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Synthesis of Cationic Iridium(I) Complexes of Water-Soluble Phosphine Ligands, $[Ir(CO)(TPPMS)_3]CF_3SO_3$, $[Ir(CO)(H_2O)(TPPTS)_2]CF_3SO_3$, and $[Ir(CO)_2(TPPMS)_3]ClO_4$ (TPPMS = $PPh_2(m\text{-}C_6H_4SO_3K)$, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$)

David P. Paterniti, Laura W. Francisco, and Jim D. Atwood*

Department of Chemistry, University at Buffalo, State University of New York,
Buffalo, New York 14260-3000

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Several new water-soluble iridium(I) complexes were synthesized and their reactivities with small molecules (H_2 or CO) in polar solvents (DMSO or H_2O) examined. Reaction of H_2 with $[Ir(CO)(TPPMS)_3]CF_3SO_3$ (TPPMS = $P(C_6H_5)_2(m\text{-}C_6H_4SO_3K)$) in DMSO or H_2O produces [*cis,mer*-$Ir(CO)(H)_2(TPPMS)_3]CF_3SO_3$, while the reaction of CO with $[Ir(CO)(TPPMS)_3]CF_3SO_3$ in water yields $[Ir(CO)_2(TPPMS)_3]CF_3SO_3$. Carbonylation of $[Ir(CO)_2(TPPMS)_3]ClO_4$ in DMSO produces $[Ir(CO)_3(TPPMS)_2]ClO_4$ and TPPMS; no reaction is observed in H_2O. Hydrogenation of $[Ir(CO)_2(TPPMS)_3]ClO_4$ in DMSO or H_2O yields [*cis,mer*-$Ir(CO)(H)_2(TPPMS)_3]ClO_4$, while reaction of H_2 with an aqueous solution of $[Ir(CO)(H_2O)(TPPTS)_2]CF_3SO_3$ produces $[Ir(CO)(H_2O)(H)_2(TPPTS)_2]CF_3SO_3$. Reaction of *trans*-$Ir(CO)ClL_2$ (L = TPPMS or TPPTS) with excess L in H_2O produces $[Ir(CO)L_3]Cl$, while no reaction occurs in DMSO. $[Ir(CO)_3(TPPMS)_2]Cl$ reacts irreversibly with TPPMS in H_2O to produce $[Ir(CO)_2(TPPMS)_3]Cl$.

Introduction

Organic media have been used for homogeneous catalysis because of their solvating abilities toward organometallic compounds. Concerns over hazardous waste generated during catalytic reactions and separation of product and catalyst led to the development of systems that employ water as solvent. In these catalytic systems, organometallic complexes are made water-soluble through the use of hydrophilic ligands.[1−3] The benefits gained from using water-based catalytic systems include easier product separations, decreased price, increased safety, and more efficient catalyst recycling.[4−6]

Hydrophilic ligands such as TPPMS and TPPTS are electronically similar to PPh_3, as indicated by their ^{31}P NMR resonances.[7−9] These similarities in electronic properties allow for easy routes to prepare water-soluble complexes by exchange of TPPMS or TPPTS for PPh_3.[10] The presence of the sulfonate group changes the solubility of a metal complex in water, allowing direct comparison of reactions in polar and nonpolar media.

The use of water-soluble organometallic complexes as catalysts for hydroformylation[5,6,11] and hydrogenation[12] of alkenes continues to increase. This, in part, has been attributed to the success of the Ruhrchemie/Rhône-Poulenc process,[13] where propylene is converted to butanal via hydroformylation using $Rh(CO)_2(H)(TPPTS)_2$. While mechanistic knowledge has been accumulated over the years from hydroformylations utilizing $Rh(CO)_2(H)(PPh_3)_2$, in organic solvents,[14] systematic investigations into the effects of water on key reaction steps (oxidative addition of H_2, carbonylation, and reductive elimination) are lacking.

In contrast to most organic solvents, water is not innocuous. Protonation, hydrogen exchange, and nucleophilic attack may be expected in aqueous solution.[15] Recent studies have shown water to be an active participant in several reactions (oxidative addition of H_2 to *trans*-$Ir(CO)X(L)_2$ (X = Cl,[16,17] OH,[18] or CH_3;[19] L = TPPMS[16,18] or TPPTS[17]); carbonylation of *trans*-Ir-

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(CO)X(L)$_2$ (X = Cl,[18,20,21] OH;[18] L = TPPMS,[18,20] TPPMS-Na,[19] or TPPTS[21])). In this article, we report the synthesis and characterization of several new cationic iridium(I) complexes ([Ir(CO)(TPPMS)$_3$]CF$_3$SO$_3$, [*trans*-Ir(CO)(H$_2$O)(TPPTS)$_2$]CF$_3$SO$_3$ and [Ir(CO)$_2$(TPPMS)$_3$]-ClO$_4$) and their reactions with H$_2$ or CO in DMSO and H$_2$O. Reactions of *trans*-Ir(CO)Cl(L)$_2$ (L = TPPMS or TPPTS) with excess L in DMSO or H$_2$O and reactions of CO with [Ir(CO)$_2$(TPPMS)$_3$]ClO$_4$ in DMSO and H$_2$O are also described.

