Synthesis, Properties, and Reactions of Monosulfonated Triphenylphosphine ($PPh_2(m\text{-}C_6H_4SO_3K)$ = TPPMS) Complexes of Iridium(I). Crystal and Molecular Structure of $[N(CH_2C_6H_5)(C_2H_5)_3^+][PPh_2(m\text{-}C_6H_4SO_3)^-]\cdot H_2O$

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Iridium complexes containing the TPPMS ligand (TPPMS = $PPh_2(m\text{-}C_6H_4SO_3K)$) have been prepared and studied in DMSO and H_2O as a comparison to the PPh_3 analogues in toluene. Measurements of the pH of the complexes show that most are almost neutral, but $Ir(CO)(H)(TPPMS)_3$ is basic (pH = 10.7). The basicity of $Ir(CO)(H)(TPPMS)_3$ is confirmed by its reaction with H_2O to give $Ir(CO)(H)_2(TPPMS)_3^+$. In aqueous solution, reaction of *trans*-$Ir(CO)(OH)(TPPMS)_2$ with H_2 produces only *fac*-$Ir(CO)(H)_3(TPPMS)_2$ not the usual mixture of facial and meridional isomers. This is attributed to a hydrogen-bonding interaction between the two *cis*-TPPMS ligands in H_2O. Reaction of *trans*-$Ir(CO)(Cl)(TPPMS)_2$ with CO in water produces $[Ir(CO)_2(TPPMS)_2^+]Cl^-$ and $[Ir(CO)_3(TPPMS)_2^+]Cl$ sequentially in a reaction that is pH dependent. Reaction of *trans*-$Ir(CO)(OH)(TPPMS)_2$ with CO results in products based on the water gas shift-reaction. These complexes of TPPMS are spectroscopically very similar to the PPh_3 analogues, but display significantly different reactions in H_2O.

Research aimed at catalysis in water or at a water/organic solvent interface has greatly expanded in recent years.[1−5] The impetus derives from reducing the role of organic solvents and from easier separation of products. The advantages of water as a solvent in organic reactions were summarized as decreased price, increased safety, and simplified protection−deprotection processes, product isolation, and catalyst recycling.[5] Industrial production of butanal using rhodium catalysts with a water-soluble phosphine ($P(m\text{-}C_6H_4SO_3Na)_3$ = TPPTS) in a hydroformylation reaction provides an example of a catalytic reaction, with reported benefits including facile separation of butanal from the catalytic medium and more efficient use of propylene and synthesis gas.[4,6]

The most numerous studies of catalytic reactions by organometallic complexes in aqueous solution involve the use of water-soluble phosphine ligands. Reviews covering metal complexes of water-soluble phosphines have appeared.[1−4,7] Several studies have examined hydrogenation of substrates in aqueous solution[8−11] and other catalytic reactions.[12−14]

The growing area of homogeneous catalysis in water has not been accompanied by systematic studies of organometallic reactions in aqueous solution. In this manuscript, we report the synthesis and characterization of iridium(I) complexes *trans*-$Ir(CO)X(TPPMS)_2$ (X = Cl, OH, and CH_3) and $Ir(CO)H(TPPMS)_3$ and several reactions of these complexes.

Experimental Section

Materials. $IrCl_3\cdot 3H_2O$ was purchased or borrowed from Johnson Matthey. Triphenylphosphine, fuming sulfuric acid (20% and 30% SO_3), tri-*n*-octylamine, benzyltriethylammonium chloride, and trifluoroacetic acid were purchased from Aldrich Chemical Company. Deuterated solvents were purchased from Cambridge Isotope Labs, Aldrich Chemical Company, or MSD Labs. Gases (CO, H_2) were purchased from Matheson. All of these materials were used as received without further purification unless otherwise noted.

Solvents. Solvents used outside of the glovebox were used as received without further drying or purification unless otherwise noted. Solvents used within the glovebox were prepared as follows: benzene, toluene, THF, and diethyl ether were refluxed in a nitrogen atmosphere over Na/benzophenone until the solution turned blue or purple in color. Hexane and pentane were refluxed overnight in a nitrogen atmosphere over finely divided CaH_2. CD_2Cl_2 and $CDCl_3$ were stirred overnight

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over finely divided CaH_2, followed by vacuum distillation into an oven-dried pressure tube fitted with a Teflon stopcock. Water was triply distilled and deionized. D_2O and DMSO-d_6 were degassed on the high-vacuum line (three freeze−pump−thaw cycles) in a pressure tube fitted with a Teflon stopcock.

