Synthesis of Cationic Iridium(I) Complexes of Water-Soluble Phosphine Ligands, [Ir(CO)(TPPMS)₃]CF₃SO₃, [Ir(CO)(H₂O)(TPPTS)₂]CF₃SO₃, and $[Ir(CO)_2(TPPMS)_3]ClO_4$ (TPPMS = $PPh_2(m-C_6H_4SO_3K), TPPTS = P(m-C_6H_4SO_3Na)_3)$

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 (H₂ or CO) in polar solvents (DMSO or H₂O) examined. Reaction of H₂ with $[Ir(CO)(TPPMS)_3]CF_3SO_3(TPPMS = P(C_6H_5)_2(m-C_6H_4SO_3K))$ in DMSO or H₂O produces [cis,mer-Ir(CO)(H)₂(TPPMS)₃]CF₃SO₃, while the reaction of CO with [Ir(CO)(TPPMS)₃]-CF₃SO₃ in water yields [Ir(CO)₂(TPPMS)₃]CF₃SO₃. Carbonylation of [Ir(CO)₂(TPPMS)₃]ClO₄ in DMSO produces [Ir(CO)₃(TPPMS)₂]ClO₄ and TPPMS; no reaction is observed in H₂O. Hydrogenation of [Ir(CO)₂(TPPMS)₃]ClO₄ in DMSO or H₂O yields [cis,mer-Ir(CO)(H)₂- $(TPPMS)_3$ ClO₄, while reaction of H₂ 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 H₂O produces [Ir(CO)L₃]Cl, while no reaction occurs in DMSO. $[Ir(CO)_3(TPPMS)_2]Cl$ reacts irreversibly with TPPMS in H₂O 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 watersoluble 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 PPh₃, as indicated by their ³¹P 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 PPh₃.¹⁰ The presence of the sulfonate group changes the solubil-

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ity 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 hydrogenation¹² 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 H₂, 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 H₂ to trans-Ir(CO)X(L)₂ (X = Cl,^{16,17} OH,¹⁸ or CH₃;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 TPPTS²¹)). In this article, we report the synthesis and characterization of several new cationic iridium(I) complexes ([Ir(CO)(TPPMS)₃]CF₃SO₃, [*trans*-Ir(CO)(H₂O)(TPPTS)₂]CF₃SO₃ and [Ir(CO)₂(TPPMS)₃]-ClO₄) and their reactions with H₂ or CO in DMSO and H₂O. Reactions of *trans*-Ir(CO)Cl(L)₂ (L = TPPMS or TPPTS) with excess L in DMSO or H₂O and reactions of CO with [Ir(CO)₂(TPPMS)₃]ClO₄ in DMSO and H₂O are also described.

Experimental Section

Materials. IrCl₃·3H₂O was purchased or borrowed from Johnson Matthey. Triphenylphosphine, n-octylamine, fuming sulfuric acid (20% and 30% SO3 w/w), and CH3Li 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. H₂ 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 D₂O and DMSO-d₆ 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 N₂ atmosphere over Na/benzophenone until the solution turned blue or purple. Hexane was refluxed overnight in a N2 atmosphere over finely divided CaH₂. DMSO was refluxed over finely divided CaH₂ 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(PPh₃)₂]ClO₄,²² and TPPMS¹⁸ 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 CaF₂ (DMSO or H₂O) cells while solid-state spectra were recorded as KBr disks. All spectra are reported in wavenumbers (cm⁻¹).

¹H and ³¹P NMR spectra were recorded on Varian VXR-400 or 500 MHz spectrometers. ¹H 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. ³¹P NMR spectra were referenced to an external sample of 85% H₃PO₄ in D₂O (reference was set to 0.0 ppm) and were proton decoupled. For ¹H and ³¹P NMR spectra that were recorded in H₂O, a sealed D₂O reference was placed into the sample for signal locking. Solvent suppression techniques were utilized during the acquisition of ¹H 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 $\mathrm{E}+\mathrm{R}$ 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]CF₃SO₃. The complexes *trans*-Ir(CO)-(CF₃SO₃)(PPh₃)₂²³ and [Ir(CO)(PPh₃)₃]CF₃SO₃²⁴ were prepared