Experimental Section

Materials. IrCl$_3$·3H$_2$O was purchased or borrowed from Johnson Matthey. Triphenylphosphine, *n*-octylamine, fuming sulfuric acid (20% and 30% SO$_3$ w/w), and CH$_3$Li were purchased from Aldrich Chemical. Deuterated solvents were purchased from Cambridge Isotope Labs, Aldrich Chemical Co., or MSD Labs and were used as received unless otherwise noted. H$_2$ and CO were obtained from Matheson. Solvents used outside the glovebox were used as received without further drying or purification unless otherwise noted. Water was triply distilled and deionized, while D$_2$O and DMSO-d_6 were degassed on a high-vacuum line (three freeze−pump−thaw cycles) in a pressure tube fitted with a Teflon stopcock. Solvents used within the glovebox were prepared as follows: THF and diethyl ether were refluxed in a N$_2$ atmosphere over Na/benzophenone until the solution turned blue or purple. Hexane was refluxed overnight in a N$_2$ atmosphere over finely divided CaH$_2$. DMSO was refluxed over finely divided CaH$_2$ until dry and then distilled at reduced pressure while maintaining a temperature of less than 90 °C. The compounds *trans*-Ir(CO)Cl(TPPMS)$_2$,[18] [Ir(CO)$_3$(PPh$_3$)$_2$]ClO$_4$,[22] and TPPMS[18] were prepared as previously described.

Instrumental Measurements. Infrared spectra were obtained using a Mattson Polaris Fourier transform spectrometer or a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Solution spectra were recorded using 0.5 mm NaCl or 0.1 mm CaF$_2$ (DMSO or H$_2$O) cells while solid-state spectra were recorded as KBr disks. All spectra are reported in wavenumbers (cm^{-1}).

^{1}H and ^{31}P NMR spectra were recorded on Varian VXR-400 or 500 MHz spectrometers. ^{1}H NMR spectra were referenced to residual solvent resonances in the deuterated solvent, and all NMR spectra contained resonances corresponding to aromatic protons, but these resonances were not assigned unless otherwise noted. ^{31}P NMR spectra were referenced to an external sample of 85% H$_3$PO$_4$ in D$_2$O (reference was set to 0.0 ppm) and were proton decoupled. For ^{1}H and ^{31}P NMR spectra that were recorded in H$_2$O, a sealed D$_2$O reference was placed into the sample for signal locking. Solvent suppression techniques were utilized during the acquisition of ^{1}H NMR spectra in water. All chemical shifts (δ) are reported in ppm, and all coupling constants (J) are reported in Hz.

Elemental analyses were provided by E + R Microanalytical Laboratory, Inc.

Syntheses. All syntheses, preparations, and reactions, unless otherwise noted, were performed in an argon-filled glovebox or via Schlenk techniques.

[Ir(CO)(TPPMS)$_3$]CF$_3$SO$_3$. The complexes *trans*-Ir(CO)-(CF$_3$SO$_3$)(PPh$_3$)$_2$[23] and [Ir(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$[24] were prepared by procedures similar to the literature procedures. In preparing *trans*-Ir(CO)(CF$_3$SO$_3$)(PPh$_3$)$_2$, silver salt metathesis, in the absence of light, was performed on 199.3 mg (0.2554 mmol) of *trans*-Ir(CO)Cl(PPh$_3$)$_2$ with 65.3 mg (0.254 mmol) of AgCF$_3$SO$_3$ in 15 mL of toluene. After stirring the solution for 45 min, the AgCl precipitate was removed on a medium sintered-glass filter and the volume was reduced to ∼5 mL; *trans*-Ir(CO)-(CF$_3$SO$_3$)(PPh$_3$)$_2$ was precipitated by addition of hexanes (yield 210.6 mg, 92%). [Ir(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$ was prepared by reacting a 1:1 molar ratio of *trans*-Ir(CO)(OCF$_3$SO$_2$)(PPh$_3$)$_2$ (196.5 mg (0.220 mmol)) with PPh$_3$ (57.2 mg (0.220 mmol)) in 15 mL of toluene. The deep orange [Ir(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$ precipitate was collected after 2 h on a medium sintered-glass filter and washed with toluene and hexanes (yield 254.0 mg, 99%). The exchange of PPh$_3$ with TPPMS was performed using 244.4 mg (0.211 mmol) of [Ir(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$ and 252.4 mg (0.662 mmol, 3.1 equiv) of TPPMS in 25 mL of THF. After stirring the solution overnight, the orange [Ir(CO)(TPPMS)$_3$]-CF$_3$SO$_3$ precipitate was collected and washed with THF, diethyl ether, and hexanes (yield 255.4 mg, 80%). The characteristic data for *trans*-Ir(CO)(OCF$_3$SO$_2$)(PPh$_3$)$_2$ and [Ir(CO)-(PPh$_3$)$_3$]CF$_3$SO$_3$ (Table 1) were in agreement with previously reported values.[23,25,26] The ^{31}P NMR resonances of [Ir(CO)-(TPPMS)$_3$]CF$_3$SO$_3$ integrated in a 1:2 ratio for *cis* phosphine to *trans* phosphines (Figure 1), and the infrared and ^{31}P NMR data were similar to [Ir(CO)(PPh$_3$)$_3$]CF$_3$SO$_3$ (Table 1). [Ir(CO)(TPPMS)$_3$]CF$_3$SO$_3$ can be recrystallized in 1:1 ethanol/cyclohexane (yield 48%). Elemental anal. Found: C(43.7), H(4.1), and P(5.6). Requires: C(43.7), H(3.9), and P(5.5) for a formula of [Ir(CO)(P(C$_6$H$_5$)$_2$(C$_6$H$_4$SO$_3$K·H$_2$O))$_3$]CF$_3$SO$_3$·3CH$_3$CH$_2$OH.