Instrumental Measurements. ^1H and ^{31}P NMR spectra were recorded using a Varian VXR-400 NMR spectrometer. ^1H NMR spectra were referenced to residual solvent resonances in the deuterated solvent. All NMR spectra contained resonances corresponding to aromatic protons; however, these resonances were not assigned unless otherwise noted. ^{31}P NMR spectra were referenced to an external sample of 85% H_3PO_4 in D_2O (reference was set to 0.0 ppm) and are proton decoupled. All chemical shifts (δ) are reported in ppm and all coupling constants (J) are reported in Hz.

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 0.10 mm CaF_2 (used for spectra obtained in DMSO, 2-methoxyethanol, and water) solution cells. Solid state spectra were recorded as KBr disks. All spectral data are reported in wavenumbers (cm^{-1}).

All pH measurements were made with a Fisher Scientific Accumet pH meter utilizing a glass pH electrode with a silver/silver chloride reference electrode. The pH meter was referenced to three buffers (pH = 4, 7, 10) before all measurements. The error limit on the pH measurements was ±0.02.

TPPMS.[15] A 100 mL Schlenk flask equipped with a stir bar was flushed with N_2 gas for 15 min. Twenty milliliters of 30% SO_3:H_2SO_4 was added under $N_2(g)$ purge. The flask was cooled on an ice bath for 15 min under a $N_2(g)$ atmosphere. The flask was maintained on an ice bath, and 10.0 g of PPh_3 was added under a $N_2(g)$ purge. (Addition of the triphenylphosphine was conducted over a period of 1 h.) Once all of the triphenylphosphine was in solution, the flask was heated to 90 °C in a water bath for 2 h. The reaction mixture was then poured into 200 mL of deaerated water, and 15 mL of tri-*n*-octylamine was added to the solution under $N_2(g)$ flow. The reaction mixture was allowed to cool to room temperature under nitrogen.

The water solution was then extracted with approximately 200 mL of toluene in a 500 mL separatory funnel. The toluene solution was then extracted with approximately 400 mL of 5% KOH(aq). The solvent volume was reduced and the solution was placed in the refrigerator. The product was collected on a sintered glass frit yielding 9.16 g of TPPMS (58%). ^{31}P NMR spectra were obtained in DMSO-d_6 and D_2O. Each spectrum contained a single resonance located at $\delta = -5.1$ (s) -5.4 (s) ppm, respectively. Anal. Calcd for $PPh_2(C_6H_4SO_3K{\cdot}H_2O)$: C, 54.26; H, 4.05; P, 7.77; S, 8.05; K, 9.81. Found: C, 55.36; H, 4.12; P, 8.09; S, 8.02; K, 9.83.

Benzyltriethylammonium−TPPMS. A Schlenk flask equipped with a stir bar was flushed with $N_2(g)$ for 15 min. The flask was loaded with 0.22 g (0.53 mmol) of TPPMS and 0.28 g (1.2 mmol) of benzyltriethylammonium chloride. Fifty milliliters of deaerated H_2O was added, and the mixture stirred overnight. Initially the solution was clear but turned cloudy after several minutes of stirring.

The reaction mixture was filtered on a 30 mL fine porosity sintered glass frit. The white precipitate was washed with a small amount of water. The product was dissolved in a minimum amount of CH_2Cl_2. The solution was transferred to a H-tube for crystallization, with pentane as the cosolvent.

After 1 week, large colorless crystals were isolated on a medium porosity sintered glass frit. The crystals were characterized by ^{31}P NMR spectroscopy and an X-ray crystallographic analysis. The ^{31}P NMR spectrum, obtained using CD_2Cl_2 as the solvent, contained a single resonance at $\delta = -3.8$ (s) ppm.

