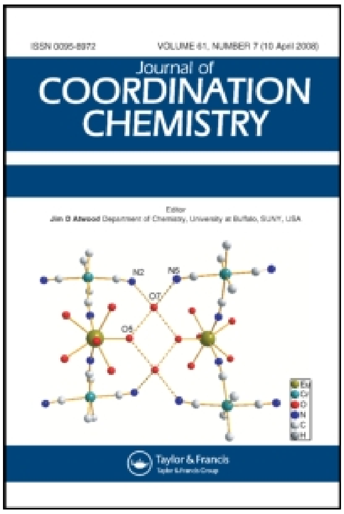

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REACTIONS OF CARBON MONOXIDE WITH *trans*-Ir(CO)(Cl)(TPPMS)$_2$ (TPPMS = PPh$_2$(C$_6$H$_4$SO$_3$K)) IN DMSO AND WATER, RATE AND MECHANISTIC STUDIES

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Reaction of CO with *trans*-Ir(CO)(Cl)L$_2$ (L = PPh$_3$ in toluene and DMSO; L = TPPMS in DMSO and H$_2$O, TPPMS = PPh$_2$(*m*-C$_6$H$_4$SO$_3$Na)) reversibly produces Ir(CO)$_2$(Cl)L$_2$ or [Ir(CO)$_3$L$_2$]Cl depending on the solvent polarity. The solvent polarity has a small effect on the rate of reaction with CO; the rate constants in toluene, DMSO and H$_2$O are all within a factor of two. Comparison to the reaction with H$_2$ shows that the selectivity for CO is much greater ($k_{CO}/k_{H_2} = 150$) in toluene than in water ($k_{CO}/k_{H_2} = 5$).

Keywords: Water soluble; carbon monoxide; phosphine ligands; TPPMS; iridium; carbonylation

INTRODUCTION

Reactions of carbon monoxide are fundamental to important homogeneously catalyzed reactions such as hydroformylation and alcohol homologation.[1–3] The basic reaction of CO in each catalyzed reaction is addition to a 16e$^-$ intermediate. In this manuscript we explore reactions of CO with *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in DMSO and H$_2$O to evaluate the solvent effect for carbonylation.

The commercial process for hydroformylation in water[4] increases the need to understand the role of water on organometallic reactions. We previously

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reported using *trans*-Ir(CO)(Cl)L_2 (L = TPPMS or P(*m*-$C_6H_4SO_3Na)_3$) reacting with H_2 to define the role of solvent in hydrogenation.[5] Hydrogen reacts a factor of 45 faster in H_2O than in toluene with the Ir(I) complexes. In hydroformylation CO and H_2 compete for intermediates and a factor of 45 rate enhancement could affect the catalytic process. Thus this manuscript examines the effect of water on carbonylation.

EXPERIMENTAL

trans-Ir(CO)(Cl)$(TPPMS)_2$ was prepared as previously described.[6] Water was triply-distilled and deionized. DMSO-d^6 and D_2O were purchased from Cambridge Isotope Labs. DMSO was dried over CaH_2 and distilled under reduced pressure. Carbon monoxide solubility in toluene,[7] DMSO[8] and H_2O[7,9] have been previously evaluated.

Infrared spectra were obtained on a Mattson Polaris FTIR in 0.5 mm NaCl (toluene) or a Perkin Elmer Paragon 1000 FTIR with 0.1 mm CaF_2 (DMSO or H_2O) cells. ^1H and ^{31}P NMR spectra were obtained on Varian VXR-400 or -500 MHz spectrometers.

The CO uptake by *trans*-Ir(CO)(Cl)L_2 was examined by UV-visible stopped flow techniques at the following wavelengths: 440 nm for L = PPh_3 in toluene; 438 nm for L = PPh_3 and L = TPPMS in DMSO; and 427 nm for L = TPPMS in H_2O. In toluene, solutions of Ir(CO)(Cl)L_2 were 3×10^{-4} M, while in DMSO and H_2O 4×10^{-5} M solutions were used. At least five half-lives were followed (see Figure 1) under *pseudo* first order conditions. The k_{obs} values were then plotted *vs.* [CO] to give plots shown in Figure 2. The rate constants are shown in Table I. Error limits in the rate constants are reported as 95% confidence limits.

RESULTS AND DISCUSSION

Carbon monoxide reacts with square-planar iridium complexes to give two products depending on the solvent.

$$trans\text{-Ir(CO)(Cl)(PPh}_3)_2 + \text{CO} \overset{\text{toluene}}{\rightleftharpoons} \text{Ir(CO)}_2\text{(Cl)(PPh}_3)_2 \qquad (1)$$

$$trans\text{-Ir(CO)(Cl)(TPPMS)}_2 + 2\text{CO} \overset{\text{H}_2\text{O}}{\rightleftharpoons} [\text{Ir(CO)}_3\text{(TPPMS)}_2^+]\text{Cl}^- \qquad (2)$$

In DMSO *trans*-Ir(CO)(Cl)L_2, L = PPh_3 or TPPMS, gives both products with the ionic favored for L = TPPMS. In all cases the addition was

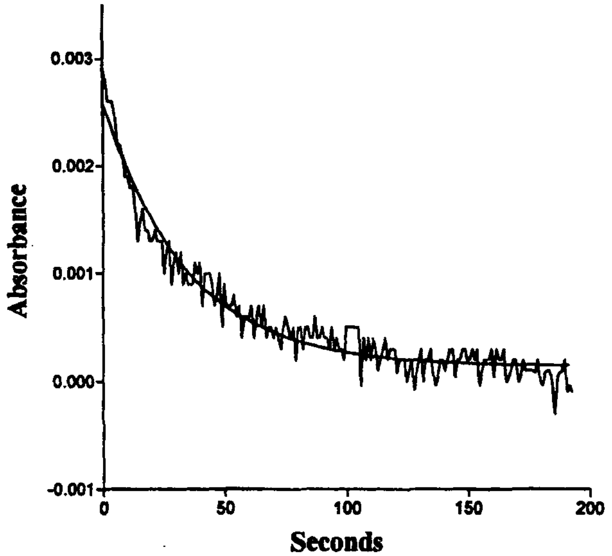

FIGURE 1 A plot of absorbance *vs.* time for loss of 1.84×10^{-5} M *trans*-Ir(CO)(Cl)$(TPPMS)_2$ with 4.0×10^{-4} M CO (pressure of 566 mm CO) at 20°C in H_2O.