[Ir(CO)$_2$(TPPMS)$_3$]ClO$_4$. Using a previously published method,[22] with slight modification, [Ir(CO)$_2$(PPh$_3$)$_3$]ClO$_4$ was synthesized by reacting 51.7 mg (0.0444 mmol) of [Ir(CO)$_3$-(PPh$_3$)$_2$]ClO$_4$ with 25.85 mg (0.0985 mmol, 2.2 equiv) of PPh$_3$ in a 50:50 THF/methanol solution. After the reaction was complete (overnight), the solvent was pumped off, leaving a lemon yellow product. The crude product was then suspended in 10 mL of THF and precipitated with hexane, where it was collected on a fine sintered-glass filter and washed with THF, diethyl ether, and hexanes (yield 32.1 mg, 52%). The exchange of PPh$_3$ with TPPMS was performed using 32.1 mg (0.0230 mmol) of [Ir(CO)$_2$(PPh$_3$)$_3$]ClO$_4$ with 33.5 mg (0.0879 mmol, 3.8 equiv) of TPPMS in 25 mL of THF (the solution was stirred overnight before collecting the product on a fine sintered-glass filter, where it was washed with THF, diethyl ether, and hexane (yield 40.6 mg, 99%). Elemental anal. Found: C(45.2), H(3.0), P(6.2), and S(6.2). Requires: C(45.2), H(2.8), P(6.2), and S(6.5) for a formula of [Ir(CO)$_2$(P(C$_6$H$_5$)$_2$(C$_6$H$_4$SO$_3$K))$_3$]ClO$_4$. The spectral characteristics of [Ir(CO)$_2$(TPPMS)$_3$]ClO$_4$ (Table 1) were similar to [Ir(CO)$_2$(PPh$_3$)$_3$]ClO$_4$ (Table 1).

[*trans*-Ir(CO)(H$_2$O)(TPPTS)$_2$]CF$_3$SO$_3$. In the absence of light, silver salt metathesis was performed on *trans*-Ir(CO)-Cl(TPPTS)$_2$. In this reaction, 12 mg (0.0467 mmol) of AgCF$_3$SO$_3$ and 70 mg (0.0500 mmol) of *trans*-Ir(CO)Cl-(TPPTS)$_2$ were dissolved in 2 mL of deionized water. The resulting silver chloride precipitate was collected after 1 h on a fine sintered-glass filter, and [*trans*-Ir(CO)(H$_2$O)(TPPTS)$_2$]-CF$_3$SO$_3$ was recovered after the water was removed via vacuum (yield 86%[27]). The ^{31}P NMR and infrared data (Table 1) were similar to [*trans*-Ir(CO)(H$_2$O)(PPh$_3$)$_2$]CF$_3$SO$_3$.[28]

Reactions. The reactions with H$_2$, CO, and L (L = TPPTS or TPPMS), unless otherwise noted, were accomplished by

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Table 1. Infrared and NMR Data for Compounds Discussed (All Infrared Data Are for Carbonyl Stretching Frequencies Unless Otherwise Indicated). L = TPPMS; L′ = TPPTS