***trans*-Ir(CO)Cl(TPPMS)$_2$.** In the drybox, a 125 mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 0.530 g (1.3 mmol) of TPPMS and 0.500 g (0.64 mmol) of *trans*-Ir(CO)(Cl)$(PPh_3)_2$.[16] Fifty milliliters of THF was added, and the reaction mixture stirred overnight in the glovebox. The yellow precipitate was collected using a fine porosity, sintered glass frit and washed with approximately 75 mL of benzene to remove any unreacted starting complex or free triphenylphosphine. After the precipitate was dried overnight under vacuum, 0.42 g of yellow powder remained (60% yield based on the starting Ir complex). The product was pure as isolated, but can be recrystallized from 2-methoxyethanol:2-propanol or DMSO:THF. The small crystals obtained were not of crystallographic quality. Anal. Calcd for $Ir(CO)Cl(K(TPPMS){\cdot}H_2O)_2$: C, 42.6; H, 3.4; P, 5.8; S, 5.7; K, 7.1. Found: C, 42.2; H, 3.1; P, 5.9; S, 6.1; K, 7.4.

An infrared spectrum showed a single absorbance in the carbonyl region at 1962 cm^{-1} in KBr, 1964 cm^{-1} in DMSO, 1967 cm^{-1} in 2-methoxyethanol and 1974 (br) cm^{-1} in H_2O. A ^{31}P NMR spectrum obtained in DMSO-d_6 showed a single resonance at $\delta = 25.6$ (s) ppm. Mass spectral analysis using FAB as the ionization mode, NBA (*n*-butanol) as the matrix, and DMSO as the solvent yielded a parent peak at m/e = 1016.8. The (M + 1) peak calculated for *trans*-Ir(CO)(Cl)-(TPPMS)$_2$ is 1017. A peak at m/e = 1054.5 corresponds to the (M + K^+) species. The observed isotope pattern for the peak at m/e = 1016.8 matches that calculated for *trans*-Ir(CO)(Cl)-(TPPMS)$_2$.

The compound was previously prepared through a laborious procedure and only characterized by its ν_{CO}[17] and more recently by a procedure nearly identical to ours.[18]

***trans*-Ir(CO)(OH)(TPPMS)$_2$.** In the drybox, a 125 mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 0.547 g of TPPMS (1.3 mmol) and 0.500 g of *trans*-Ir(CO)(OH)$(PPh_3)_2$[19] (0.66 mmol). Fifty milliliters of THF was added, and the reaction mixture stirred overnight in the drybox. The yellow precipitate was filtered from the reaction mixture using a fine, sintered glass frit and washed with approximately 75 mL of benzene to remove any unreacted starting complex or free triphenylphosphine. After the precipitate was dried overnight in the drybox, 0.564 g of yellow powder (60% yield) was isolated.

The product was pure as isolated and was recrystallized from 2-methoxyethanol:2-propanol or DMSO:THF. The small crystals obtained are not of crystallographic quality. IR (KBr) = 1944 cm^{-1}; (DMSO) = 1934 cm^{-1}; (H_2O) = 1952 cm^{-1}. A ^{31}P NMR spectrum taken in DMSO-d_6 or in D_2O had a single resonance at $\delta = 26.6$ (s) ppm. ^1H NMR (DMSO-d_6): δ 0.17 (t, $J_{P-H} = 6.8$ Hz).

***trans*-Ir(CO)(CH$_3$)(TPPMS)$_2$.** In the glovebox, 0.106 g (0.14 mmol) of *trans*-Ir(CH$_3$)(CO)$(PPh_3)_2$[20] was suspended in 20 mL of THF and 0.090 g (0.226 mmol) of TPPMS was added. The solution was stirred overnight. The canary yellow precipitate was collected on a fine, sintered glass filter and washed first with THF and then with benzene, yield 103.4 mg or 87%. IR(DMSO): ν_{CO} 1937 cm^{-1}. ^{31}P NMR (DMSO-d_6): δ 31.5 (br). ^1H NMR (DMSO-d_6): $\delta(CH_3) = -0.4$ (t, $J_{P-H} = 9$ Hz). All ^{31}P and ^1H NMR resonances were consistent with those of the PPh_3 analogue.[20] Anal. Calcd for *trans*-Ir(CO)(CH$_3$)-$(P(C_6H_5)_2(C_6H_4SO_3K))_2$: C, 45.82; H, 3.14; P, 6.22; S, 6.44. Found: C, 45.84; H, 3.71; P, 6.20; S, 6.34.

