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Carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ and Reactivity of [Ir(CO)$_2$(TPPTS)$_3$]Cl (TPPTS = P(*m*-$C_6H_4SO_3Na$)$_3$) in DMSO and Water

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Reaction of CO with *trans*-Ir(CO)(Cl)(TPPTS)$_2$ in DMSO and H_2O give [Ir(CO)$_3$(TPPTS)$_2$]Cl (H_2O and DMSO) and Ir(CO)$_2$(Cl)(TPPTS)$_2$ (DMSO only). In both solvents the carbonylation is reversed by passing N_2 through the solution. In water, further reactions occur slowly, including water-gas-shift reactions and formation of Ir(CO)$_2$(TPPTS)$_3^+$. This trisphosphine complex was independently prepared to examine its reactions. In DMSO, reaction with CO readily forms Ir(CO)$_3$(TPPTS)$_2^+$; no reaction with CO is observed in water. Reaction of Ir(CO)$_2$(TPPTS)$_3^+$ with H_2 occurs through TPPTS dissociation giving Ir(CO)$_2$(H)$_2$(TPPTS)$_2^+$ initially before reaction with free TPPTS gives Ir(CO)(H)$_2$(TPPTS)$_3^+$ as the final product. Hydrogen bonding from water to the sulfonated phosphine ligands provides a reasonable explanation for the differing ligand substitution behavior in DMSO and H_2O.

Introduction

Activation of carbon monoxide is an integral step in industrially important reactions such as hydroformylation and Monsanto's acetic acid process.[1] These reactions are catalyzed by transition metal complexes; their utility has made the activation of carbon monoxide the focus of study.[2] The water-gas-shift reaction, important for its potential commercial value, also involves the activation of carbon monoxide. Unfortunately, there are relatively few examples of transition metal catalysis of this reaction by homogeneous systems.[3] Presently, high-temperature heterogeneous systems are used to catalyze the conversion of CO and water to CO_2 and H_2.[4]

The use of water as a solvent is a relatively new aspect of organometallic chemistry. Water as a solvent for reactions catalyzed by transition metal complexes has been particularly useful. Systems which catalyze selective hydrogenation, carbon−carbon bond formation, and carbonylation have appeared in the literature.[5] However, water is not an innocuous medium in which to run organometallic reactions. In fact, water has been shown to be an active participant in several reactions.[6]

One of the most attractive aspects of water-based catalytic systems is the facile separation of the product(s) from the catalyst associated with these systems. The Rhone−Poulenc hydroformylation process uses a water-based rhodium phosphine system to catalyze the hydroformylation of propene.[7] The efficiency of this system lies in the manual separation of the product phase from the catalyst phase and recycling of reactants. The development of this process sparked interest in water-soluble organometallic chemistry. Water-soluble organometallic chemistry has been the subject of recent reviews.[8]

The reactivity of Vaska's complex, *trans*-Ir(CO)Cl(PPh$_3$)$_2$, has been thoroughly studied.[9] This organometallic complex has been used to model the activation of a variety of substrates by late transition metal centers. It is within this well-developed framework that we hoped to probe the effect of water on the reactivity of organometallic complexes. We have synthesized water-soluble analogues of Vaska's complex using the water-soluble tertiary phosphines TPPMS (PPh$_2$(*m*-C_6H_4-SO_3K)) and TPPTS (P(*m*-$C_6H_4SO_3Na$)$_3$). The characterization data, as well as their reactivity in dimethyl sulfoxide, have shown these complexes to be very similar to their PPh$_3$ analogues in organic solvents,[10] although water has interesting effects on the oxidative addition of hydrogen to *trans*-Ir(CO)Cl(TPPMS)$_2$ and *trans*-Ir(CO)Cl(TPPTS)$_2$.[11]

On the basis of interest in the activation of carbon monoxide and interest in water-soluble organometallic complexes, we have extended our investigation of the effect of water on the reactivity of organometallic complexes to carbonylation reactions. A water-soluble

