmol of reactant in 25 mL of the organic phase (using a 6.71/1.0 ratio of substrate/catalyst); (b) as anticipated, use of a nitrogen instead of a carbon monoxide atmosphere results in little carbonylation (8% after 48 h) with PEG-400 as the phase-transfer agent; (c) the carbonylation reaction, using either PEG-400 or CTAB, is insensitive to the nature of the organic phase (i.e. benzene, methylene chloride, 4-methyl-2-pentanone).

It is conceivable that the initial steps (Scheme I) of the carbonylation reaction are analogous to those proposed for the double carbonylation of styrene oxide,⁷ i.e. generation of an acylcobalt carbonyl complex from the reaction of cobalt tetracarbonyl anion² with a halide followed by carbon monoxide insertion and then reaction with a thiirane (e.g. 2-phenylthiirane) to give 3 and subsequently 4. While the oxygen analogue of 4 can then experience enolization followed by carbonylation, the thio ester function of 4 can undergo hydrolysis to 5 [thiolacetates are hydrolyzed more rapidly than the corresponding esters],¹² and intramolecular cyclization of 5 would afford thietan-2-one (6). Since base is present, thietan-2-one (6) will undergo ring cleavage to 7 and the mercapto acid 2 would result by protonation.

That an acylcobalt tetracarbonyl complex and not the cobalt tetracarbonyl anion is the key catalytic species in the reaction was indicated by treating bis(triphenyl-

Scheme I



phosphine)nitrogen(1+) tetracarbonylcobaltate with methyl iodide in methylene chloride and water, cetyltrimethylammonium bromide as the phase-transfer catalyst, and then an equivalent amount of 2-phenylthiirane (room temperature, 1 atm, 18 h) to give the β -mercapto acid 2 in 41% yield. No reaction occurs under homogeneous conditions [i.e. CH_2Cl_2 but no water or phase-transfer agent] or by phase-transfer catalysis in the absence of methyl iodide [i.e., $\text{Co}(\text{CO})_4^-$ is inactive].

Thietan-2-one¹³ was prepared in order to determine its susceptibility to ring cleavage under the conditions employed for the phase-transfer-catalyzed carbonylation reaction. If thietan-2-one was treated under the standard conditions [i.e. $\text{Co}_2(\text{CO})_8/\text{CO}/\text{C}_6\text{H}_6/3 \text{ N KOH}/\text{PEG-400}/\text{CH}_3\text{I}/\text{room temperature}/1 \text{ atm}/18 \text{ h}$], 3-mercapto-propionic acid was isolated in quantitative yield. The same result was obtained when the reaction was repeated without both cobalt carbonyl and methyl iodide. If thietan-2-ones are indeed generated in the thiirane/ $\text{Co}_2(\text{CO})_8$ catalyzed reaction, then this would be another example of a metal-catalyzed ring-expansion carbonylation reaction.^{7,14,15}

In conclusion, PEG-400 enables one to effect the regiospecific carbonylation of thiiranes to β -mercapto acids under exceptionally mild conditions. Other synthetic approaches to β -mercapto acids are known, including the reaction of unsaturated acids with benzyl mercaptan followed by debenzoylation with sodium in liquid ammonia,¹¹ but the present method has a number of advantages including simplicity in execution and workup, as well as regiospecificity. This reaction constitutes the first example of a metal complex catalyzed carbonylation reaction of a thiirane. It has been generally considered that reactions involving organosulfur reactants cannot be effectively catalyzed by transition-metal complexes as the catalyst is poisoned by the sulfur atom of the substrate. However, the results described above, together with those for the carbonylation of mercaptans under more stringent conditions,^{16,17} demonstrate that cobalt carbonyl is a valuable

(9) Alper, H.; Januszkievicz, K.; Smith, D. J. H. *Tetrahedron Lett.* 1985, 26, 2263.

(10) Li, P.; Alper, H. *J. Org. Chem.* 1986, 51, 4354.

(11) (a) Field, L.; Giles, P. M., Jr. *J. Med. Chem.* 1970, 13, 317. (b) Lajler, W. A.; Siguango, F. F. U.S. 2402639, 1946.

