Water-Soluble Organometallic Compounds. 3. Kinetic Investigations of Dissociative Phosphine Substitution Processes Involving Water-Soluble Group 6 Metal Derivatives in Miscible Aqueous/Organic Media

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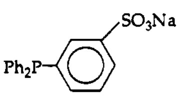
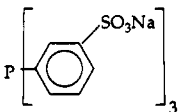
Mechanistic aspects of ligand substitution reactions of group 6 metal carbonyl derivatives containing the trisulfonated phosphine P(*m*-$C_6H_4SO_3Na)_3$ (hereafter referred to as TPPTS) in pure water and water/THF media have been investigated by examination of the reactions of these derivatives with carbon monoxide as an incoming ligand. The reactions, which were carried out under 500 psi of CO in the temperature range 110-160 °C, were monitored in situ by infrared spectroscopy employing a cylindrical internal reflectance reactor. Kinetic measurements show the reactions are first-order in metal complex concentration and independent of CO pressure at high CO pressures, and the rates are retarded by added TPPTS. The activation parameters for TPPTS dissociation from $M(CO)_5$TPPTS derivatives (M = Mo, W), e.g., in 1:1 THF/H_2O, $\Delta H^{\ddagger} = 28.8 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = -4.2 \pm 3.5$ eu and $\Delta H^{\ddagger} = 31.8 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -0.73 \pm 3.6$ eu, respectively were shown to be quite similar to those determined for the analogous processes involving the nonsulfonated PPh_3 ligand in the same solvent systems. In addition only small solvent effects were noted in going from aqueous to organic solvents for these dissociative processes. For the *cis*-$Mo(CO)_4[TPPTS]_2$ derivative, in which the sodium ions are encapsulated by a cryptand, kryptofix-221, a steric acceleration of TPPTS dissociation is noted relative to its PPh_3 analog. The steric requirements of the TPPTS ligand were defined by X-ray structural data obtained on [Na-kryptofix-221]$_3[W(CO)_5P(C_6H_4SO_3)_3]$ and $Fe(CO)_4$-TPPTS. By way of contrast for the *cis*-$Mo(CO)_4[TPPTS]_2$ derivative in which the Na^+ ions are free to interact with the sulfonate groups, a stabilizing effect is noted which is attributed to intramolecular interligand interactions via the Na^+ cations. In the case of *cis*-$W(CO)_4[TPPTS]_2$ and *cis*-$W(CO)_4[PPh_3]_2$ an intramolecular rearrangement to the corresponding trans product was observed.

Introduction

Research efforts in the area of water-soluble organometallic chemistry continue to expand at an accelerated rate. Seventeen years following the initial synthesis of sulfonated phosphines[1] $Ph_2P(m\text{-}C_6H_4SO_3Na)$, **1**, and $P(m\text{-}C_6H_4SO_3Na)_3$, **2**, the Rhone-Poulenc/Ruhrchemie biphasic hydroformylation catalyst HRh-$(CO)L_3$ (L = **2**) spurred the development in this field.[2,3] Although this rhodium phosphine complex is possibly the most well-known of the water-soluble phosphine catalysts, other similar water-based organometallic catalysts have been employed for a variety of important chemical processes.[4] Several of the processes which make use of the sulfonated triphenylphosphine ligands are indicated in eqs 1-3.

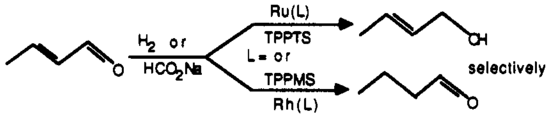


(TPPMS)
1

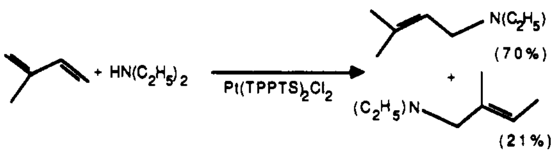


(TPPTS)
2

$$CH_2CHCH_3 + CO + H_2 \xrightarrow{HRh(CO)(TPPTS)_3} \begin{matrix} n\text{-butanol } (95\%) \\ iso\text{-butanol } (4\%) \end{matrix} \qquad (1)$$



(2)



(3)

A fundamental understanding of the mechanistic aspects of these various processes, especially in comparison with analogous processes involving nonsulfonated phosphines, is needed in order to fully exploit the role of these water-soluble phosphine complexes in homogeneous catalysis. Spectral comparisons (ν(CO), ^{13}C and ^{31}P NMR) between complexes containing the sulfonated phosphines **1** and **2** and triphenylphosphine have been reported.[4a,c,5,6] These measurements indicate the $-SO_3^-$ substituents to have only a minor electronic influence on the nature of the M-P bond. This conclusion is further supported by M-P bond distances obtained from crystallographic data.[5,7] On the other hand, there is a scarcity of kinetic data on ligand substitution reactions of these water-soluble phosphine complexes. The most notable observation with respect to ligand substitution reactions involving water-soluble phosphine complexes thus far has been presented by Horvath and co-workers.[6] These researchers have

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(1) Ahrland, S.; Chatt, J.; Davies, N.; Williams, A. *J. Chem. Soc.* **1958**, 276.
(2) Kuntz, E. G. Fr. Patent 2314910, 1975.
(3) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570.
(4) (a) Herrmann, W. A.; Kulpe, J. A.; Kellner, J.; Riepl, H.; Bahrmann, H.; Konkol, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 391. (b) Herrmann, W. A; Kulpe, J. A.; Bahrmann, H.; Konkol, W. *J. Organomet. Chem.* **1990**, *389*, 85. (c) Herrmann, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103. (d) Joo, F.; Benyei, A. *J. Organomet. Chem.* **1989**, *363*, C19. (e) Russell, M. *Platinum Met. Rev.* **1988**, *32*, 179. (f) Joo, F.; Toth, Z.; Beck, M. T. *Inorg. Chim. Acta* **1986**, *42*, 153. (g) Joo, F.; Toth, Z. *J. Mol. Catal.* **1980**, *369*. (h) Borowski, A.; Cole-Hamilton, D.; Wilkinson, G. *Nouv. J. Chem.* **1977**, *2*, 137. (i) Joo, F.; Beck, M. T. *Magy. Foly.* **1973**, *79*, 189. (j) Okano, T.; Uchida, I.; Nakagaki, T.; Konishi, H.; Kiji, J. *J. Mol. Catal.* **1989**, *54*, 65. (k) Fache, E.; Senocq, F.; Santini, C.; Basset, Jean-Marie *J. Chem. Soc., Chem. Commun.* **1990**, *24*, 1776.
(5) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1144.
(6) Horvath, I.; Kastrup, R.; Oswald, A.; Mozeleski, E. *Catal. Lett.* **1989**, *2*, 85.
(7) Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324.