complex	IR (cm^{-1})	31P δ (ppm)	1H δ (IrH) (ppm); coupling constants (Hz)
$[Ir(CO)L_3]CF_3SO_3$	2011(br)[a]	15.2(br), 18.2(br)[b,c]	
	2011[d]		
$[Ir(CO)L_3]ClO_4$	2013(br)[a]	15.4(br), 18.3(br)[a,c]	
$[Ir(CO)L_3]Cl$	2013(br)[a]	15.8(br), 18.6(br)[a,c]	
$[Ir(CO)L'_3]Cl$	2023(br)[a]	16.5(br), 19.8(br)[a,c]	
trans-$Ir(CO)(OCF_3SO_2)(PPh_3)_2$	1985[b]	27.4(br)[e]	
$[Ir(CO)(PPh_3)_3]CF_3SO_3$	2002[b]	15(d), 17.5(t)[c,e;] $J_{PP} = 29$ Hz	
[*trans*-$Ir(CO)(H_2O)L'_2]CF_3SO_3$	1993(br)[a]	29.7(s)[a]	
[*trans*-$Ir(CO)(DMSO\text{-}d_6)L_2]CF_3SO_3$	1979[f]	28.7(br)[g]	
$[Ir(CO)_2L_3]CF_3SO_3$	1966(w), 2005[a]	−2.1(s)[a]	
$[Ir(CO)_2L_3]ClO_4$	1966(w), 2003(s)[a]	−2.1(s)[a]	
	1967(w), 2002(s)[b]		
$[Ir(CO)_2(PPh_3)_3]ClO_4$	1964(w), 2002(s)[f]	−2.2(s)[g]	
$[Ir(CO)_3L_2]ClO_4$	2003, 2015(sh)[a]	−2.4(s)[a]	
$Ir(CO)_2H(L)_2$	n/a	6.9(br)[g]	−11.2(t) ($J_{PH} = 10.4$)[g]
		7.2(br)[a]	−11.2(m)[a,h]
$[Ir(CO)(H_2O)(H)_2L'_2]CF_3SO_3$	2024(br), 2115(br)[a,i]	18.9(s)[a]	−6.8(td) ($J_{PH} = 17.7$; $J_{HH} = 5.0$); −23(td) ($J_{PH} = 14.2$; $J_{HH} = 5.0$)[a,j]
[*cis,trans*-$Ir(CO)_2(H)_2L_2]ClO_4$	n/a	4.6(s)[a]	−9.96(t) ($J_{PH} = 14.6$)[a]
		4.4(br)[a]	−10.2(t) ($J_{PH} = 11.6$)[a]
cis,trans-$Ir(CO)Cl(H)_2L_2$	n/a	14.8(s)[a]	−7.7(td) ($J_{PH} = 17.5$; $J_{HH} = 5.0$); −19.3(td) ($J_{PH} = 13.5$; $J_{HH} = 5.0$)[a,j]
cis,trans-$Ir(CO)(OClO_3)(H)_2L_2$	n/a	11.3(s)[g]	−7.4(td) ($J_{PH} = 17.4$; $J_{HH} = 4.3$); −18.4(td) ($J_{PH} = 13.9$; $J_{HH} = 4.3$)[g,j]
fac-$Ir(CO)(H)_3L'_2$	n/a	8.6(s)[a]	−10.7(t) ($J_{PH} = 22$); −11.8(2nd order dd) ($J_{PH} = 21$)[a]
[*cis,mer*-$Ir(CO)(H)_2L_3]CF_3SO_3$	2011(br), 2109(br)[f,i]	3.4(br), −0.5(br)[c,g]	−9.6(qd) ($J_{PH} = 14.5$, $J_{HH} = 4.5$); −11.5(dtd) ($J_{PH(cis)} = 18.1$, $J_{PH(trans)} = 116$, $J_{HH} = 4.5$)[g,j]
	2018(br), 2115(br)[a,i]	3.7(br), 0.5(br)[a,c]	−9.6(q) ($J_{PH} = 15$); −11.6(dt) ($J_{PH(cis)} = 20$, $J_{PH(trans)} = 120$)[a,j]
[*cis,mer*-$Ir(CO)(H)_2L_3]ClO_4$	2018(br), 2110(br)[f,i]	3.7(br), −0.1(br)[c,g]	−9.6(qd) ($J_{PH} = 19$, $J_{HH} = 4$); −11.5(dtd) ($J_{PH(cis)} = 18.5$, $J_{PH(trans)} = 119$, $J_{HH} = 3.4$)[g,j]
	2019(br), 2113(br)[a,i]	3.7(br), 0.5(br)[a,c]	−9.8(qd) ($J_{PH} = 17.4$); −11.7(dt) ($J_{PH(cis)} = 18$, $J_{PH(trans)} = 112$)[a,j]
TPPMS		−5.2[a]	
OTPPMS		26.9[g]	

[a] H_2O. [b] D_2O. [c] The NMR resonances integrated in a 2:1 ratio for *trans* and *cis* phosphines. [d] KBr. [e] CD_2Cl_2. [f] DMSO. [g] DMSO-d_6. [h] No coupling constants were calculated because of the poorly resolved spectrum. [i] (Ir−H). [j] The hydrides integrated in a 1:1 ratio.