(12) Idoux, J. P.; Hwang, P. T. R.; Hancock, C. K. *J. Org. Chem.* 1973, 38, 4239.

(13) Lin'Kova, M. G.; Patrino, N. D.; Kunnyants, I. L. *Dokl. Akad. Nauk. SSR* 1959, 127, 564.

(14) Roberto, D.; Alper, H. *Organometallics* 1984, 3, 1767.

(15) Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* 1983, 105, 6737.

(16) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* 1985, 50, 147.

(17) Antebi, S.; Alper, H. *Organometallics* 1986, 5, 596.

Table I. β -Mercapto Acids from $\text{Co}_2(\text{CO})_8$ and PEG-400 Catalyzed Carbonylation of Thiranes

reactant	halide	reactn time, h	product, ^a %	IR, ^b cm^{-1}	NMR δ^c	MS, m/e
1	CH_3I	18	$\text{PhCH}_2\text{CH}_2\text{SH}$, 78	2580 (SH), 1740 (CO)	1.10 (t, 1 H, SH, $J = 8$ Hz), 3.30 (dd, 2 H, CH_2), 4.61 (m, 1 H, CH), 7.25 (s, 5 H, Ph), 10.00 (s (br), 1 H, COOH)	182 $[\text{M}]^+$, 164 $[\text{M} - \text{H}_2\text{O}]^+$, 149 $[\text{M} - \text{SH}]^+$, 311 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
2- <i>p</i> -tolyl-thiirane	PhCH_2Br	18	$\text{PhCH}_2\text{CH}_2\text{SH}$, 55	2585 (SH), 1740 (CO)	1.15 (t, 1 H, SH, $J = 8$ Hz), 2.25 (s, 3 H, CH_3), 3.35 (dd, 2 H, CH_2), 4.62 (m, 1 H, CH), 7.19 (s, 4 H, aromatic), 10.10 (s (br), 1 H, COOH)	196 $[\text{M}]^+$, 181 $[\text{M} - \text{CH}_3]^+$, 178 $[\text{M} - \text{H}_2\text{O}]^+$, 163 $[\text{M} - \text{SH}]^+$, 325 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
cyclohexene sulfide	PhCH_2Br	60	2-mercapto-1-cyclohexanecarboxylic acid, ^d 55	2610 (SH), 1715 (CO)	1.20 (d, 1 H, SH, $J = 7$ Hz), 1.35-2.20 (m, 8 H, CH_2 protons), 2.70-2.90 (m, 2 H, CH protons), 10.90 (s (br), 1 H, COOH)	289 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
1-methylcyclohexene sulfide	CH_3I	48	2-mercapto-1-ethyl-1-cyclohexanecarboxylic acid, ^e 24	2610 (SH), 1715 (CO)	1.90 (d, 1 H, SH, $J = 7$ Hz), 1.22-2.40 (m, 11 H, CH_2 and CH protons), 2.95 (m, 1 H, CH), 10.65 (s (br), 1 H, COOH)	303 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
cyclopentene sulfide	PhCH_2Br	60	2-mercapto-1-cyclopentanecarboxylic acid, ^e 33	2610 (SH), 1720 (CO)	1.30-2.50 (m, 7 H, SH and methylene protons), 2.80-3.05 (m, 2 H, CH protons), 11.50 (s (br), 1 H, COOH)	275 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
cyclooctene sulfide	CH_3I	60	2-mercapto-1-cyclooctanecarboxylic acid, ^e 24	2610 (SH), 1715 (CO)	1.20-2.30 (m, 13 H, SH and methylene protons), 2.75-3.00 (m, 2 H, CH protons), 11.05 (s (br), 1 H, COOH)	317 $[\text{M} - \text{CH}_3]^+$ of bis-SiMe ₃ derivative
2-hexyl-thiirane	CH_3I	60	$\text{C}_6\text{H}_{13}\text{CH}_2\text{SH}$ and $\text{C}_6\text{H}_{13}\text{CH}_2\text{COOH}$, 27	2650 (SH)	0.90-2.05 (m, 28 H, SH and $\text{CH}_2(\text{CH}_2)_6$), 3.35-3.62 (m, 6 H, $\text{CH}(\text{COOH})$, CH_2SH , and $\text{CH}(\text{SH})\text{CH}_2\text{COOH}$), 11.20 (s (br), 2 H, COOH) ^f	190 $[\text{M}]^+$
	PhCH_2Br	48	$\text{C}_6\text{H}_{13}\text{CH}_2\text{SH}$ and $\text{C}_6\text{H}_{13}\text{CH}_2\text{COOH}$, 49			