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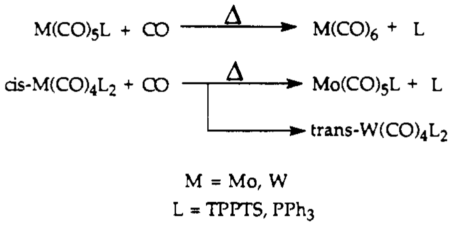
Scheme I



suggested that the higher barrier revealed for phosphine dissociation in $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ vs $HRh(CO)[PPh_3]_3$, a pivotal step in the hydroformylation reaction, is due to an intramolecular association of the sulfonate groups on adjacent phosphine ligands via hydrogen bonding through the aqueous medium.

The first paper in this series reported upon the synthesis, spectral data, and crystal structure of $[Na\text{-kryptofix-}221]_3[W(CO)_5P(C_6H_4SO_3)_3]$.[5] This structure provided a good model for the steric environment of an isolated metal-bound TPPTS ligand as would be expected in an aqueous solution, where the Na^+ ion may be completely hydrated. The second member of the series presented catalytic studies of the reactions depicted in eq 2 employing 1,3,5-triaza-7-phosphaadamantane complexes of Ru(II) and Rh(I) as catalysts in biphasic aqueous/organic medium.[8] This present contribution contains the basic solution chemistry of group 6 metal carbonyl complexes of $P(C_6H_4SO_3Na)_3$, in particular $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ (L = 2), including quantitative measurements for phosphine dissociation (Scheme I). Comparisons between the mono- and bis-substituted complexes containing TPPTS and its nonsulfonated analog, PPh_3, are incorporated.

Experimental Section

Reagents. Methanol and ethanol were purchased from Fischer (spectrophotometric grade) and were dried by distillation over magnesium and I_2 under a N_2 atmosphere. Tetrahydrofuran, hexane, and diethyl ether were purchased from Fischer Scientific and purified over sodium benzophenone ketyl under a N_2 atmosphere. Water was triply distilled, deionized, and degassed with N_2. Tungsten and molybdenum hexacarbonyl were purchased from Strem Chemical Co. Kryptofix-221 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane), 2-methoxyethanol, TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine), and carbon monoxide were obtained from EM Science, Aldrich Chemical Co., Exxon Corporate Research, and Airco Inc., respectively. Unless otherwise stated all chemicals were used without further purification.

Instrumentation. Infrared spectra were collected on either an IBM 85 or a Mattson 6020 spectrometer. Aqueous infrared spectra were taken employing a CIRCLE (cylindrical internal reflectance) cell, furnished by Spectra Tech Inc. Other infrared spectra in methanol and 2-methoxyethanol were taken with both the CIRCLE and standard 0.1-mm CaF solution cells. Kinetic measurements were made using a REACTOR cell, furnished by Spectra Tech Inc. NMR spectra were collected using both Varian XL-200 (^{13}C and ^1H) and a Varian XL-200E (^{31}P) spectrometers. All manipulations were performed using a Vacuum Atmospheres glovebox or a nitrogen/vaccum Schlenk line.

Preparations. $M(CO)_5TPPTS$ (M = Mo, W). A typical preparation is described herein. A solution of $W(CO)_6$ was prepared by dissolving 0.654 g (2.0 mmol) in 75 mL of MeOH. This solution was placed in a photolysis vessel and irradiated with a 400-W UV lamp for 30 min to yield the very substitutionally labile $W(CO)_5{\cdot}MeOH$ species as identified by IR spectroscopy (ν(CO) 2074 (w), 1932 (s), and 1887 cm^{-1} (m)). The methanol adduct was added by cannula to a flask containing 1 equiv (1.06 g, 2.0 mmol) of the solid TPPTS ($P(m\text{-}C_6H_4SO_3Na)_3{\cdot}3H_2O$) ligand. The reaction was monitored by the disappearance of the ν(CO) infrared bands associated with the methanol adduct, with concomitant appearance of ν(CO) bands due to $W(CO)_5TPPTS$. After being filtered through Celite, the compound was precipitated by the addition of isopropyl alcohol to yield a very flocculent pale yellow solid. The compound was centrifuged and the supernatant ligand decanted to yield a wet yellow paste. Final drying of the compound was accomplished under vacuum at ambient temperature over a 24-h period. Data for $W(CO)_5TPPTS$ are as follows. ν(CO) in H_2O: 2073 (w), 1946 (s), and 1932 (m, sh) cm^{-1}. $\delta(^{31}P)$ NMR in H_2O: 26.9 ppm. Anal. Calcd for $[W(CO)_5P(m\text{-}C_6H_4SO_3Na)_3{\cdot}3H_2O]$: C, 29.19; H, 1.92. Found: C, 28.96; H, 1.86. Data for $Mo(CO)_5$-TPPTS are as follows. ν(CO) in H_2O: 2075 (w), 1955 (s), and 1941 (m, sh) cm^{-1}. Anal. Calcd for $[Mo(CO)_5P(m\text{-}C_6H_4SO_3Na)_3{\cdot}3H_2O]$: C, 32.18; H, 2.11. Found: C, 32.10; H, 2.08.

$[Na\text{-kryptofix-}221]_3[W(CO)_5P(C_6H_4\text{-}m\text{-}SO_3)_3]$. A slurry of $W(CO)_5$-TPPTS (200 mg, 0.220 mmol) in 25 mL of THF was placed in a 50-mL Schlenk flask and allowed to stir with slow addition of 2-methoxyethanol (7 mL) until the solid was completely dissolved. Filtration of the resultant solution through Celite produced a pristine yellow solution which was perfectly transparent. Three equivalents of kryptofix-221 (0.59 g, 0.67 mmol) dissolved in acetonitrile (5 mL) were added to the solution, which was allowed to stir over a 24-h period. Solvent was stripped off under vacuum to leave a yellow glass. The complex dissolved completely in CH_3CN to give a bright yellow solution with IR ν(CO) bands at 2075 (w), 1946 (s), and 1938 cm^{-1} (m, sh).