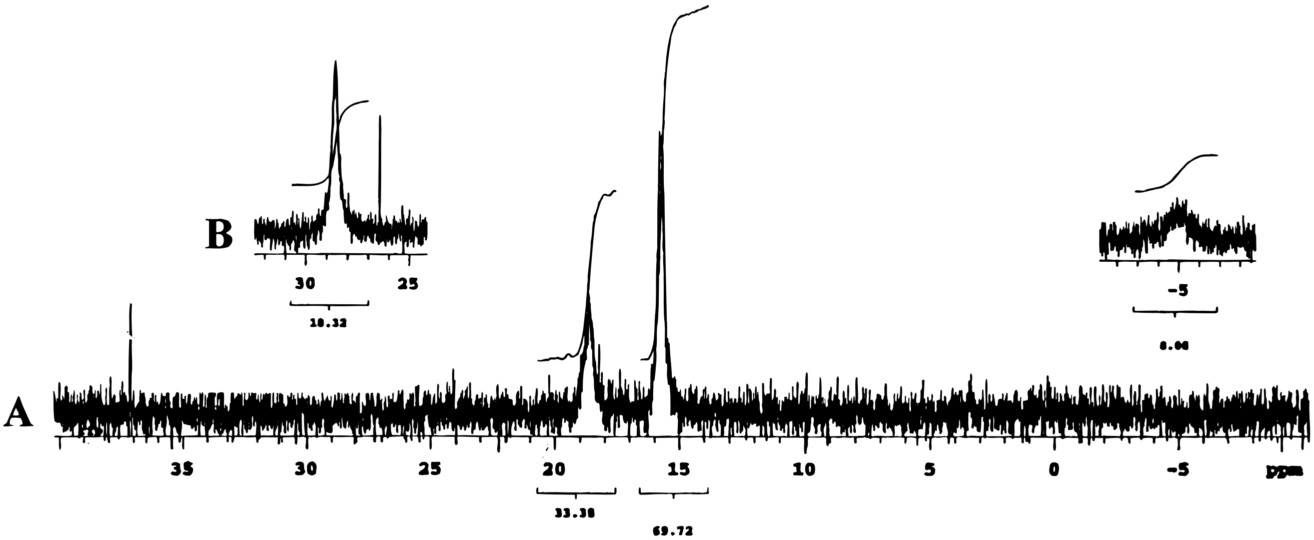

Figure 1. (A) ^{31}P NMR spectrum of $[Ir(CO)(TPPMS)_3]^+\text{-}CF_3SO_3^-$ recorded in water (δ(*trans* TPPMS) = 15.8(br) ppm; δ(*cis* TPPMS) = 18.6(br) ppm). (B) ^{31}P NMR spectrum of [*trans*-$Ir(CO)(DMSO\text{-}d_6)L_2]^+CF_3SO_3^-$ ($\delta = 28.7$(br) ppm) and L ($\delta = -5.2$(br) ppm) from the reaction of $[Ir(CO)(TPPMS)_3]CF_3SO_3$ with DMSO-d_6.

NMR-scale procedures (in a 10 mL beaker, ~30 mg of the iridium complex was suspended in ~1 mL of DMSO-d_6, D_2O, or H_2O; the solution was transferred to an NMR tube, sealed, and removed from the glovebox. Gases were added from a high-vacuum line).

Results and Discussion

Synthesis. The cationic complexes of iridium(I) with TPPMS ($[Ir(CO)(TPPMS)_3]CF_3SO_3$ and $[Ir(CO)_2(TPPMS)_3]ClO_4$) can be prepared by exchange of PPh_3 with TPPMS using stoichiometric amounts of iridium(I) complex and TPPMS in THF; the iridium(I) TPPMS-containing complex precipitates from THF. The characterization data shown in Table 1 confirm the product formulations.

Reactions. When $[Ir(CO)(TPPMS)_3]CF_3SO_3$ is dissolved in DMSO-d_6, [*trans*-$Ir(CO)(DMSO\text{-}d_6)(TPPMS)_2]CF_3SO_3$ and TPPMS are produced in a 1:1 ratio (eq 1).

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(27) The product was contaminated with a minor amount of unreacted starting material (*trans*-$Ir(CO)Cl(TPPTS)_2$; ^{31}P NMR(H_2O); $\delta = 26.9$(br) ppm).

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$$[\mathrm{Ir(CO)L_3}]\mathrm{CF_3SO_3} \xrightarrow{\text{DMSO-}d_6} [\textit{trans}\text{-}\mathrm{Ir(CO)(DMSO\text{-}d_6)L_2}]\mathrm{CF_3SO_3} + \mathrm{L} \quad (1)$$