^a Yields are of analytically pure materials (satisfactory C, H, S analyses). ^b CHCl_3 solution. ^c CDCl_3 with Me₃Si as internal standard. ^d Reference 11a. ^e Reference 11b. ^f ¹³C NMR (CDCl_3): δ 13.97, 22.49, 25.74 ($\text{CH}_3\text{CH}_2\text{CH}_2$ of both isomers), 28.82, 29.22, 31.65, 31.67, 35.91, 36.49 ($-\text{CH}_2\text{CH}_2\text{CH}_2$), 41.19, 41.32 (C-COOH), 61.65, 61.75 (CSH), 169.46, 172.42 (COOH).

catalyst for the carbonylation of organic sulfur compounds.

Experimental Section

General Remarks. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. Varian EM360A and XL300 instruments were used for NMR spectral determinations, and a VG5050 micromass spectrometer was used for recording mass spectra. Reactant halides, cobalt carbonyl, and phase-transfer agents were purchased from commercial sources. Thiiranes were prepared by literature methods.^{18,19} Bis(triphenylphosphine)nitrogen(1+) tetracarbonylcobaltate was synthesized according to the procedure of Gladysz and co-workers.²⁰ Solvents were dried and distilled by standard techniques.

General Procedure for the Carbonylation of Thiiranes. Carbon monoxide was bubbled through a 3 N KOH (15 mL) solution containing 0.3 mmol of PEG-400. After 15 min, a degassed solution of $\text{Co}_2(\text{CO})_8$ (0.3 mmol) in benzene (20 mL) was added followed 1 h later by the halide (2 mL) and 30 min later by the thiirane (2.0 mmol) in benzene (5 mL). The reaction mixture was stirred under carbon monoxide at room temperature and one atmosphere (see Table I for reaction times). Standard workup [separation of the phases, acidification of the aqueous phase (1 M HCl), ether extraction (4 × 25 mL), and flash chromatography of the concentrated ether extract (Al_2O_3 ; $\text{C}_6\text{H}_{14}/\text{CH}_3\text{COOC}_2\text{H}_5$ as eluant)] gave pure β -mercapto acid.

Reaction of 2-Phenylthiirane with Bis(triphenylphosphine)nitrogen(1+) Tetracarbonylcobaltate. Carbon monoxide was bubbled, for 15 min, through an aqueous solution (15 mL) of cetyltrimethylammonium bromide (0.364 g, 1.0 mmol). Bis(triphenylphosphine)nitrogen(1+) tetracarbonylcobaltate (0.709 g, 1.0 mmol), in degassed methylene chloride (20 mL), was added, and the solution was stirred under carbon monoxide for 1 h.

Methyl iodide (2 mL) was added, followed 30 min later by a methylene chloride (5 mL) solution of 2-phenylthiirane (0.136 g, 1.0 mmol). The reaction mixture was stirred under carbon monoxide for 18 h at room temperature and one atmosphere. The phases were separated, the aqueous phase was extracted with ether, the combined organic phase was concentrated, and flash chromatography of the crude product on alumina using hexane/ethyl acetate as the eluant afforded the pure β -mercapto acid in 41% yield.