***cis*-$Mo(CO)_4(TPPTS)_2$.** The preparation of *cis*-$Mo(CO)_4(TPPTS)_2$ is a modification of a previously reported synthesis, employing the substitutionally labile *cis*-$Mo(CO)_4(piperidine)_2$, to produce *cis*-$Mo(CO)_4L_2$, where L = phosphine or phosphite.[9] In the glovebox, a 50-mL Schlenk flask was loaded with 0.436 g (1.15 mmol) of *cis*-$Mo(CO)_4(piperidine)_2$, which was dissolved in 15 mL of freshly distilled THF. Degassed H_2O (30 mL) was added to 1.31 g (2.3 mmol) of fluffy white TPPTS in a 50-mL round bottom flask. Upon cannulation of the TPPTS solution into *cis*-$Mo(CO)_4(piperidine)_2$, a cloudy yellow solution resulted. After the solution was stirred for approximately 10 min, the solvents were removed by vacuum overnight to yield a dark yellow glass.

Recrystallization of *cis*-$Mo(CO)_4(TPPTS)_2$ was accomplished by first dissolving the yellow glass in a minimum of degassed H_2O. The yellow solution was then filtered through Celite to yield a pristine light yellow solution. A flocculent yellow solid was precipitated by the addition of 40 mL of EtOH. After the solid was allowed to settle out, the supernatant liquid was removed and the solid washed with three portions of Et_2O (20 mL). Finally the compound was dried under vacuum. IR (2-methoxyethanol): ν(CO) 2025 (w), 1931 (m, sh), 1914 (s), and 1898 (m, sh) cm^{-1}. Anal. Calcd for *cis*-$Mo(CO)_4(TPPTS)_2{\cdot}9H_2O$: C, 31.88; H, 2.81. Found: C, 32.21; H, 3.13.

$[Na\text{-kryptofix-}221]_6[cis\text{-}Mo(CO)_4\{P(C_6H_4\text{-}m\text{-}SO_3)_3\}_2]$. This compound was prepared by placing 0.125 g (0.090 mmol) of *cis*-$Mo(CO)_4(TPPTS)_2$ in a 50-mL Schlenk flask and adding 15 mL of CH_3CN, affording a very heterogeneous suspension. Addition of 2 mL of a 0.334 M solution of kryptofix-221 in CH_3CN yielded a clear light yellow solution within 5 min. This solution was filtered through Celite and dried under vacuum to give an amber glass. IR (CH_3CN): ν(CO) 2023 (w), 1911 (m, sh), 1909 (m, sh), 1859 (m) cm^{-1}.

***cis*-$W(CO)_4(TPPTS)_2$.** This complex was prepared by loading a photolysis flask with 150 mg (0.43 mmol) of $W(CO)_6$, after which it was dissolved in 200 mL of freshly distilled THF and photolyzed for approximately 2 h with strong bubbling of N_2. IR spectroscopy was used to determine the extent of the reaction. Initially, the bright yellow $W(CO)_5{\cdot}THF$ complex was formed, ν(CO) 2073 (w), 1929 (s), 1890 (m) cm^{-1}. Continued photolysis afforded the disappearance of the ν(CO) bands for the monosubstituted product and the concomitant formation of the orange *cis*-$W(CO)_4{\cdot}(THF)_2$ complex, ν(CO) 2013 (w), 1876 (vs), 1830 (m) cm^{-1}. Once the maximum amount of *cis*-$W(CO)_4{\cdot}2THF$ had been produced, the solution was cannulated into a flask containing 485 mg (0.85 mmol) of TPPTS dissolved in 15 mL of degassed H_2O. It has not been possible to form 100% *cis*-$W(CO)_4{\cdot}2THF$. The solvent was stripped off under vacuum to yield a dark yellow brown glass. Recrystallization of the glass was accomplished by dissolving the compound in a minimum of degassed H_2O and filtering through Celite. A yellow brown solid was produced upon the addition of 30 mL of EtOH. Finally the complex was dried under vacuum. IR (MeOH): ν(CO) 2024 (w), 1925.1 (m, sh), 1906 (s), and 1895 (m, sh) cm^{-1}.

***cis*-$W(CO)_4(PPh_3)_2$.** This compound could not be produced by the same route as for *cis*-$Mo(CO)_4(PPh_3)_2$, due to major contamination by the trans species.[9] The complex was prepared by dissolving 250 mg of $W(CO)_5PPh_3$ (0.43 mmol) and 111 mg of PPh_3 (0.43 mmol) in a photolysis vessel in 200 mL of freshly distilled hexane. The solution was photolyzed for approximately 30 min to yield a light yellow solid on the walls of the

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[8] Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 1990.

[9] Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

photoreactor. The resultant solid was scraped off the photolysis vessel and dissolved in CH_2Cl_2 for recrystallization. Isolation of the complex was accomplished by the addition of Et_2O, followed by drying under vacuum at room temperature. IR (THF): ν(CO) 2017 (w), 1915 (m, sh), 1898 (s), and 1878 (m, sh) cm^{-1}.

Kinetic Measurements for Phosphine Displacement. When elevated temperatures or pressures were not required, reactions were performed in a 50-mL Schlenk flask. Typically, the flask was loaded with the solid sample in the glovebox and brought out, and the sample dissolved with dry degassed solvent (5 mL). Addition of carbon monoxide was accomplished by bubbling the gas through the solution for 2 min. An atmosphere of CO was kept over the solution, for the duration of the reaction. The flask was then lowered into a thermostated water bath, which held temperatures to within 0.1 °C. Samples were withdrawn with a glass syringe and monitored by infrared spectroscopy in the ν(CO) region. Progress of the reaction was followed by monitoring the disappearance of a weak isolated band in the starting material.

Reactions requiring higher temperatures and higher pressures were performed in a REACTOR (CIRCLE) cell furnished by Spectra Tech Inc. The stainless steel reactor was fitted with septa and evacuated. Addition of the metal complex solution, previously prepared under N_2, was accomplished by cannula. The cell was then placed in the spectrometer and pressurized with carbon monoxide, and the temperature was ramped to the desired point. The temperature was held to within 1 °C by a Parr temperature controller and was monitored by an Omega thermocouple. The Mattson Galaxy 6020 spectrometer automatically took spectra at predetermined intervals for the duration of the reaction. Reaction progress was ascertained by analysis of the disappearance of the strong ν(CO) band in the starting complex.