by procedures similar to the literature procedures. In preparing *trans*-Ir(CO)(CF₃SO₃)(PPh₃)₂, silver salt metathesis, in the absence of light, was performed on 199.3 mg (0.2554 mmol) of trans-Ir(CO)Cl(PPh₃)₂ with 65.3 mg (0.254 mmol) of AgCF₃-SO₃ 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)-(CF₃SO₃)(PPh₃)₂ was precipitated by addition of hexanes (yield 210.6 mg, 92%). [Ir(CO)(PPh₃)₃]CF₃SO₃ was prepared by reacting a 1:1 molar ratio of trans-Ir(CO)(OCF₃SO₂)(PPh₃)₂ (196.5 mg (0.220 mmol)) with PPh₃ (57.2 mg (0.220 mmol)) in 15 mL of toluene. The deep orange [Ir(CO)(PPh₃)₃]CF₃SO₃ 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 PPh₃ with TPPMS was performed using 244.4 mg (0.211 mmol) of [Ir(CO)(PPh₃)₃]CF₃SO₃ 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]-CF₃SO₃ precipitate was collected and washed with THF, diethyl ether, and hexanes (yield 255.4 mg, 80%). The characteristic data for trans-Ir(CO)(OCF₃SO₂)(PPh₃)₂ and [Ir(CO)- $(PPh_3)_3$ [CF₃SO₃ (Table 1) were in agreement with previously reported values.^{23,25,26} The ³¹P NMR resonances of [Ir(CO)-(TPPMS)₃]CF₃SO₃ integrated in a 1:2 ratio for *cis* phosphine to trans phosphines (Figure 1), and the infrared and ³¹P NMR data were similar to [Ir(CO)(PPh₃)₃]CF₃SO₃ (Table 1). [Ir(CO)(TPPMS)₃]CF₃SO₃ 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(C₆H₅)₂(C₆H₄SO₃K·H₂O))₃]CF₃SO₃· 3CH₃CH₂OH.

[Ir(CO)2(TPPMS)3]ClO4. Using a previously published method,²² with slight modification, [Ir(CO)₂(PPh₃)₃]ClO₄ was synthesized by reacting 51.7 mg (0.0444 mmol) of [Ir(CO)₃-(PPh₃)₂]ClO₄ with 25.85 mg (0.0985 mmol, 2.2 equiv) of PPh₃ 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 PPh₃ with TPPMS was performed using 32.1 mg (0.0230 mmol) of [Ir(CO)₂(PPh₃)₃]ClO₄ 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 $[Ir(CO)_2(P(C_6H_5)_2(C_6H_4SO_3K))_3]CIO_4$. The spectral characteristics of [Ir(CO)₂(TPPMS)₃]ClO₄ (Table 1) were similar to [Ir(CO)₂(PPh₃)₃]ClO₄ (Table 1).

[*trans*-Ir(CO)(H₂O)(TPPTS)₂]CF₃SO₃. 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 AgCF₃SO₃ 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)(H₂O)(TPPTS)₂]-CF₃SO₃ was recovered after the water was removed via vacuum (yield 86%²⁷). The ³¹P NMR and infrared data (Table 1) were similar to [*trans*-Ir(CO)(H₂O)(PPh₃)₂]CF₃SO₃.²⁸