Ir(CO)(H)(TPPMS)$_3$. (A) In the drybox, a 125 mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 0.300 g of TPPMS (0.72 mmol) and 0.25 g of *trans*-Ir(CO)-

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(H)(PPh_3)$_3$[21] (0.25 mmol). Fifty milliliters of THF was added and the reaction mixture stirred for 2 weeks in the drybox. The pale yellow precipitate was filtered from the reaction mixture using a fine, sintered glass frit and washed with approximately 75 mL of benzene to remove any unreacted starting complex or free triphenylphosphine. After the precipitate was dried overnight in a drybox, 0.210 g of yellow powder remained (58% yield). The product was pure as isolated and could be recrystallized from 2-methoxyethanol: 2-propanol or DMSO:THF. Infrared spectral analysis in KBr revealed two absorbances at 2064 and 1927 cm^{-1}, which were assigned as the iridium−hydride and carbonyl stretches, respectively. IR (H_2O): ν_{CO} 1926 cm^{-1}. The ^{31}P NMR spectrum showed a single resonance at $\delta = 14.9$ (s) in DMSO-d_6 and $\delta = 15.6$ (s) in D_2O. The hydride region of the ^{1}H NMR spectrum showed a single resonance at $\delta = -11.0$ (q, $J_{P-H} = 21.3$ Hz) in DMSO-d_6 and $\delta = -10.8$ (q, $J_{P-H} = 21.9$ Hz) in D_2O.

(B) In the glovebox, a 100 mL Schlenk flask equipped with a stir bar was loaded with 0.373 g of Ir(CO)H(PPh_3)$_3$ (0.37 mmol) and 0.462 g of TPPMS (1.16 mmol). Sixty milliliters of THF was added and the flask was sealed under an Ar(g) atmosphere and removed from the box. On the Schlenk line, the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux under a N_2(g) atmosphere. After the mixture was refluxed for 9 days, the contents of the flask were allowed to cool to room temperature. The flask was then taken into the inert atmosphere glovebox where the reaction mixture was filtered on a medium porosity, sintered glass frit. The pale yellow powder isolated was washed with 15 mL of THF and 30 mL of diethyl ether. After the precipitate was dried on the frit, 0.551 g of the pale yellow powder was recovered. The characterization was the same as described in A, with the exception that there was approximately 5% free TPPMS in the product.

[*cis,mer*-Ir(CO)(H)$_2$(TPPMS)$_3$]CF_3COO. In the glovebox, a 100 mL Schlenk flask equipped with a stir bar was charged with 0.223 g of Ir(CO)H(TPPMS)$_3$. On the Schlenk line, 50 mL of deaerated H_2O was added under N_2(g) purge. The result was a rich yellow solution. Several drops of CF_3COOH were added under N_2(g) purge. The solution immediately became colorless. This colorless solution was allowed to stir overnight. The solvent was pumped off at room temperature resulting in a "wet" solid. The flask was sealed and pumped into the glovebox under vacuum.

In the glovebox, 25 mL of diethyl ether was added to the flask. This mixture was allowed to stir for 1 h. An off-white powder was isolated on a medium porosity sintered glass frit. The product was characterized by infrared and ^{31}P and ^{1}H NMR spectroscopies. An infrared spectrum obtained as a KBr pellet showed the following absorbances: $\nu_{Ir-H} = 2118$ cm^{-1}; ν_{C-O} (terminal carbonyl) = 2019 cm^{-1}; and ν_{C-O} (trifluoroacetate carbonyl) = 1666 cm^{-1}. The infrared spectrum in H_2O showed $\nu_{Ir-H} = 2110$ (br) and $\nu_{CO} = 2016$ (br) cm^{-1}. The assignments of the resonances recorded in the ^{31}P and ^{1}H NMR spectra are ^{1}H NMR (DMSO-d_6) $\delta = -9.6$ (q, $J_{P-H} = 13.6$ Hz, 1H); $\delta = -11.5$ (dt, $J_{P-H-trans} = 115.2$ Hz, $J_{P-H-cis} = 18.3$ Hz, 1H). The coupling between the two hydrides was observed in some especially well-resolved spectra and was approximately 4 Hz. ^{31}P NMR spectrum (DMSO-d_6): δ 3.09 (d, $J_{P-P} = 13.7$ Hz, 2P); δ 0.70 (t, $J_{P-P} = 13.7$ Hz, 1P). ^{1}H NMR (D_2O): $\delta = -9.6$ (q, $J_{P-H} = 16.3$ Hz, 1H); δ −11.5 (dt, $J_{P-H-trans} = 114.4$ Hz, $J_{P-H-cis} = 18.5$ Hz, 1H). ^{31}P NMR (D_2O): $\delta = 3.5$ (d, $J_{P-P} = 8.8$ Hz); 0.1 (br).