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Table 1. Comparison of Infrared Data for Iridium Complexes with TPPTS and PPh_3

complex	ν (CO) (cm^{-1})	ν (IrH) (cm^{-1})
$[Ir(CO)_3(TPPTS)_2]Cl$	2004(s), 2016(sh), 2075(w)[c]	
	2018(s), 2029(sh), 2082(w)[a]	
$[Ir(CO)_3(PPh_3)_2]ClO_4$	1977(s), 2020(s), 2070(w)[b]	
cis,trans-$[Ir(CO)_2(H)_2(TPPTS)_2]Cl$	2052(s), 2086(s)[b]	2147(s), 2166(sh)[b]
	2060(s), 2092(s)[a]	2152(s), 2171(sh)[a]
cis,trans-$[Ir(CO)_2(H)_2(PPh_3)_2]BPh_4$	2045(s), 2085(s)[d]	2150, 2177[d]
	2041(s), 2083(s)[e]	2136, 2154(sh)[e]
$[Ir(CO)_2(TPPTS)_3]Cl$	2018(s), 1980(m)[a]	
$[Ir(CO)_2(PPh_3)_3]ClO_4$[22]	2030, 1975(sh)	

[a] H_2O. [b] KBr. [c] DMSO. [d] $CHCl_3$. [e] Nujol.

analogue of Vaska's complex was chosen to model the activation of carbon monoxide by organometallic complexes in water. In this contribution, we describe the reactions of *trans*-$Ir(CO)Cl(TPPTS)_2$ with carbon monoxide in dimethyl sulfoxide and in water.

Experimental Section

Chemicals, solvents, and spectroscopic measurements were obtained as previously described.[11b] All gases were added at 1 atm.

Reaction of *trans*-$Ir(CO)Cl(TPPTS)_2$ with CO in DMSO. In the glovebox, 0.046 g of *trans*-$Ir(CO)Cl(TPPTS)_2$ was loaded into a 100 mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed and removed from the glovebox. In the fume hood, 5 mL of CO(g)-saturated DMSO was added to the flask under CO(g) purge. The flask was sealed under a CO(g) atmosphere, and the solution was allowed to stir at room temperature. After 10 min, an aliquot of the solution was transferred to an IR cell under CO(g) purge and an IR spectrum recorded. Absorbances corresponding to $[Ir(CO)_3(TPPTS)_2]^+$ and $Ir(CO)_2Cl(TPPTS)_2$ were observed. After 3 days, the IR spectrum of the reaction solution was unchanged. A ^{31}P NMR spectrum was recorded, and resonances corresponding to $Ir(CO)_2Cl(TPPTS)_2$ and $[Ir(CO)_3(TPPTS)_2]^+$ were observed along with a very small amount of free TPPTS.

Reaction of *trans*-$Ir(CO)Cl(TPPTS)_2$ with CO in D_2O. In the glovebox, 0.030 g of *trans*-$Ir(CO)Cl(TPPTS)_2$ was dissolved in 1 mL of D_2O in a NMR tube fitted with an adaptor for use on the high-vacuum line. On the high-vacuum line, the solution was degassed (three freeze−pump−thaw cycles) and 0.74 atm of CO(g) was introduced into the tube with the solution frozen and the tube flame sealed. The tube was allowed to thaw, and the reaction was followed by ^{31}P spectroscopy. After 1 h the resonance corresponding to the starting material comprised 20% of the integrated ^{31}P NMR resonances and was broadened. The major resonances observed in the ^{31}P NMR spectrum were assigned as *trans*-$Ir(CO)Cl(TPPTS)_2$, $[Ir(CO)_3(TPPTS)_2]^+$, and $[Ir(CO)_2(TPPTS)_3]^+$.

After 14 days there was no evidence of starting material in the ^{31}P NMR spectrum. The resonances which comprised the spectrum at this point corresponded to *cis,trans*-$[Ir(CO)_2(D)_2(TPPTS)_2]^+$, $[Ir(CO)_3(TPPTS)_2]^+$, and $[Ir(CO)_2(TPPTS)_3]^+$. These resonances integrated 1:2:1, respectively. A small amount of *cis,mer*-$[Ir(CO)(D)_2(TPPTS)_3]^+$ was observed.