Results

The rates of substitution of the water-soluble phosphine ligand in the complexes $M(CO)_5TPPTS$ (M = Mo and W) by carbon monoxide were determined in both pure water and mixture of water/tetrahydrofuran (eq 4). The reactions were monitored in

$$M(CO)_5TPPTS + CO \xrightarrow{k_1} M(CO)_6 + TPPTS \qquad (4)$$

$$\text{rate} = k_1[M(CO)_5TPPTS] \qquad (5)$$

situ by infrared spectroscopy over a temperature range 110–160 °C. Kinetic measurements were carried out over a pressure range 200–500 psi of carbon monoxide at 130 °C.[10] At these high pressures of CO the reactions went to completion and the rate constants changed by less than 5% (see Table I). Hence, all reactions were followed at 500 psi of carbon monoxide. Under these conditions the reactions were observed to be first-order in metal complex and zero-order in the concentration of carbon monoxide. A representative rate plot is illustrated in the supplementary material for the reaction of $W(CO)_5TPPTS$ with carbon monoxide, while a corresponding Eyring plot for data determined over a 30° temperature range may be seen in Figure 1.

These reactions were observed to be quite clean with metal hexacarbonyl being the only metal-containing product. Although formation of the metal hexacarbonyls could not be observed spectroscopically for reactions carried out in water or THF/water mixtures due to their limited solubilities in these solvents, a white crystalline solid could be seen floating on the surface of the reaction mixture upon opening the reactor. The solid was isolated, and upon dissolving it in hexane was identified as $M(CO)_6$ by infrared spectroscopy. Figure 2 represents overlay spectra of a kinetic run of $W(CO)_5TPPTS$ reacting with CO in a 1:1 mixture of THF/H_2O, demonstrating not only that the reaction goes to completion but also that the CIRCLE cell has the capability to monitor effectively the substitution reaction in an aqueous solvent mixture.

Table I. Rate Constants for the Dissociation of Phosphines from $M(CO)_5L$, Where M = Mo and W[a]

M	L	temp, °C	10^4k_1, s^{-1}	solvent
W	$P(C_6H_4SO_3Na)_3$	155	4.110	H_2O
W	$P(C_6H_4SO_3Na)_3$	115	0.119	THF/H_2O (1:1)
		120	0.237	
		125	0.430	
		130	0.726	
		130	0.708[b]	
		130	0.698[c]	
		135	0.967	
		140	1.78	
		145	2.36	
W	$P(C_6H_4SO_3Na)_3$	117	0.219	THF/H_2O (2:1)
		123	0.263	
		134	1.14	
		138	1.25	
W	$[Na\text{-kryptofix-}221]_3$-$[C_6H_4SO_3)_3]$	135	1.79	CH_3CN
W	PPh_3	120	0.038	THF/H_2O (1:1)
		128	0.198	
		130	0.357	
		150	0.979	
W	PPh_3	125	0.490	CH_3CN
Mo	TPPTS	110	0.720	THF/H_2O (1:1)
		125	3.28	
		135	7.22	
Mo	PPh_3	110	0.731	THF/H_2O (1:1)
		125	3.15	
		135	8.60	

[a] Reactions were carried out in CO-saturated solutions at 500 psi of carbon monoxide. [b] This run was carried out in a CO-saturated solution at 400 psi of carbon monoxide. [c] This run was carried out in a CO-saturated solution at 200 psi of carbon monoxide.

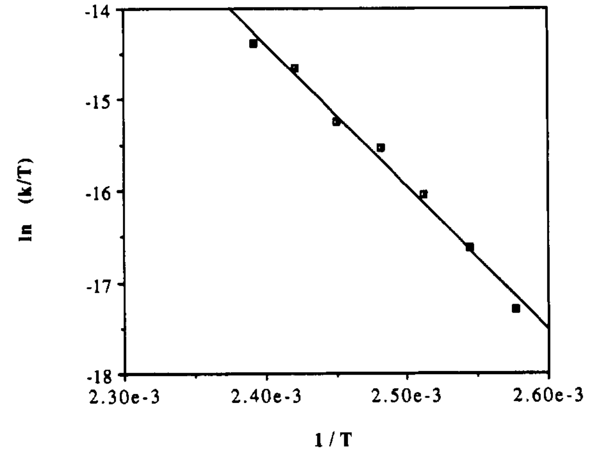

Figure 1. Eyring plot for the dissociation of TPPTS from $W(CO)_5TPPTS$ under 500 psi of CO in the temperature range between 115 and 145 °C in a 1:1 mixture of THF/H_2O.

The first-order rate constant for dissociative loss of the TPPTS ligand from $M(CO)_5TPPTS$ are compiled in Table I for the various solvents and solvent mixtures examined. In addition, kinetic data for the acetonitrile-soluble derivative $[Na\text{-kryptofix-}221]_3$-$[W(CO)_5P(C_6H_4SO_3)_3]$ along with its PPh_3 analog are included in Table I. Activation parameters for several of these processes are consolidated in Table II together with the corresponding first-order rate constants at 135 °C. Because of the low solubility of carbon monoxide in *pure* water, it was necessary to determine the k_1 value from the initial portion of the reaction in an effort to lessen the contribution from the reverse process.

In an attempt to investigate possible interligand interactions between two adjacent phosphine ligands via the sulfonate groups, the *cis*-$M(CO)_4L_2$ complexes were synthesized and their reactivities toward phosphine ligand substitution investigated. Upon reaction of these derivatives with carbon monoxide in 2-methoxyethanol, complexes of molybdenum and tungsten differ in their reactivity in that *cis*-$Mo(CO)_4[TPPTS]_2$ undergoes a

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(10) Reactions carried out at atmospheric carbon monoxide pressure reached a steady-state with a sizable quantity of starting $M(CO)_5TPPTS$ complex remaining in solution.

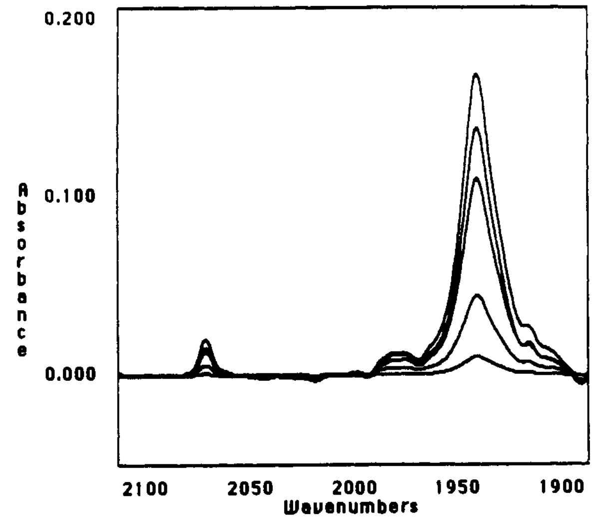

Figure 2. Representative portion of the infrared spectra in the ν(CO) region accumulated during a kinetic run of $W(CO)_5TPPTS$ in a 1:1 mixture of THF/H_2O.