$$\mathrm{L} = \mathrm{TPPMS}$$

The PPh_3 analogue ([Ir(CO)(DMSO)(PPh_3)$_2$]ClO_4) was prepared by dissolving *trans*-Ir(CO)($OClO_3$)(PPh_3)$_2$ in DMSO.[25] The tris(triphenylphosphine) complex [Ir(CO)(PPh_3)$_3$]$^+$, while readily characterized in nonpolar solvents ($^{31}P(CDCl_3)$: 15.5(t) and 12.9(d) ppm with J_{P-P} = 30 Hz and a 1:2 integration), shows only a broadened resonance at 29 ppm in DMSO. The trisphosphine complex [Ir(CO)(TPPMS)$_3$]CF_3SO_3 is stable in H_2O. Figure 1 shows the ^{31}P NMR spectra recorded in DMSO-d_6 and H_2O with clear distinction between the complexes in the two solvents. The preference for [Ir(CO)(TPPMS)$_3$]$^+$ in water versus DMSO-d_6 is not entirely understood, but may indicate hydrogen bonding between adjacent TPPMS ligands. A crystal structure of $[N(CH_2C_6H_5)(C_2H_5)_3{}^+][P(C_6H_5)_2(m\text{-}C_6H_4SO_3)^-]\cdot H_2O$ confirmed that a system of hydrogen bonding links the $[P(C_6H_5)_2(m\text{-}C_6H_4SO_3)^-]$ anions through H_2O molecules of solvation.[18] The *cis* orientation of the TPPMS ligands around [Ir(CO)(TPPMS)$_3$]CF_3SO_3 puts them in proximity to each other, which could allow for solvation hydrogen bonding. A similar explanation may account for the stability of $[Ir(CO)_2L_3]^+$ (L = TPPTS or TPPMS) versus $[Ir(CO)_3L_2]^+$ in water.[20,21]

Reaction of H_2 with [Ir(CO)(TPPMS)$_3$]CF_3SO_3 in H_2O or DMSO-d_6 produces [*cis,mer*-Ir(CO)(H)$_2$(TPPMS)$_3$]CF_3SO_3. The reaction in water proceeds cleanly to product (eq 2),

$$[\mathrm{Ir(CO)L_3}]\mathrm{CF_3SO_3} + \mathrm{H_2} \xrightarrow{\mathrm{H_2O}} [\textit{cis,mer}\text{-}\mathrm{Ir(CO)(H)_2L_3}]\mathrm{CF_3SO_3} \quad (2)$$

$$\mathrm{L} = \mathrm{TPPMS}$$

while the reaction in DMSO-d_6 initially produces [*trans*-Ir(CO)(DMSO-d_6)(TPPMS)$_2$]CF_3SO_3 and TPPMS (eq 1), which then reacts with H_2 (eq 3).

$$[\textit{trans}\text{-}\mathrm{Ir(CO)(DMSO\text{-}d_6)L_2}]\mathrm{CF_3SO_3} + \mathrm{L} \xrightarrow[\text{DMSO-}d_6]{\mathrm{H_2}} [\textit{cis,mer}\text{-}\mathrm{Ir(CO)(H)_2L_3}]\mathrm{CF_3SO_3} \quad (3)$$

$$\mathrm{L} = \mathrm{TPPMS}$$

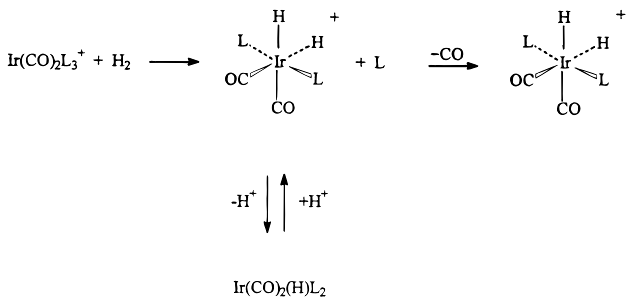
Reaction of [*trans*-Ir(CO)(H_2O)(TPPTS)$_2$]CF_3SO_3 with H_2 in H_2O produces [*cis,trans*-Ir(CO)(H_2O)(H)$_2$(TPPTS)$_2$]CF_3SO_3 (eq 4).

$$[\textit{trans}\text{-}\mathrm{Ir(CO)(H_2O)L_2}]\mathrm{CF_3SO_3} + \mathrm{H_2} \xrightarrow{\mathrm{H_2O}} [\textit{cis,trans}\text{-}\mathrm{Ir(CO)(H_2O)(H)_2L_2}]\mathrm{CF_3SO_3} \quad (4)$$

$$\mathrm{L} = \mathrm{TPPTS}$$

The aquo complex slowly undergoes further reaction with H_2 to *fac*-Ir(CO)(H)$_3$(TPPTS)$_2$[29] and a proton or with TPPTS to form [*cis,mer*-Ir(CO)(H)$_2$(TPPMS)$_3$]CF_3SO_3 (Table 1).[17] The use of triflate[30] allowed generation of relatively pure [*cis,trans*-Ir(CO)(H_2O)(H)$_2$(TPPTS)$_2$]CF_3SO_3 characterized by infrared and NMR. Water coordination to other six-coordinate water-soluble dihydride complexes has been observed in [Rh(H_2O)(H)$_2$(TPPTS)$_3$]Cl,[31] Ru(H_2O)(H)$_2$(TPPTS)$_3$,[32] and [*mer*-Ir(H_2O)(H)$_2$(PMe_3)$_3$]Cl.[33]