Reaction of *trans*-$Ir(CO)Cl(TPPTS)_2$ with CO in H_2O. In the glovebox, 0.060 g of *trans*-$Ir(CO)Cl(TPPTS)_2$ was loaded into a 100 mL Schlenk flask equipped with a magnetic stir bar. In the fume hood, 5 mL of CO(g)-saturated H_2O was added to the flask under CO(g) purge. The flask was sealed under an atmosphere of CO(g), and the reaction was allowed to stir at room temperature. After 30 min, ^{31}P and ^1H NMR spectra showed resonances corresponding to *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$, $[Ir(CO)_3(TPPTS)_2]^+$ (major), and $[Ir(CO)_2(TPPTS)_3]^+$.

After 30 min under a CO(g) atmosphere, 1 mL of the solution was transferred to a 50 mL Schlenk flask that had been flushed with N_2(g) for 15 min. The flask was purged with N_2(g) for 90 min, during which the colorless solution turned yellow. In the infrared spectrum, the absorbances assigned as $[Ir(CO)_3(TPPTS)_2]^+$ disappeared. Only an absorbance assigned as *trans*-$Ir(CO)Cl(TPPTS)_2$ was observed.

After 3 days of carbonylation, a NMR sample was prepared from the reaction solution and ^{31}P and ^1H NMR spectra recorded. The ^{31}P NMR spectrum was comprised of resonances corresponding to *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$ and $[Ir(CO)_3(TPPTS)_2]^+$ which integrated 1.0:1.7, respectively. The ^{31}P NMR spectrum with the hydrides remaining coupled was recorded. The only change observed was that the resonance assigned as *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$ was observed as a triplet ($J_{PH} = 15$ Hz). The hydride region of the ^1H NMR spectrum contained a single resonance assigned as *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$. An aliquot of the solution was transferred to an IR cell under CO(g) purge, and an IR spectrum was recorded. Absorbances corresponding to *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$ and $[Ir(CO)_3(TPPTS)_2]^+$ were observed.

After 2 weeks, the solvent was removed from a portion of the sample. IR and NMR spectra showed *trans*-$Ir(CO)Cl(TPPTS)_2$, *cis,trans*-$[Ir(CO)Cl(H)_2(TPPTS)_2$ (only in DMSO-d_6), *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$ (only in D_2O), $Ir(CO)_2(H)(TPPTS)_2$, TPPTS (minor), and $OP(m\text{-}C_6H_4SO_3Na)_3$ (minor).

After 24 days of carbonylation, ^{31}P and ^1H NMR spectra indicated no further reaction and 1 drop of 5% KOH(aq) was added to this NMR sample. ^{31}P and ^1H NMR spectra were recorded. The ^{31}P and ^1H NMR spectra were comprised of resonances assigned as TPPTS oxide (minor), $Ir(CO)H(TPPTS)_3$, and $Ir(CO)_2H(TPPTS)_2$. The resonances assigned to $Ir(CO)_2H(TPPTS)_2$ and $Ir(CO)H(TPPTS)_3$ integrated 5.8:1.0, respectively.

***trans*-$Ir(CO)Cl(TPPTS)_2$ + CO + TPPTS + H_2 in H_2O.** In the glovebox, 0.030 g of *trans*-$Ir(CO)Cl(TPPTS)_2$ (0.020 mmol) was loaded into a 100 mL Schlenk flask equipped with a magnetic stir bar. In the fume hood, 5 mL of CO(g)-saturated H_2O was added to the flask under CO(g) purge. The flask was sealed under an atmosphere of CO(g), and the reaction was allowed to stir at room temperature for 15 min, during which the rich yellow solution turned colorless. Under CO(g) purge, 0.020 g of TPPTS (0.032 mmol) was added to the flask. The solution turned pale yellow, and CO(g) evolution was observed. After 20 min, a NMR sample showed $[Ir(CO)_2(TPPTS)_3]^+$. An aliquot of the solution was transferred to an IR cell under CO(g) purge, and an IR spectrum was recorded, showing $[Ir(CO)_2(TPPTS)_3]^+$.