Table II. Comparative Rate Constants and Activation Parameters[a] for Dissociative Processes in $M(CO)_5L$ (M = Mo, W)

M	L/solvent	10^4k_1-(135 °C), s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu
W	TPPTS/1:1 THF/H_2O	0.967	31.8 ± 1.5	−0.73 ± 3.6
W	TPPTS/2:1 THF/H_2O	1.14[b]	29.8 ± 4.8	−5.7 ± 12.0
W	PPh_3/1:1 THF/H_2O	0.264[b]	32.6 ± 9.9	−1.4 ± 24.6
Mo	TPPTS/1:1 THF/H_2O	7.22	28.8 ± 1.4	−4.2 ± 3.5
Mo	PPh_3/1:1 THF/H_2O	8.60	30.5 ± 0.8	0.17 ± 2.0

[a] Errors on activation parameters represent 95% confidence limits. [b] Rate values were interpolated from data in Table I.

substitution of TPPTS by CO, whereas *cis*-$W(CO)_4[TPPTS]_2$ sustains an intramolecular rearrangement to the trans isomer (eqs 6 and 7).

$$cis\text{-}Mo(CO)_4[TPPTS]_2 + CO \rightarrow Mo(CO)_5TPPTS + TPPTS \quad (6)$$

$$cis\text{-}W(CO)_4[TPPTS]_2 + CO \rightarrow trans\text{-}W(CO)_4[TPPTS]_2 \quad (7)$$

The ligand substitution reactions involving *cis*-$Mo(CO)_4[TPPTS]_2$ was found to be first-order in metal complex and zero-order in CO for reactions carried out in a large excess of CO. Addition of free TPPTS retarded the rate of phosphine substitution (see Table III). Hence, the dissociative mechanism outlined in eqs 8 and 9, which lead to the rate expressions in eqs 10 and 11, is consistent with these observations. Figure 3 contains a plot of $1/k_{obsd}$ vs [TPPTS] at constant CO pressure.

$$cis\text{-}Mo(CO)_4[TPPTS]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo(CO)_4TPPTS] + [TPPTS] \quad (8)$$

$$[Mo(CO)_4TPPTS] + [CO] \xrightarrow[k_2]{\text{(fast)}} Mo(CO)_5TPPTS \quad (9)$$

$$\text{rate} = \left[\frac{k_1k_2[CO]}{k_{-1}[TPPTS] + k_2[CO]}\right][Mo(CO)_4(TPPTS)_2] \quad (10)$$

$$\text{rate} = k_{obsd}[Mo(CO)_4(TPPTS)_2] \quad (11)$$

The first-order rate constants for the dissociation of TPPTS from *cis*-$Mo(CO)_4[TPPTS]_2$ are listed in Table III for a wide range of temperatures. The addition of 25% water to the 2-methoxyethanol solution did not significantly affect the rate of phosphine dissociation. From the data in Table III for the *cis*-$Mo(CO)_4[TPPTS]_2$ derivative as a function of [TPPTS] under a constant pressure of CO, $k_{-1}/k_2[CO]$ was determined to be 9.94. If [CO] in 2-methoxyethanol at 60 °C is taken to be 0.00719 M- atm^{-1}, then, k_{-1}/k_2 = 0.072.[11] Included in Table III are comparable rate data as a function of temperature for the kryptofix-221 encapsulated TPPTS and PPh_3 derivatives. Activation parameters for all three derivatives are listed in Table IV along with comparative rate constants at 65 °C. All reactions appeared to go very cleanly to the $Mo(CO)_5L$ complexes with no formation of the *trans*-$Mo(CO)_4L_2$ species; however, it should be noted that the ν(CO) regions for both cis and trans isomers grossly overlap, thus small quantities of the trans isomer are difficult to detect. On the contrary the reaction of the tungsten derivative *cis*-$W(CO)_4[TPPTS]_2$ under a CO atmosphere led exclusively to the trans isomer (eq 7) with no production of $W(CO)_5TPPTS$. Hence, the isomerization reaction does not occur via phosphine dissociation and thus is an *intramolecular* process. Reaction 7 obeys first-order kinetics with regard to the tungsten complex.

Table III. Rate Contants for the Dissociation of a Phosphines in *cis*-$Mo(CO)_4L_2$ in the Presence of a CO-Saturated Solution

L	temp, °C	10^3k_1, s^{-1}	solvent
TPPTS	50	0.105	2-methoxyethanol
	55	0.193	
	60	0.257	
	65	0.693	
	70	1.19	
	80	4.92	
TPPTS	60	0.492	2-methoxyethanol/H_2O (3:1)
	60[a]	0.417	
	60[b]	0.384	
	60[c]	0.284	
[Na-kryptofix-221]$_3$-[$P(C_6H_4SO_3)_3$]	40	0.232	2-methoxyethanol
	45	0.517	
	55	1.457	
	65	6.400	
PPh_3	55	0.231	2-methoxyethanol
	60	0.465	
	65	0.903	
	70	1.666	

[a] [TPPTS] = 0.0188 M. [b] [TPPTS] = 0.0325 M. [c] [TPPTS] = 0.0738 M.

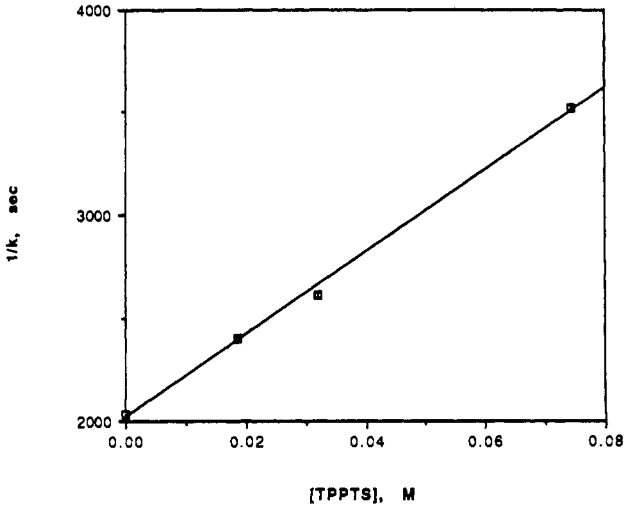

Figure 3. Plot of k_{obsd}^{-1} versus [TPPTS] at a constant CO pressure of 1 atm. Reactions were carried out in 2-methoxyethanol at 60 °C.