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 ₃ SO 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 ₃ SO ₂)(PPh ₃) ₂	1985 ^b	27.4(br) ^e	
[Ir(CO)(PPh ₃) ₃]CF ₃ SO ₃	2002 ^b	15(d), 17.5(t) ^{c,e;}	
		$J_{\rm PP} = 29 \; {\rm Hz}$	
[trans-Ir(CO)(H2O)L'2]CF3SO3	1993(br) ^a	29.7(s) ^a	
[trans-Ir(CO)(DMSO-d ₆)L ₂]CF ₃ SO ₃	1979 ^{<i>f</i>}	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	$-11.2(t) (J_{\rm PH} = 10.4)^{g}$
		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) ₂ L ₂]ClO ₄	n/a	4.6(s) ^a	$-9.96(t) (J_{\rm PH} = 14.6)^a$
		4.4(br) ^a	$-10.2(t) (J_{\rm PH} = 11.6)^a$
cis, trans-Ir(CO)Cl(H)2L2	n/a	14.8(s) ^a	-7.7 (td) ($J_{\text{PH}} = 17.5$; $J_{\text{HH}} = 5.0$); -19.3 (td) ($J_{\text{PH}} = 13.5$; $J_{\text{HH}} = 5.0$) ^{a,j}
cis, trans-Ir(CO)(OClO ₃)(H) ₂ L ₂	n/a	11.3(s) ^g	-7.4 (td) ($J_{\text{PH}} = 17.4$; $J_{\text{HH}} = 4.3$); -18.4 (td) ($J_{\text{PH}} = 13.9$; $J_{\text{HH}} = 4.3$) ^{gJ}
fac-Ir(CO)(H) ₃ L' ₂	n/a	8.6(s) ^a	$-10.7(t)$ ($J_{\rm PH} = 22$); $-11.8(2$ nd order dd) ($J_{\rm PH} = 21$) ^a
[cis,mer-Ir(CO)(H) ₂ L ₃]CF ₃ SO ₃	2011(br), 2109(br) ^{f,i}	3.4(br), -0.5(br) ^{c,g}	$-9.6(qd)$ ($J_{PH} = 14.5$, $J_{HH} = 4.5$); $-11.5(dtd)$ ($J_{PH(cis)} = 18.1$,
	2018(br), 2115(br)a,i	3.7(br), 0.5(br) ^{a,c}	$J_{\rm PH(trans)} = 116, J_{\rm HH} = 4.5)$ gj
			$-9.6(q) (J_{PH} = 15); -11.6(dt) (J_{PH(cis)} = 20, J_{PH(trans)} = 120)^{aj}$
$[cis, mer-Ir(CO)(H)_2L_3]ClO_4$	2018(br), 2110(br) ^{f,i}	3.7(br), -0.1(br) ^{c,g}	$-9.6(qd)$ ($J_{PH} = 19$, $J_{HH} = 4$); $-11.5(dtd)$ ($J_{PH(cis)} = 18.5$,
	2019(br), 2113(br) ^{a,i}	3.7(br), 0.5(br) ^{a,c}	$J_{\rm PH(trans)} = 119, \ J_{\rm HH} = 3.4)^{gj}$
			$-9.8(qd)$ ($J_{PH} = 17.4$); $-11.7(dt)$ ($J_{PH(cis)} = 18$, $J_{PH(trans)} = 112$) ^{a,j}
TPPMS		-5.2^{a}	· · · · · · · · · · · · · · · · · · ·
OTPPMS		26.9^{g}	

^{*a*} H₂O. ^{*b*} D₂O. ^{*c*} The NMR resonances integrated in a 2:1 ratio for *trans* and *cis* phosphines. ^{*d*} KBr. ^{*e*} CD₂Cl₂. ^{*f*} DMSO. ^{*g*} DMSO- d_{6} . ^{*h*} No coupling constants were calculated because of the poorly resolved spectrum. ^{*j*} (Ir–H). ^{*j*} The hydrides integrated in a 1:1 ratio.



Figure 1. (A) ³¹P NMR spectrum of $[Ir(CO)(TPPMS)_3]^+$ -CF₃SO₃⁻ recorded in water (δ (*trans* TPPMS) = 15.8(br) ppm; δ (*cis* TPPMS) = 18.6(br) ppm). (B) ³¹P NMR spectrum of [*trans*-Ir(CO)(DMSO-*d*₆)L₂]+CF₃SO₃⁻ (δ = 28.7(br) ppm) and L (δ = -5.2(br) ppm) from the reaction of [Ir(CO)(TPPMS)_3]CF₃SO₃ with DMSO-*d*₆.

NMR-scale procedures (in a 10 mL beaker, \sim 30 mg of the iridium complex was suspended in \sim 1 mL of DMSO- d_6 , D₂O, or H₂O; 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]CF₃SO₃ and [Ir(CO)₂-

 $(TPPMS)_3$]ClO₄) can be prepared by exchange of PPh₃ 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 , $[trans-Ir(CO)(DMSO-d_6)(TPPMS)_2]$ -CF₃SO₃ and TPPMS are produced in a 1:1 ratio (eq 1).