After 24 h, the NMR tube was uncapped and placed into a 500 mL Schlenk flask, which was then flushed with H_2(g) for 15 min. The NMR tube was removed from the flask and capped, and ^{31}P and ^1H NMR spectra were recorded. The following products were assigned based on resonances observed in the ^{31}P NMR spectrum: *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$, $[Ir(CO)_2(TPPTS)_3]^+$, and TPPTS. The major product determined by integration of the ^{31}P NMR spectrum was *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$. There were very minor resonances assigned as *cis,mer*-$[Ir(CO)(H)_2(TPPTS)_3]^+$. The major resonance in the hydride region of the ^1H NMR spectrum was

Table 2. Comparison of ^{1}H NMR Data (Hydride Resonances) for Iridium–Hydride Complexes

iridium–hydride complex	δ (ppm)	J_{PH} (Hz)
cis,trans-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl	−10.0(t)[a]	15
cis,trans-[Ir(CO)$_2$(H)$_2$(PPh$_3$)$_2$]BPh$_4$	−9.8(t)[b]	15
cis,mer-[Ir(CO)(H)$_2$(TPPTS)$_3$]Cl	−9.5(q)[a]	18.3
	−11.3(dt)[a]	*trans*-115, *cis*-18.3
cis,mer-[Ir(CO)(H)$_2$(PMePh$_2$)$_3$]BPh$_4$[13]	−9.0(q)[b]	16.7
	−11.6(dt)[b]	*trans*-119, *cis*-17.7

[a] D$_2$O. [b] CDCl$_3$.

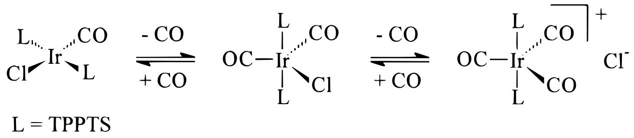

Figure 1. Carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ in DMSO.

assigned as *cis,trans*-[Ir(CO)$_2$(*H*)$_2$(TPPTS)$_2$]$^+$. Again, there were minor resonances assigned as *cis,mer*-[Ir(CO)(*H*)$_2$(TPPTS)$_3$]$^+$.

The flask containing the reaction solution was purged with H$_2$(g) for 20 min. An aliquot of the solution was transferred to an IR cell under CO(g) purge, and an IR spectrum was recorded. This IR spectrum was assigned as *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]$^+$. The flask was sealed under an atmosphere of H$_2$(g) and allowed to stir at room temperature.

After 4 days, the major resonances in the ^{31}P and ^{1}H NMR spectra were assigned as *cis,mer*-[Ir(CO)(H)$_2$(TPPTS)$_3$]$^+$. An IR spectrum of the solution also showed *cis,mer*-[Ir(CO)(H)$_2$(TPPTS)$_3$]$^+$ based on comparison with spectral data available for *cis,mer*-[Ir(CO)(H)$_2$(PMePh$_2$)$_3$]$^+$ (see Tables 1 and 2).

Results and Discussion

Reaction of *trans*-Ir(CO)Cl(TPPTS)$_2$ with carbon monoxide (1 atm) in dimethyl sulfoxide leads to an equilibrium mixture of the dicarbonyl complex, Ir(CO)$_2$Cl(TPPTS)$_2$, and cationic tricarbonyl complex, [Ir(CO)$_3$(TPPTS)$_2$]Cl (see Figure 1). The same reaction was observed for the TPPMS analogue.[12] Reversible formation of a cationic tricarbonyl complex, [Ir(CO)$_3$(L)$_2$]Cl (L = PMePh$_2$), was observed when *trans*-Ir(CO)Cl(L)$_2$ was carbonylated in acetone.[13] However, in nonpolar solvents, only the dicarbonyl complex, Ir(CO)$_2$Cl(L)$_2$, is observed when L is triphenylphosphine.[14] The cationic tricarbonyl complex, [Ir(CO)$_3$(TPPTS)$_2$]Cl, was not independently synthesized but was identified by comparison of its infrared spectrum with that observed for the triphenylphosphine analogue (see Table 1).[15] The chemical shift of the singlet observed for this complex in the ^{31}P NMR spectrum is also consistent with this assignment.