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[11] (a) This value for [CO] in 2-methoxyethanol at 60 °C is taken from an extrapolation of the temperature-dependent data reported by Calderazzo and Cotton[11b] in diethoxydiethyl ether. (b) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30.

Table IV. Comparative Rate Constants and Activation Parameters for Dissociative Processes in $Mo(CO)_4L_2$ in 2-Methoxyethanol under CO[a]

L	10^3k_1(65 °C)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
TPPTS	0.693	30.0 ± 2.0	14.7 ± 6.1
[Na-kryptofix-221]$_3$-[P($C_6H_4SO_3$)$_3$]	6.40	27.1 ± 1.7	9.3 ± 5.2
PPh_3	0.903	29.5 ± 0.3	12.7 ± 1.0

[a] Errors on activation parameters represent 95% confidence limits.

Table V. Rate Constants for the Isomerization of *cis*-$W(CO)_4L_2$ to *trans*-$W(CO)_4L_2$ in the Presence of a CO-Saturated Solution

LK	temp, °C	10^3k_1, s^{-1}	solvent
TPPTS	50	0.087	2-methoxyethanol
	65	0.278	
	70	0.601	
PPh_3	40	0.063	2-methoxyethanol
	50	0.134	
	70	0.801	

Table VI. Comparative Rate Constants and Activation Parameters for the Intramolecular Isomerization Processes for *cis*-$W(CO)_4L_2$ in 2-Methoxyethanol under CO

L	10^4k_1(50 °C)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
TPPTS	0.87	20.2 ± 3.6	−16.7 ± 10.9
PPh_3	0.903	18.3 ± 1.2	−21.5 ± 3.6

[a] Errors on activated parameters represent 95% confidence limits.

Tables V and VI contain the corresponding rate constants as a function of temperature for the TPPTS derivative, as well as its PPh_3 analog, and the activation parameters for the isomerization reactions, respectively.

The steric requirements of the TPPTS ligand in various environments were estimated by calculating Tolman cone angles from crystallographic data for [Na-kryptofix-221]$_3$[W(CO)$_5$-P($C_6H_4SO_3$)$_3$][5] and Fe(CO)$_4$TPPTS.[12] In order to be internally consistent, the analogous cone angle for the PPh_3 ligand was reassessed.[13] Cone angle calculations were carried out by first setting the M–P bond distance to 2.28 Å, the value used by Tolman.[14,15] The half-cone-angle was then defined by the M–P bond axis and the tangent to the van der Waals radii of the outermost atom or the atom which would describe the largest angle as depicted in Figure 4.[16] In order to obtain the tangential point, the bond distance for the outermost lying atom was extended by the value of its van der Waals radius.[17] The cone angle defined for the TPPTS ligand was 166–178° depending upon the nature of the counterion associated with it.

Discussion

The ligand substitution reaction defined in eq 4 involving the replacement of P(*m*-$C_6H_4SO_3Na$)$_3$ by carbon monoxide has been shown to proceed via a dissociative (D) mechanism. This is manifested by the first-order dependence of the reaction on the concentration of M(CO)$_5$TPPTS and independence on the pressure of CO at high pressures of CO, as well as its retardation by added quantities of the leaving ligand. Furthermore, consistent with this description of the reaction pathway are the magnitudes of the values determined for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. That is, $\Delta H^{\ddagger}$ for these processes was found to be ~30 kcal/mol with $\Delta S^{\ddagger}$ being close to zero. These activation parameters are indicative of a transition state with a greatly lengthened M–P bond with restricted translational motion of the two molecular fragments, i.e., $\Delta G^{\ddagger}$ should be similar to the free energy of formation (ΔG°) of the five-coordinate intermediate.[18] In addition the enhanced reactivity of the molybdenum derivatives (about 1 order of magnitude in rate) relative to their tungsten analogs is in agreement with the anticipated weaker Mo–P bond. This is evident in a slightly lower enthalpy of activation in the case of molybdenum of about 2 kcal/mol. For example, the corresponding $\Delta H^{\ddagger}$ value for TPPTS dissociation in M(CO)$_5$TPPTS derivatives in a 1:1 mixture of THF and H_2O are 28.8 ± 2.4 kcal mol^{-1} and 31.8 ± 1.5 kcal mol^{-1} for molybdenum and tungsten, respectively. Comparative studies of triphenylphosphine analogs of molybdenum and tungsten in the same solvent system indicate an impressive similarity in the rate and activation parameters with those determined for the corresponding TPPTS complexes That is, the $\Delta G^{\ddagger}$ values for phosphine dissociation in Mo(CO)$_5$PPh$_3$ and Mo(CO)$_5$TPPTS in 1:1 THF/H_2O are nearly identical at 30.1 and 30.4 kal/mol, respectively.

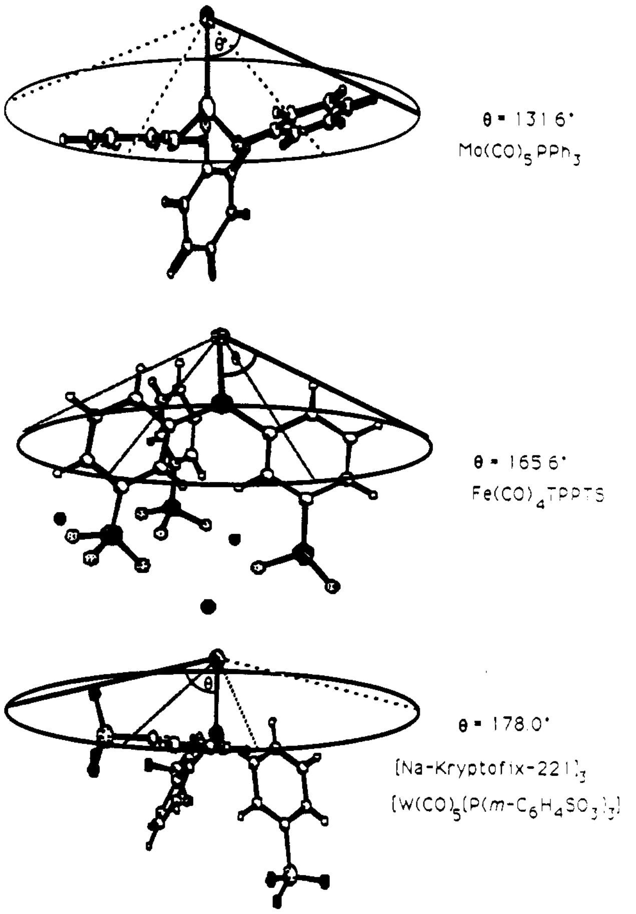

Figure 4. Calculated cone angles from crystallographic data.