Scheme 1



[Ir(CO)$_2$(TPPMS)$_3$]ClO_4 reacts with H_2 in H_2O (or DMSO) to produce initially [*cis,cis,trans*-Ir(CO)$_2$(H)$_2$(TPPMS)$_2$]ClO_4 and TPPMS via substitution of TPPMS with H_2. Reaction of TPPMS with [*cis,cis,trans*-Ir(CO)$_2$(H)$_2$(TPPMS)$_2$]ClO_4 slowly generates [*cis,mer*-Ir(CO)(H)$_2$(TPPMS)$_3$]ClO_4 and CO. In addition, [*cis,cis,trans*-Ir(CO)$_2$(H)$_2$(TPPMS)$_2$]ClO_4, which is a weak acid, establishes an equilibrium with H_3O^+ and Ir(CO)$_2$H(TPPMS)$_2$. The reaction sequences are shown in Scheme 1. In a different study,[20,34] carbonylation of aqueous *trans*-Ir(CO)Cl(TPPMS)$_2$ produces [Ir(CO)$_3$(TPPMS)$_2$]Cl (major product) and [Ir(CO)$_2$(H_2O)(TPPMS)$_2$]Cl and [*cis,cis,trans*-Ir(CO)$_2$(H)$_2$(TPPMS)$_2$]Cl as minor products. Similarly, protonation of Ir(CO)$_2$H(PPh_3)$_2$ at 60 °C in a 1% ethanolic solution of perchloric acid produces [Ir(CO)$_2$(H)$_2$(PPh_3)$_2$]ClO_4.[22] Addition of 2 drops of 5% KOH to an aqueous solution containing [*cis,cis,trans*-Ir(CO)$_2$(H)$_2$(TPPMS)$_2$]Cl results in Ir(CO)$_2$H(TPPMS)$_2$ as the equilibrium is shifted.[34]

Carbonylation of [Ir(CO)(TPPMS)$_3$]CF_3SO_3 in water produces [Ir(CO)$_2$(TPPMS)$_3$]CF_3SO_3 (eq 5).

$$[\mathrm{Ir(CO)L_3}]\mathrm{CF_3SO_3} + \mathrm{CO} \xrightarrow{\mathrm{H_2O}} [\mathrm{Ir(CO)_2L_3}]\mathrm{CF_3SO_3} \quad (5)$$

$$\mathrm{L} = \mathrm{TPPMS}$$

Analogously, Reed et al.[25] reported CO reacts with [Ir(CO)(PPh_3)$_3$]ClO_4 to produce [Ir(CO)$_2$(PPh_3)$_3$]ClO_4 in ethanol.

Induced decarbonylation of an aqueous solution of [Ir(CO)$_2$(TPPMS)$_3$]ClO_4 by refluxing in a nitrogen atmosphere produces [Ir(CO)(TPPMS)$_3$]ClO_4 (eq 6);

$$[\mathrm{Ir(CO)_2L_3}]\mathrm{ClO_4} \xrightarrow[\text{reflux}]{\mathrm{N_2/H_2O}} [\mathrm{Ir(CO)L_3}]\mathrm{ClO_4} + \mathrm{CO} \quad (6)$$

$$\mathrm{L} = \mathrm{TPPMS}$$

decarbonylation of [Ir(CO)$_2$(PPh_3)$_3$]ClO_4 under similar conditions yields [Ir(CO)(PPh_3)$_3$]ClO_4.[25] [*cis,mer*-Ir(CO)(H)$_2$(TPPMS)$_3$]ClO_4 was a minor product (~6%) of reaction 6; its formation occurs through a series of reactions that, initially, involves attack of OH^- on a carbonyl

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carbon of $[Ir(CO)_2(TPPMS)_3]ClO_4$ to produce $Ir(C(O)OH)(CO)(TPPMS)_3$ and a proton. Loss of CO_2 generates $Ir(CO)H(TPPMS)_3$,[35] which is protonated to form [*cis,mer*-$Ir(CO)(H)_2(TPPMS)_3]ClO_4$ (eq 7).

$$[\mathrm{Ir(CO)_2L_3}]^+ \xrightarrow{\mathrm{H_2O}} \mathrm{Ir(C(O)OH)(CO)L_3} + \mathrm{H}^+ \xrightarrow{-\mathrm{CO_2}} \mathrm{Ir(CO)H(L)_3} \xrightarrow{\mathrm{H^+}} [\mathrm{Ir(CO)(H)_2L_3}]^+ \quad (7)$$

$$\mathrm{L = TPPMS}$$

Reaction of CO with $[Ir(CO)_2(TPPMS)_3]ClO_4$ in DMSO produces $[Ir(CO)_3(TPPMS)_2]ClO_4$ and TPPMS (eq 8), but no reaction occurs in H_2O (eq 9).

$$[\mathrm{Ir(CO)_2L_3}]\mathrm{ClO_4} + \mathrm{CO} \xrightarrow{\mathrm{DMSO}\text{-}d_6} [\mathrm{Ir(CO)_3L_2}]\mathrm{ClO_4} + \mathrm{L} \quad (8)$$

$$\mathrm{L = TPPMS}$$

$$[\mathrm{Ir(CO)_2L_3}]\mathrm{ClO_4} + \mathrm{CO} \xrightarrow{\mathrm{H_2O}} \mathrm{NR} \quad (9)$$

$$\mathrm{L = TPPMS}$$

Consistent with reactions 8 and 9, TPPMS reacts irreversibly with $[Ir(CO)_3(TPPMS)_2]ClO_4$ in water to produce $[Ir(CO)_2(TPPMS)_3]ClO_4$ and CO (eq 10).