In water, carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ leads, initially, to quantitative formation of [Ir(CO)$_3$(TPPTS)$_2$]Cl. This reaction was completely reversible when the CO atmosphere was purged with nitrogen (see Figure 2). The intermediate, neutral, dicarbonyl complex, Ir(CO)$_2$Cl(TPPTS)$_2$, was not observed. Unlike the reaction in DMSO, the cationic tricarbonyl complex slowly undergoes further reaction with water to generate a cationic dihydride complex, *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl. This complex was not independently synthesized but was characterized by spectroscopic data which agreed with the analogous triphenylphosphine complex (see Table 1).[13]

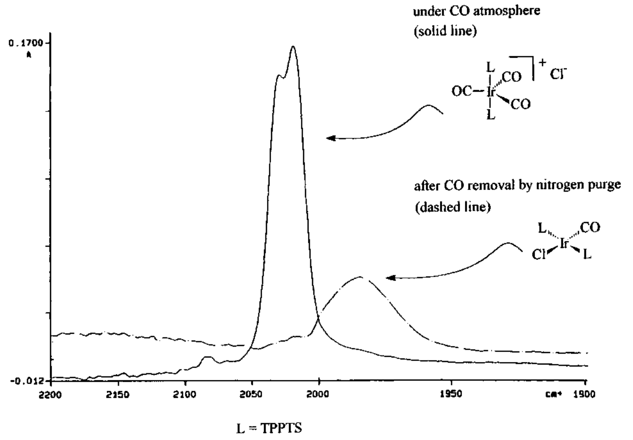

Figure 2. Reversible carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ in water.

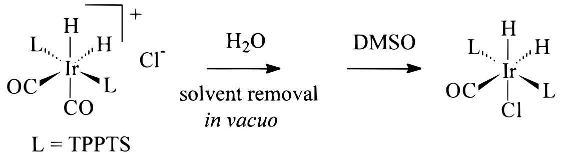

Figure 3. Chloride displacement of CO on dissolution of [Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]$^+$ in DMSO.

The shift of the equilibrium (see Figure 1) in water favoring formation of [Ir(CO)$_3$(TPPTS)$_2$]Cl is expected from hydration of the ions. While no data are available on the enthalpies of hydration of [Ir(CO)$_3$(TPPTS)$_2$]$^+$, the enthalpy of hydration of a chloride ion is −77 kcal/mol,[16] which is sufficiently large to facilitate Cl$^-$ dissociation.[17]

cis,trans-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl behaved differently when dissolved in water and DMSO. In DMSO, *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl underwent CO dissociation with the chloride counterion substituting in the vacant coordination site (see Figure 3). However, in water, *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl was stable. The stability of *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl in water but not in DMSO may indicate more rapid CO dissociation in DMSO or may result from hydration of the ions.

The products resulting from carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ could be explained by nucleophilic attack of hydroxide or a water molecule on a carbonyl carbon of [Ir(CO)$_3$(TPPTS)$_2$]Cl leading to formation of the unobserved intermediate Ir(CO)$_2$(C(O)OH)(TPPTS)$_2$. This hydroxycarbonyl complex would decarboxylate leaving another unobserved intermediate, Ir(CO)$_2$H(TPPTS)$_2$, which could be protonated to generate the observed product, *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl. This reaction scheme is depicted in Figure 4. Nucleophilic attack on a carbonyl carbon and decarboxylation have literature precedent,[18] and we have shown that Ir-

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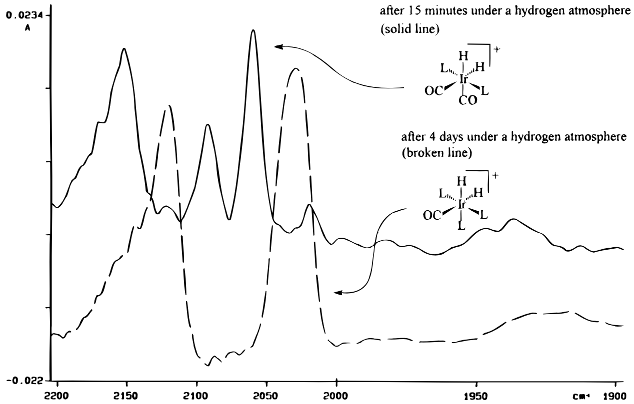

Figure 4. Hydroxide attack on $[Ir(CO)_3(TPPTS)_2]^+$.

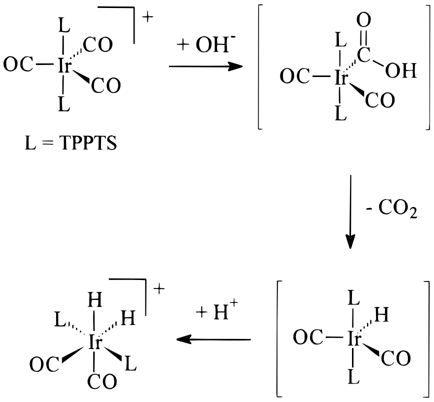

Figure 5. Hydrogenation of $[Ir(CO)_2(TPPTS)_3]^+$ in water.