An additional striking feature of these ligand substitution reactions is the lack of influence of solvent or solvent mixture on rates, which further substantiates the intimate mechanism as D in character. That is, the range of rate constant values for phosphine dissociation in (CO)$_5$WP(*m*-$C_6H_4SO_3Na$)$_3$ span only a factor of ~2, i.e., (4.11–10.2) × 10^{-4} s^{-1} at 155 °C, in THF/water mixtures and pure water. Furthermore, the cryptated encapsulated [Na-kryptofix-221]$_3$[W(CO)$_5$P(*m*-$C_6H_4SO_3$)$_3$] dissolved in CH_3CN displayed a first-order rate constant for phosphine dissociation quite similar to that noted for the sodium salt in THF/H_2O solution. Similarly, k_1 for PPh_3 dissociation

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(12) Darensbourg, D. J.; Bischoff, C. J. Unpublished results.

(13) Cotton, F. A.; Darensbourg, D. J.; Ilsley, G. *Inorg. Chem.* **1981**, *20*, 578.

(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(15) Measurements were also taken which indicate that the cone angle for the phosphine in [Na-kryptofix-221]$_3$[W(CO)$_5${P($C_6H_4SO_3$}$_3$] decreases by only 5° for every 0.3-Å increase in M–P bond length. Thus, at the true bond length of 2.55 Å for this complex, the cone angle is calculated to be 173°.

(16) DeLerno, J. R.; Trefonas, L. M.; Darensbourg, M. Y.; Majeste, R. J. *Inorg. Chem.* **1976**, *15*, 816.

(17) Modifications to the crystal structures, i.e. changes in bond lengths, were carried out using ChemX and SHELXTL software performed on a micro VAX II computer.

(18) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1979**, *184*, 77.

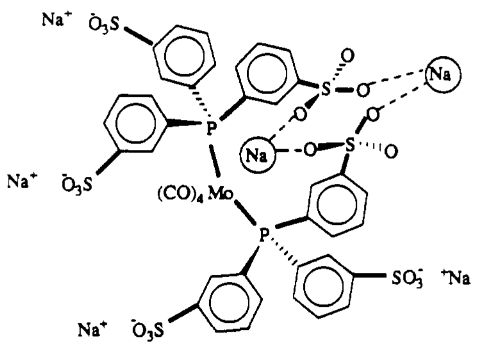


Figure 5. Schematic of proposed intramolecular interligand interactions of adjacent SO_3^- groups via Na^+ bridges in *cis*-$Mo(CO)_4[TPPTS]_2$.

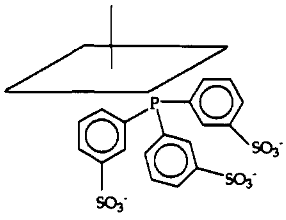
from $W(CO)_5PPh_3$ in 1:1 THF/water is only three times slower than that observed in the highly nucleophilic solvent, CH_3CN.

The influence of *intramolecular interligand* interactions, i.e., via hydrogen-bonding or $O^{\delta-}\cdots Na^+\cdots O^{\delta-}$ ion-pairing between neighboring phosphines, on the rate of TPPTS dissociation from molybdenum was assessed by examining ligand substitution reactions involving the *cis*-$Mo(CO)_4[TPPTS]_2$ derivative (eq 6). As observed for the monosubstituted derivative, the reaction obeys a rate law which is first-order in metal complex, and zero-order in CO at high CO pressure and is retarded by free phosphine ligand. These results are consistent with earlier studies involving dissociation of a phosphine ligand from *cis*-$Mo(CO)_4L_2$ complexes.[9,19,20]

The rate constants for phosphine dissociation at 65 °C in 2-methoxyethanol (Table III) exhibit small, but systematic, variations with the nature of the phosphine ligand, with $[Na\text{-kryptofix-}221]_3[P(C_6H_4SO_3)_3] > PPh_3 \geq TPPTS$. The 7-fold decrease in phosphine dissociation rates in proceeding from *cis*-$Mo(CO)_4[P(m\text{-}C_6H_4SO_3)_3]_2^{6-}$ to *cis*-$Mo(CO)_4[PPh_3]_2$ can be attributed to the increase in steric requirements for the sulfonated derivative, where the cryptated encapsulated TPPTS ligand has a cone angle ~30% greater than that of PPh_3. That is, it is anticipated that some lengthening of the Mo–P bond from its equilibrium position occurs because of the steric requirements of the two bulky phosphine ligands. Indeed this is evident upon comparing the $\Delta H^{\ddagger}$ values (Table IV) for the cryptated encapsulated TPPTS and PPh_3. It has previously been well documented that a lengthening of the Mo–P bond, as well as distortions in the P–Mo–P bond angle, occurs with increasing cone angle of the ligands (L) for *cis*-$Mo(CO)_4L_2$ complexes.[21] Furthermore, these effects correlated well with kinetic parameters for phosphine dissociation in these derivatives.[20,22]

On the other hand there is a slight stabilizing effect of about 1–2 kcal/mol of having two TPPTS ligands bound to the metal center in close proximity to one another.[23] This is illustrated by the kinetic parameters for reaction 6 in the absence of a sodium ion sequestering reagent, where k_1 decreases by a factor of 10 in going from $[Na\text{-kryptofix-}221]_6$[*cis*-$Mo(CO)_4[P(m\text{-}C_6H_4SO_3)_3]_2$] to $[Na]_6$[*cis*-$Mo(CO)_4[P(m\text{-}C_6H_4SO_3)_3]_2$]. The aforementioned stabilization is likely due to an intramolecular interligand interaction, possibly bridging through Na^+ as represented schematically in Figure 5. The intervention of hydrogen bonding via solvent molecules as well may be occurring. An analogous intermolecular interligand interaction has been noted in the solid-state structure of $Fe(CO)_4TPPTS$[12] and $Pd[PPh_2(m\text{-}C_6H_4\text{-}SO_3Na)]_3$.[7] In an attempt to determine whether added water has an influence on the rate of TPPTS dissociation from *cis*-$Mo(CO)_4[TPPTS]_2$, reaction 6 was examined in a 3:1 mixture of 2-methoxyethanol and water. This solvent mixture could in principle afford a medium in which the sodium cations are hydrated and thus removed from interaction at the sulfonate sites. However, only a slight increase in the rate constant was observed upon water addition (Table III). Hence, the reactivity data suggest that the sodium ions selectively interact with the sulfonate substituents as opposed to being completely solvated by water.