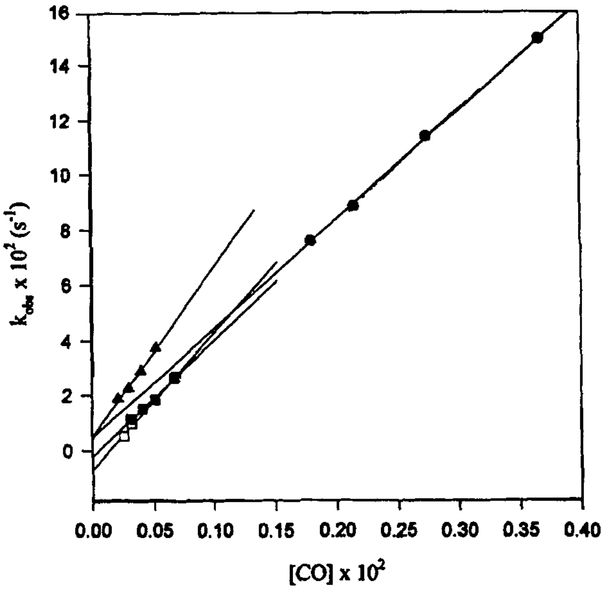

FIGURE 2 Plots of k_{obs} *vs.* [CO] for reaction of *trans*-Ir(CO)(Cl)L_2 in various solvents at 20°C (●, L = PPh_3 in toluene; ■, L = PPh_3 in DMSO; □, L = TPPMS in DMSO; ▲, L = TPPMS in H_2O).

TABLE I Rate constants for reactions of iridium complexes with CO in various solvents at 20°C

Complex	$[M] \times 10^5$	$k\ (M^{-1}s^{-1})$	*Solvent*
trans-Ir(Cl)(CO)$(PPh_3)_2$	15	40 ± 3	Toluene
trans-Ir(Cl)(CO)$(PPh_3)_2$	1.9	42 ± 6	DMSO
trans-Ir(Cl)(CO)$(TPPMS)_2$	2.3	50 ± 5	DMSO
trans-Ir(Cl)(CO)$(TPPMS)_2$	1.8	62 ± 4	Water
$[Ir(CO)_2(H_2O)(TPPMS)_2]^+Cl^-$*	1.5	4.0 ± 0.6	Water

Reported at the 95% confidence level.
* The rate is measured for $[Ir(CO)_3(TPPMS)_2]Cl$ formation; this is the presumed intermediate.

reversible; removal of CO resulted in reformation of *trans*-Ir(CO)(Cl)L_2. In water a slower reaction involving nucleophilic attack by H_2O on a carbonyl results in water gas shift type reactions.

The kinetics for reactions (1) and (2) show a dependence on both reactants,

$$\text{rate} = k[\textit{trans}\text{-Ir(CO)(Cl)}L_2][\text{CO}]$$

with the second order rate constants shown in Table I. Our value for k in toluene with $L = PPh_3$, $k = 40 \pm 3\ s^{-1}M^{-1}$ is in excellent agreement with the value reported by Vaska,[10] $k = 43\ s^{-1}M^{-1}$. Carbonylation in DMSO gave rate constants quite similar for $L = PPh_3$ and TPPMS and very similar to the reaction for $L = PPh_3$ in toluene. In DMSO, $Ir(CO)_2(Cl)L_2$ formed initially with the cation forming more slowly. In H_2O for L = TPPMS the rate constant was somewhat larger ($k = 62 \pm 4\ s^{-1}M^{-1}$) with no evidence for $Ir(CO)_2(Cl)(TPPMS)_2$, but a different intermediate formed enroute to $[Ir(CO)_3(TPPMS)_2^+]Cl^-$. The characterization data for the intermediate are not conclusive ($\nu_{CO} = 2004\ cm^{-1}$; ^{31}P, $\delta = -0.9$(s) ppm), but would be consistent with $Ir(CO)_2(H_2O)(TPPMS)_2^+$. This intermediate further reacts with CO to give $Ir(CO)_3(TPPMS)_2^+$ with a rate constant of $4.0 \pm 0.6\ s^{-1}M^{-1}$ as measured from the rate of formation of $Ir(CO)_3(TPPMS)_2^+$.

The rate of reaction of CO with *trans*-Ir(CO)(Cl)L_2 is very little affected by solvent with toluene, DMSO and water within a factor of 2. This indicates very little change in polarity from the ground state to the transition state with the transition state involving interaction of CO with the 16-electron, square-planar complex. The minor solvent effect is in marked contrast to the reactions of H_2 where the change from toluene to water was a factor of 45.[5] Such a marked change in rates of reactions of H_2 and CO in different solvents could have important ramifications for catalytic reactions involving both gases (hydroformylation, water-gas shift reactions and synthesis gas reactions) if these reactions with iridium(I) are general to other organometallic centers. In toluene the ratio of rate constants, $k_{CO}/k_{H_2} = 150$, while in water the ratio is 5, a dramatic change in selectivity with change in solvent.

Acknowledgments

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