$(CO)H(TPPTS)_3$ is readily protonated in water to yield *cis,mer*-$[Ir(CO)(H)_2(TPPTS)_3]^+X^-$ ($X = OH^-, CF_3COO^-$).[11b]

Reaction of the cationic tricarbonyl complex with water to generate a dihydride complex is similar to the water-gas-shift reaction. The reduction of protons has been proposed for production of hydrogen in water-gas-shift reactions catalyzed by a rhodium/acetic acid system.[3c] A mechanism based on reductive elimination of hydrogen from a dihydride complex was offered as an alternative for the aforementioned rhodium system and for a $Fe(CO)_5$/NaOH system.[3b,c] Kalck speculates that a rhodium dihydride complex is an intermediate in water-based, water-gas-shift reactions catalyzed by $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(TPPTS)_2$.[19] The characterization of *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]Cl$ as a product of the carbonylation of *trans*-$Ir(CO)Cl(TPPTS)_2$ in water supports such speculation and may give insight into the mechanism of this reaction when catalyzed by late transition metal complexes.

During the carbonylation reactions, $[Ir(CO)_2(TPPTS)_3]Cl$ was a product. To better understand its formation in the absence of excess TPPTS, it was prepared quantitatively by adding 1 equiv of TPPTS, under CO, to $[Ir(CO)_3(TPPTS)_2]Cl$, generated *in situ* from reaction of an aqueous solution of *trans*-$Ir(CO)Cl(TPPTS)_2$ with an atmosphere of CO for 15 min. The characterization of this complex was consistent with data available for the triphenylphosphine complex (see Table 1). Phosphine substitution by CO is not observed (see Figure 6); a water solution of $[Ir(CO)_2(TPPTS)_3]Cl$, generated *in situ*, is stable under an atmosphere of CO. The TPPMS analogue shows the same reactivity such that the attempted synthesis of $[Ir(CO)_3(TPPMS)_2]ClO_4$ results in the isolation of $[Ir(CO)_2(TPPMS)_3]ClO_4$ (although these salts did not show any tendency to explode, perchlorate salts should always be handled carefully). This trisphosphine product reacted with an atmosphere of carbon monoxide in DMSO to form the cationic tricarbonyl complex, $[Ir(CO)_3(TPPMS)_2]ClO_4$, and uncomplexed TPPMS. No phosphine substitution by CO is observed when $[Ir(CO)_2(TPPMS)_3]ClO_4$ is reacted with CO in water.[20]

Although $[Ir(CO)_2(TPPTS)_3]Cl$ does not react with CO in water, it can be hydrogenated in water yielding *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]Cl$ and free TPPTS. Subsequently, CO was displaced by TPPTS resulting in formation of *cis,mer*-$[Ir(CO)(H)_2(TPPTS)_3]Cl$ (see Figure 5). Initial oxidative addition to the saturated complex, $[Ir(CO)_2(TPPTS)_3]Cl$, evidently requires phosphine dissociation. Once hydrogen has oxidatively added, CO substitution by TPPTS generates the final product (see Figure 6).

Reaction with H_2 suggests that $[Ir(CO)_2(TPPTS)_3]Cl$ dissociates a phosphine to produce an unsaturated intermediate. Observation of $[Ir(CO)_2(H)_2(TPPTS)_2]^+$ as the inital product in the reaction of $[Ir(CO)_2(TPPTS)_3]Cl$ with H_2 (see Figure 6) supports this speculation. This 16-electron intermediate, $Ir(CO)_2(TPPTS)_2{}^+$, or the 18-electron aquo complex, while very reactive with hydrogen, shows no reactivity toward CO (see Figure 4). In DMSO, the TPPMS analogue shows no such selectivity;[20] reaction with CO is rapid. The methyldiphenylphosphine analogue reacts with H_2 to directly form *cis,mer*-$[Ir(CO)(H)_2(PMePh_2)_3]^+$.[13] This product may arise by CO dissociation from $[Ir(CO)_2(PMePh_2)_3]^+$ to form $[Ir(CO)(PMePh_2)_3]^+$, which oxidatively adds H_2 to generate the observed product. The intermediate suggested in Figure 6 may be trapped by oxidative addition of dihydrogen resulting in a stable dihydride, *cis,trans*-$[Ir(CO)_2(H)_2(TPPTS)_2]^+$.