⁽²⁷⁾ The product was contaminated with a minor amount of unreacted starting material (*trans*-Ir(CO)Cl(TPPTS)₂; ³¹P NMR(H₂O); δ = 26.9(br) ppm).

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The PPh₃ analogue ([Ir(CO)(DMSO)(PPh₃)₂]ClO₄) was prepared by dissolving trans-Ir(CO)(OClO₃)(PPh₃)₂ in DMSO.²⁵ The tris(triphenylphosphine) complex [Ir(CO)-(PPh₃)₃]⁺, while readily characterized in nonpolar solvents (³¹P(CDCl₃): 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]CF₃SO₃ is stable in H₂O. Figure 1 shows the ³¹P 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 $[N(CH_2C_6H_5)(C_2H_5)_3^+][P(C_6H_5)_2(m-C_6H_4SO_3)^-]\cdot H_2O$ confirmed that a system of hydrogen bonding links the $[P(C_6H_5)_2(m-C_6H_4SO_3)^-]$ anions through H₂O molecules of solvation.¹⁸ The *cis* orientation of the TPPMS ligands around [Ir(CO)(TPPMS)₃]CF₃SO₃ 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- $Ir(CO)(H)_2(TPPMS)_3]$ -CF₃SO₃. The reaction in water proceeds cleanly to product (eq 2),

$$[Ir(CO)L_{3}]CF_{3}SO_{3} + H_{2} \xrightarrow{H_{2}O} [cis, mer-Ir(CO)(H)_{2}L_{3}]CF_{3}SO_{3} (2)$$
$$L = TPPMS$$

while the reaction in DMSO- d_6 initially produces [*trans*-Ir(CO)(DMSO- d_6)(TPPMS)₂]CF₃SO₃ and TPPMS (eq 1), which then reacts with H₂ (eq 3).

$$[trans-Ir(CO)(DMSO-d_6)L_2]CF_3SO_3 + L \xrightarrow{H_2}_{DMSO-d_6} [cis,mer-Ir(CO)(H)_2L_3]CF_3SO_3 (3)$$
$$L = TPPMS$$

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).

$$[trans-Ir(CO)(H_2O)L_2]CF_3SO_3 + H_2 \xrightarrow{H_2O} [cis, trans-Ir(CO)(H_2O)(H)_2L_2]CF_3SO_3 (4)$$
$$L = TPPTS$$

The aquo complex slowly undergoes further reaction with H₂ to *fac*-Ir(CO)(H)₃(TPPTS)₂²⁹ and a proton or with TPPTS to form [*cis,mer*-Ir(CO)(H)₂(TPPMS)₃]-CF₃SO₃ (Table 1).¹⁷ The use of triflate³⁰ allowed generation of relatively pure [*cis,trans*-Ir(CO)(H₂O)(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(H₂O)(H)₂(TPPTS)₃,^{32} and [*mer*-Ir-(H₂O)(H)₂(PMe_3)_3]Cl.^{33}

 $[Ir(CO)_2(TPPMS)_3]ClO_4$ reacts with H₂ in H₂O (or DMSO) to produce initially [cis, cis, trans-Ir(CO)₂(H)₂-(TPPMS)₂|ClO₄ and TPPMS via substitution of TPPMS with H₂. Reaction of TPPMS with [cis, cis, trans-Ir(CO)₂-(H)₂(TPPMS)₂]ClO₄ slowly generates [cis, mer-Ir(CO)-(H)₂(TPPMS)₃]ClO₄ and CO. In addition, [cis, cis, trans- $Ir(CO)_2(H)_2(TPPMS)_2|CIO_4$, which is a weak acid, establishes an equilibrium with H_3O^+ and $Ir(CO)_2H^-$ (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(H₂O)(TPPMS)₂]Cl and [cis, cis, trans-Ir(CO)₂(H)₂(TPPMS)₂]Cl as minor products. Similarly, protonation of $Ir(CO)_2H(PPh_3)_2$ at 60 °C in a 1% ethanolic solution of perchloric acid produces [Ir(CO)₂(H)₂(PPh₃)₂]ClO₄.²² 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)₂H(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).