Phase-Transfer-Catalyzed Cleavage of Thietan-2-one. Carbon monoxide was bubbled through a solution of potassium hydroxide (15 mL, either 0.1 or 3.0 M) and PEG-400 (0.12 g, 0.30 mmol). After 15 min, a degassed solution of benzene (20 mL) was added, followed by thietan-2-one (0.176 g, 2.0 mmol) in benzene (5 mL). The reaction mixture was stirred overnight at room temperature (1 atm). The phases were separated, and the aqueous phase was acidified with 1 M HCl and then extracted with ether (4 × 25 mL). The ether extract was dried (MgSO_4) and concentrated, and flash chromatography on alumina with hexane/ethyl acetate gave 3-mercaptopropionic acid in 94–100% yield (two runs).

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Registry No. 1, 1498-99-3; PEG-400, 25322-68-3; $\text{PhCH}(\text{CO}_2\text{H})\text{CH}_2\text{SH}$, 90536-14-4; *p*- $\text{MeC}_6\text{H}_4\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{SH}$, 108744-11-2; $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{SH}$, 108744-15-6; $\text{CH}_3(\text{C}-\text{H}_2)_5\text{CH}(\text{SH})\text{CH}_2\text{CO}_2\text{H}$, 108744-16-7; $\text{Co}_2(\text{CO})_8$, 15226-74-1; 2-*p*-tolylthiirane, 16245-83-3; 2-mercapto-1-cyclohexanecarboxylic acid, 1074-00-6; cyclohexene sulfide, 286-28-2; 1-methylcyclohexene sulfide, 7272-23-3; 2-mercapto-1-methyl-1-cyclohexanecarboxylic acid, 108744-12-3; cyclopentene sulfide, 285-75-6; 2-mercapto-1-cyclopentanecarboxylic acid, 108744-13-4; cyclooctene sulfide, 286-63-5; 2-mercapto-1-cyclooctanecarboxylic acid, 108744-14-5; 2-hexylthiirane, 5633-78-3; bis(triphenylphosphine)nitrogen(1+) tetracarbonylcobaltate, 53433-12-8; thietan-2-one, 2935-95-7; 3-mercaptopropionic acid, 107-96-0.

- (18) Van Tamelen, E. E. *J. Am. Chem. Soc.* **1951**, *73*, 3445.
 (19) Guss, C. O.; Chamberlain, D. L., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 1342.
 (20) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C., *Inorg. Chem.* **1979**, *18*, 553.

Electrochemical Oxidation of Rhenium Alkyl Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{R})$: Evidence for One-Electron Charge Transfer

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The redox properties of rhenium alkyl complexes $\text{R}-(\text{Re})$ ($(\text{Re}) = (\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)$) with $\text{R} = \text{PhCH}_2$ (1), $(\text{CH}_3)_2\text{CHCH}_2$ (2), and $\text{Ph}(\text{CH}_3)\text{CH}$ (3) are studied electrochemically. Cyclic voltammetric, peak current, heterogeneous charge transfer, and chronoamperometric studies in a variety of solvents indicate that 1–3 undergo initial one-electron oxidation to cation radicals $\text{R}-(\text{Re})^{+\bullet}$. These decompose by an EC mechanism at rates that correlate with solvent donor ability. Intermediates, possibly $\text{R}-(\text{Re}/\text{solvent})^{+\bullet}$, are detected by cyclic voltammetry. Coulometric experiments further suggest that $\text{R}-(\text{Re})^{+\bullet}$ can catalytically oxidize solvent via $\text{R}-(\text{Re}/\text{solvent})^{+\bullet}$. These data contrast with an earlier report describing evidence for a two-electron oxidation of 3.

Introduction

An earlier investigation of the electrochemical oxidation of rhenium alkyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{R})$, abbreviated here as $\text{R}-(\text{Re})$, suggested that two types of

processes take place.² Type I complexes ($\text{R} = \text{CH}_3$, CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}_2\text{Ph}$, $\text{CH}_2\text{CH}(\text{CH}_3)_2$, $\text{CH}_2\text{-C}(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)\text{CH}_2\text{Ph}$, CH_2Ph) were thought to undergo one-electron charge transfer to give $\text{R}_1-(\text{Re})^{+\bullet}$ (I),

(1) (a) University of Utah. (b) University of Trondheim.

(2) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020.