The lack of reactivity between $[Ir(CO)_2(TPPTS)_3]^+$ and CO must be related to the relative stability of the products and reactants. Since the carbonylation of *trans*-$Ir(CO)Cl(TPPTS)_2$, forming $[Ir(CO)_3(TPPTS)_2]^+$, would be expected to proceed through the intermediate, $[Ir(CO)_2(TPPTS)_2]^+$, proposed in the hydrogenation of $[Ir(CO)_2(TPPTS)_3]^+$, no kinetic barrier preventing carbonylation of $[Ir(CO)_2(TPPTS)_3]^+$ would be expected. Thus, $[Ir(CO)_2(TPPTS)_3]^+$ must be more stable than $[Ir(CO)_3(TPPTS)_2]^+$. This is the opposite of the stability of the PPh_3 analogues where $[Ir(CO)_2(PPh)_3]^+$ is difficult to prepare. A possible source of stability for $[Ir(CO)_2(TPPTS)_3]^+$ would be hydrogen bonding between the sulfonate groups. The likely geometries of $[Ir(CO)_3(TPPTS)_2]^+$ and $[Ir(CO)_2(TPPTS)_3]^+$ are shown in Figure 7. For the cationic tricarbonyl complex, the TPPTS ligands are axial (as observed for the PPh_3 analogue) and hydrogen bonding between the TPPTS ligands cannot occur. However, for any of the possible geometries for $[Ir(CO)_2(TPPTS)_3]^+$, the TPPTS ligands would be oriented for hydrogen bonding between the sulfonate groups. The hydrogen bonding may provide the extra stability for $[Ir(CO)_2(TPPTS)_3]^+$. Hydrogen bonding was also suggested for the stability of $Rh(CO)(H)(TPPTS)_3$[21] and *fac*-$Ir(CO)(H)_3(TPPTS)_2$.[11b]

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Table 3. Characterization Data for Iridium−TPPTS Complexes

iridium complex	IR(νCO) (cm^{-1})	IR(νIr−H) (cm^{-1})	^{31}P NMR δ(ppm), J(Hz)	^{1}H NMR δ(ppm), J(Hz)
trans-Ir(CO)Cl(TPPTS)$_2$	1967(s)^{e} 1982(s)^{b}		25(s,br)^{c} 26.5(s)^{d}	
Ir(CO)$_2$Cl(TPPTS)$_2$	1929(s)^{a} 1968(m)^{a}		13(s, vbr)^{c}	
[Ir(CO)$_3$(TPPTS)$_2$]$^+$	2004(s)^{a} 2016(sh)^{a} 2018(s)^{b} 2029(sh)^{b}		0.7(s)^{c} 0.06(s)^{b,d}	
[Ir(CO)$_2$(TPPTS)$_3$]$^+$	1980(m)^{b} 2018(s)^{b}		−1.9(s)^{b,d}	
Ir(CO)$_2$H(TPPTS)$_2$	1929(s)^{e}		7.6(s)^{c} 8.1(br)^{b}	−11.2(t),^{b} $J_{PH} = 6.8$
Ir(CO)H(TPPTS)$_3$			19.2(s)^{b}	−10.8(q),^{b} $J_{PH} = 21.9$
cis,trans-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]$^+$	2052(s)^{e} 2086(s)^{e} 2060(s)^{b} 2092(s)^{b}	2147(s)^{e} 2166(sh)^{e} 2152(s)^{b} 2170(sh)^{b}	5.9(s)^{d} 6.1(s)^{b}	−10.0(t),^{b,d} $J_{PH} = 15.0$
cis,mer-[Ir(CO)(H)$_2$(TPPTS)$_3$]$^+$	2029(s)^{b}	2120(s)^{b} 2144(sh)^{b}	3.5(d),^{d} $J_{PP} = 13.8$ 1.2(br)^{d} 3.9(d),^{b} $J_{PP} = 13.6$ 1.5(t),^{b} $J_{PP} = 13.6$	−9.6(q),^{b} $J_{PP} = 17.6$ −11.4(dtd),^{b} $J_{PPtrans} = 116.2$ $J_{PPcis} = 18.8$ $J_{HH} = 3$
cis,trans-Ir(CO)Cl(H)$_2$(TPPTS)$_2$			12.2(s)^{c}	−7.5(td),^{c} $J_{PPcis} = 17.2$ $J_{HH} = 4$ −18.3(td),^{c} $J_{PPcis} = 13.6$ $J_{HH} = 4$
TPPTS			−4.3(s)^{c} −5.0(s)^{b}	
TPPTS−oxide			25.9(s)^{c} 35.4(s)^{b}	