$$[Ir(CO)L_3]CF_3SO_3 + CO \xrightarrow{H_2O} [Ir(CO)_2L_3]CF_3SO_3 (5)$$
$$L = TPPMS$$

Analogously, Reed et al.²⁵ reported CO reacts with [Ir- $(CO)(PPh_3)_3$]ClO₄ to produce [Ir(CO)₂(PPh₃)₃]ClO₄ 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);

$$[Ir(CO)_{2}L_{3}]ClO_{4} \xrightarrow{N_{2}H_{2}O} [Ir(CO)L_{3}]ClO_{4} + CO (6)$$
$$L = TPPMS$$

decarbonylation of $[Ir(CO)_2(PPh_3)_3]CIO_4$ under similar conditions yields $[Ir(CO)(PPh_3)_3]CIO_4$.²⁵ [*cis,mer*-Ir(CO)-(H)₂(TPPMS)₃]CIO₄ 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).

$$[Ir(CO)_{2}L_{3}]^{+} \xrightarrow{H_{2}O} Ir(C(O)OH)(CO)L_{3} + H^{+} \xrightarrow{-CO_{2}}$$
$$Ir(CO)H(L)_{3} \xrightarrow{H^{+}} [Ir(CO)(H)_{2}L_{3}]^{+} (7)$$
$$L = TPPMS$$

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).

$$[Ir(CO)_{2}L_{3}]ClO_{4} + CO \xrightarrow{DMSO-d_{6}} [Ir(CO)_{3}L_{2}]ClO_{4} + L$$
(8)

$$L = TPPMS$$

$$[Ir(CO)_{2}L_{3}]CIO_{4} + CO \xrightarrow{H_{2}O} NR \qquad (9)$$
$$L = TPPMS$$

11 0

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).

$$[Ir(CO)_{3}L_{2}]ClO_{4} + L \xrightarrow{H_{2}O} [Ir(CO)_{2}L_{3}]ClO_{4} + CO(g)$$
(10)
$$L = TPPMS$$

Reaction of $[Ir(CO)_3(PPh_3)_2]ClO_4$ with PPh₃ in DMSOd₆ establishes an equilibrium with $[Ir(CO)_2(PPh_3)_3]ClO_4$ and CO(g), which favors the products (eq 11).

$$[Ir(CO)_{3}(PPh_{3})_{2}]ClO_{4} + PPh_{3} \xleftarrow{DMSO-d_{6}} \\ [Ir(CO)_{2}(PPh_{3})_{3}]ClO_{4} + CO(g) (11)$$

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-Ir(CO)Cl(L)₂ + L
$$\xrightarrow{H_2O}$$
 [Ir(CO)L₃]Cl (12)
L = TPPMS or TPPTS

by infrared and ³¹P NMR data,³⁶ which are spectroscopically consistent with $[Ir(CO)(TPPMS)_3]^+X$ (X = $CF_3SO_3^-$ or CIO_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-Ir(CO)Cl(L)₂ + L
$$\xrightarrow{\text{DMSO-}d_6}$$
 NR (13)

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

Similarly, no reaction was observed for *trans*-Ir(CO)Cl- $(PPh_3)_2$ with PPh₃.³⁷ The reactions of *trans*-Ir(CO)Cl- $(L)_2$ with excess L in H₂O 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]CF₃SO₃ and [Ir(CO)₂(TPPMS)₃]-ClO₄). The complexes prepared and the characterizations are remarkably similar for PPh₃ complexes and complexes of sulfonated phosphine ligands. However, for reactions in H₂O versus DMSO a number of differences are observed: (1) $Ir(CO)(TPPMS)_3^+$ is stable in H₂O 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 H₂ 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 H₂ reacts in H₂O. (4) In H₂O 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 H₂O gives $Ir(CO)_2^-$ (TPPMS)₃⁺; no reaction is observed in DMSO. (6) *trans*-Ir(CO)(Cl)(TPPMS)₂ reacts with TPPMS in H₂O 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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