$$[\mathrm{Ir(CO)_3L_2}]\mathrm{ClO_4} + \mathrm{L} \xrightarrow{\mathrm{H_2O}} [\mathrm{Ir(CO)_2L_3}]\mathrm{ClO_4} + \mathrm{CO(g)} \quad (10)$$

$$\mathrm{L = TPPMS}$$

Reaction of $[Ir(CO)_3(PPh_3)_2]ClO_4$ with PPh_3 in DMSO-d_6 establishes an equilibrium with $[Ir(CO)_2(PPh_3)_3]ClO_4$ and CO(g), which favors the products (eq 11).

$$[\mathrm{Ir(CO)_3(PPh_3)_2}]\mathrm{ClO_4} + \mathrm{PPh_3} \xrightleftharpoons{\mathrm{DMSO}\text{-}d_6} [\mathrm{Ir(CO)_2(PPh_3)_3}]\mathrm{ClO_4} + \mathrm{CO(g)} \quad (11)$$

Adding excess L (L = TPPMS or TPPTS) to an aqueous solution of *trans*-$Ir(CO)Cl(L)_2$ results in immediate formation of $[Ir(CO)L_3]Cl$ (eq 12), as indicated

$$trans\text{-}\mathrm{Ir(CO)Cl(L)_2} + \mathrm{L} \xrightarrow{\mathrm{H_2O}} [\mathrm{Ir(CO)L_3}]\mathrm{Cl} \quad (12)$$

$$\mathrm{L = TPPMS\ or\ TPPTS}$$

by infrared and ^{31}P NMR data,[36] which are spectroscopically consistent with $[Ir(CO)(TPPMS)_3]^+X$ ($X = CF_3SO_3^-$ or ClO_4^-, see Table 1) and $[Ir(CO)(PPh_3)_3]PF_6$ as reported by Williams et al.[26] No reaction is observed when *trans*-$Ir(CO)Cl(TPPTS)_2$ is dissolved with excess TPPTS in DMSO-d_6 (eq 13).

$$trans\text{-}\mathrm{Ir(CO)Cl(L)_2} + \mathrm{L} \xrightarrow{\mathrm{DMSO}\text{-}d_6} \mathrm{NR} \quad (13)$$

$$\mathrm{L = TPPMS\ or\ TPPTS}$$

Similarly, no reaction was observed for *trans*-$Ir(CO)Cl(PPh_3)_2$ with PPh_3.[37] The reactions of *trans*-$Ir(CO)Cl(L)_2$ with excess L in H_2O mark another route for preparation of the *tris*-sulfonated phosphine iridium(I) complexes.

Conclusion

The use of the hydrophilic ligand TPPMS allows preparation of water-soluble cationic iridium(I) complexes ($[Ir(CO)(TPPMS)_3]CF_3SO_3$ and $[Ir(CO)_2(TPPMS)_3]ClO_4$). The complexes prepared and the characterizations are remarkably similar for PPh_3 complexes and complexes of sulfonated phosphine ligands. However, for reactions in H_2O versus DMSO a number of differences are observed: (1) $Ir(CO)(TPPMS)_3^+$ is stable in H_2O but loses TPPMS to form $Ir(CO)(DMSO)(TPPMS)_2^+$ in DMSO. (2) $Ir(CO)(DMSO)(TPPMS)_2^+$ is an identifiable intermediate in reaction of $Ir(CO)(TPPMS)_3^+$ with H_2 in DMSO. No intermediate is seen for the hydrogenation in H_2O. (3) While H_2 and CO react with $Ir(CO)_2(TPPMS)_3^+$ in DMSO, only H_2 reacts in H_2O. (4) In H_2O $Ir(CO)_2(TPPMS)_3^+$ loses CO (water reflux) to give $Ir(CO)(TPPMS)_3^+$. In DMSO, CO and TPPMS are readily lost to give $Ir(CO)(DMSO)(TPPMS)_2^+$. (5) Reaction of $Ir(CO)_3(TPPMS)_2^+$ with TPPMS in H_2O gives $Ir(CO)_2(TPPMS)_3^+$; no reaction is observed in DMSO. (6) *trans*-$Ir(CO)(Cl)(TPPMS)_2$ reacts with TPPMS in H_2O to give $Ir(CO)(TPPMS)_3^+$; in DMSO only TPPMS exchange is observed.

The different reactions of iridium(I) complexes in H_2O in comparison to the also polar DMSO can all be attributed to unusual stability in H_2O for complexes containing three sulfonated ligands. This stability in water may indicate hydrogen bonding from water to *cis*-sulfonated phosphine groups.

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Supporting Information Available: Synthesis data and UV–vis data for compounds discussed in text (6 pages). Ordering information is given on any current masthead page.

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