^{a} DMSO. ^{b} H_2O. ^{c} DMSO-d_6. ^{d} D_2O. ^{e} KBr.

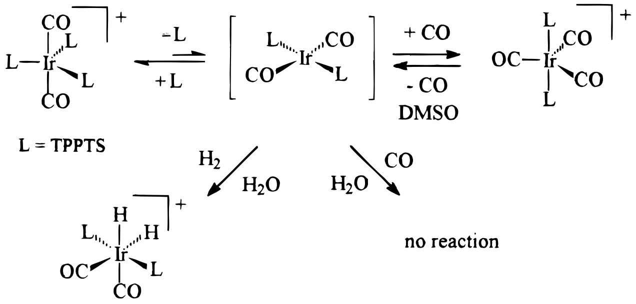

Figure 6. Observed reactivity of [Ir(CO)$_2$(TPPTS)$_3$]$^+$.

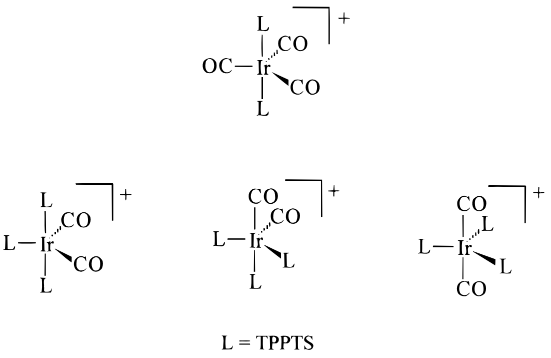

Figure 7. Geometries of TPPTS ligands of [Ir(CO)$_3$(TPPTS)$_2$]$^+$ and [Ir(CO)$_2$(TPPTS)$_3$]$^+$.

The observation of [Ir(CO)$_2$(TPPTS)$_3$]$^+$ as a product in the NMR-scale carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ in water supports the premise that phosphine addition to an intermediate with the formula [Ir(CO)$_2$(TPPTS)$_2$]$^+$ is favored over CO addition. In the NMR-scale reaction, the amount of CO in solution is limited by the capacity of the sealed NMR tube. Under these conditions, appreciable amounts of [Ir(CO)$_2$(TPPTS)$_3$]$^+$ are formed in the absence of free phosphine. The unsaturated intermediate must scavenge phosphine from solution. In reactions where the amount of CO is not limited, only trace amounts of [Ir(CO)$_2$(TPPTS)$_3$]$^+$ are observed.

Reactions of the water-soluble organoiridium complexes discussed in this manuscript indicate novel reactivity, linked to the medium in which they are carried out. The differing reactivity of *cis,trans*-[Ir(CO)$_2$(H)$_2$(TPPTS)$_2$]Cl in water and DMSO and selective reactivity of [Ir(CO)$_2$(TPPTS)$_3$]Cl in water provide examples where dissimilar reactivity is solvent related. Hydrogen bonding may provide the stability of ionic species generated in water and may be linked to the unusual selectivity observed in some reactions.

Conclusions

Carbonylation of *trans*-Ir(CO)Cl(TPPTS)$_2$ in water led to iridium−hydride products which show water plays an active role and could be used as a model for homogeneous catalysis of the water-gas-shift reaction by organotransition metal complexes.

In addition, when water is used as a solvent for organometallic reactions, the polarity, hydrogen bonding properties, protic nature, and different solubility properties all play a role in the observed reactivity. Further investigation is necessary to assess the impact these factors have on organometallic reactions in water.

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