The intermediate afforded upon TPPTS dissociation from *cis*-$Mo(CO)_4[TPPTS]_2$, species **3**, was shown to react selectively with CO as opposed to TPPTS. That is, k_{-1}/k_2, the ratio of bimolecular rate constants for **3** reacting with TPPTS vs CO, was determined to be 0.072. The discriminating ability of **3** for CO vs TPPTS can be attributed to electrostatic repulsion between **3** and an incoming TPPTS ligand, as well as enhanced solvation of the free TPPTS ligand vs the metal bound ligand. This observation is to be contrasted with the reactivity of the PPh_3 analog of **3**, species **4**. Intermediate **4** in the less-interacting hexane solvent exhibits a preference for the better nucleophile PPh_3 as compared with CO, where the k_{-1}/k_2 value has been determined to be 4.8.[24,25]



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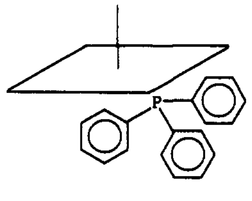

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Upon changing of the metal center in the bis(phosphine) derivatives to tungsten an alternate reaction took place. That is, in the case of *cis*-$W(CO)_4L_2$ an intramolecular nondissociative rearrangement to the trans isomer is the lower energy process. Although rearrangements of this type have been observed, nondissociative isomerization reactions involving *very* sterically demanding ligands are uncommon.[26] With enthalpy of activation values of 20.2 ± 3.6 and 18.3 ± 1.2 kcal mol^{-1} for *cis*-$W(CO)_4(TPPTS)_2$ and *cis*-$W(CO)_4(PPh_3)_2$, respectively, the rearrangement pathway is significantly lower in energy than what is anticipated for breaking the W–P bond in these derivatives. Very large negative entropies of activation (−16.7 ± 10.9 and −21.5 ± 3.6 eu for *cis*-$W(CO)_4(TPPTS)_2$ and *cis*-$W(CO)_4(PPh_3)_2$, respectively) indicate much ordering in the transition state, to be expected for sterically demanding ligands. Free energy of activation values were calculated at 25.2 and 24.7 kcal mol^{-1} for isomerization of *cis*-$W(CO)_4[TPPTS]_2$ and *cis*-$W(CO)_4(PPh_3)_2$, which are in good agreement with $\Delta G^{\ddagger}$ (26.2 kcal mol^{-1}) observed for the intramolecular isomerization of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in heptane.[27]

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(19) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

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(21) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661.

(22) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 1651.

(23) This observation supports the findings of Horvath and coworkers for phosphine dissociation in $HRh(CO)(TPPTS)_3$;[6] however, the stabilizing effect noted herein is much smaller. Certainly part of the enhanced intramolecular interligand interactions reported to occur in $HRh(CO)(TPPTS)_3$ can be attributed to the fact that each TPPTS ligand is capable of interacting with two adjacent TPPTS ligands.

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(25) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

(26) (a) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407. (b) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508 and references therein. (c) Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331. (d) Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307. (e) Fischer, H.; Motsch, A.; Markel, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726. (f) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.

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Concluding Remarks

The present study has illustrated the feasibility of obtaining quantitative infrared data at high temperatures and pressures in aqueous solvents by the in situ cylindrical internal reflectance technique. Kinetic parameters for TPPTS dissociation from $M(CO)_5TPPTS$ derivatives (M = Mo, W) are shown to be quite similar to those determined for the analogous processes involving the nonsulfonated PPh_3 ligand in the same solvent system. Furthermore, there were only small effects on the rates of reactions seen upon going from aqueous to organic solvents for these dissociative reactions. On the other hand, the larger steric requirements of the TPPTS ligand vs PPh_3 as derived from X-ray structural data become evident upon examining phosphine loss from $[Na\text{-kryptofix-}221]_6[\textit{cis}\text{-}Mo(CO)_4[P(C_6H_4SO_3)_3]_2]$, where $P(C_6H_4SO_3)_3{}^{3-}$ dissociation is enhanced over its PPh_3 counterpart. Alternatively, in the absence of encapsulating reagents for Na^+ a slight stabilizing effect was noted for the two cis TPPTS ligands in *cis*-$Mo(CO)_4[TPPTS]_2$. Additionally, we have demonstrated a greater than 10:1 selectivity for the pentacoordinate fragment, $[Mo(CO)_4TPPTS]$, for carbon monoxide vs TPPTS in 2-methoxyethanol. The effect of this preference for CO vs TPPTS is likely to be somewhat diminished in pure water where CO solubility is greatly reduced relative to its solubility in organic solvent. Finally, we have observed an intramolecular rearrangement of *cis*-$W(CO)_4L_2$ to *trans*-$W(CO)_4L_2$ for the sterically encumbering TPPTS and PPh_3 ligands.

Current efforts are directed toward understanding the origin of the added stability noted for some substrate molecules bonded adjacent to the TPPTS ligands. In this regard we have observed a stabilizing effect for the carboxylate and alkoxide ligands in complexes of the type *cis*-$W(CO)_4[TPPTS]O_2CR^-$. We are also exploring the selectivity of the $[M(CO)_4TPPTS]$ intermediates toward a variety of incoming nucleophiles of more relevance to catalysis, such as olefins, H_2, etc.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE88-17873) is greatly appreciated. We are most thankful for a gift of the ligand TPPTS from Dr. I. Horvath of Exxon Corporate Research.

Supplementary Material Available: Tables of data, along with an error analysis, from the individual kinetic runs for the reactions of $W(CO)_5$-TPPTS, $W(CO)_5PPh_3$, and $Mo(CO)_5TPPTS$ with carbon monoxide in a 1:1 THF/H_2O mixture and figures showing plots of the data (24 pages). Ordering information is given on any current masthead page.