Reactions. The reactions with H_2 and CO were accomplished by NMR-scale or preparative-scale procedures. NMR-scale reactions involved 0.030 g of the iridium complex dissolved in 1 mL of DMSO-d_6 or D_2O in the glovebox. The solution was placed into an NMR tube equipped with a teflon stopcock, removed from the glovebox, and placed on a high-vacuum line. The tube was degassed and filled with 0.7 atm of H_2 or CO and flame sealed while frozen. The reaction was followed by NMR spectroscopies.

Table 1. Crystal Data for [$NBzEt_3^+$][PPh_2(m-$C_6H_4SO_3$)$^-$]·H_2O

mol formula	$C_{31}H_{38}NO_4PS$
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14 var)
a, Å	8.514(2)
b, Å	30.060(4)
c, Å	11.821(2)
β, deg	102.531(15)
V, Å^3	2953.9(9)
Z	4
fw	551.7
D(calcd), g/cm^3	1.241
μ(Mo Kα), mm^{-1}	0.191
T, min/max	0.9319/0.9692
2θ range, deg	8.0−45.0
radiation; λ, Å	Mo Kα, 0.710 730
temperature, K	295
index ranges	h, −8 to +8
	k, −28 to +28
	l, 0 to +11
total no. of reflns	5847
no. of indep reflns	2751 (R(int) = 2.22%)
no. of obs data (>6σ)	1518
ext corr	$\chi = 0.0005(2)$
weighting scheme	$w = [\sigma^2(F) + 0.0007F^2]^{-1}$
R	5.18%
R_w	5.87%
ρ (min, max), e/Å^3	−0.42, 0.79

For preparative-scale reactions, 0.050−0.100 g of the iridium complex was placed in a 100 mL Schlenk flask equipped with a stir bar and removed from the glovebox. The desired solvent (DMSO, H_2O, etc.) was degassed by bubbling N_2 through it for 15 min and added to the iridium complex. The flask was purged with H_2 or CO and allowed to react.

pH Measurements. The water-soluble iridium complex was weighed (30 mg) into a three-necked round bottom flask in a glovebox. The flask was removed from the glovebox, and under N_2 purge, 3.0 mL of H_2O was added. The pH was measured periodically under N_2.

Collection of X-ray Diffraction Data for [$NBzEt_3^+$]-[PPh_2(m-$C_6H_4SO_3$)$^-$]·H_2O. A colorless crystal (dimensions 0.2 × 0.35 × 0.5 mm) was inserted into a thin-walled glass capillary and aligned on a Siemens R3m/V diffractometer. Determination of Laue symmetry, crystal class, and unit cell dimensions were carried out as described previously.[22] Details appear in Table 1.

Solution and Refinement of the Structure. All crystallographic calculations were performed on a VAXstation 3100 computer, with use of the Siemen's SHELXTL PLUS program package.[23] The analytical forms of the scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[24] The structure was solved by a combination of direct methods and difference-Fourier techniques and was refined to $R = 5.18\%$ and $R_w = 5.87\%$ for those data with $|F_o| > 6\sigma(|F_o|)$. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms of the organic systems were placed in the appropriate idealized trigonal or tetrahedral locations with d(C−H) = 0.96 Å.[25] The hydrogen atoms of the water molecule of solvation were located from a difference-Fourier map but were not further refined. The residual electron density on a final difference-Fourier map was in the range from −0.42 to +0.79 e/Å^3.

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Table 2. Infrared Stretching Frequencies (in cm^{-1}) for TPPMS Complexes of Iridium Compared to PPh_3 Complexes

complex	L = TPPMS	L = PPh_3
trans-$Ir(CO)(Cl)L_2$	1962[a]	1955[b,16]
trans-$Ir(CO)(OH)L_2$	1944[a]	1925[a,19]
$Ir(CO)_3L_2^+$	2078, 2022, 2007[c]	2070, 2020, 1997[a,44]
$Ir(CO)(H)L_3$	1927[a]	1927[a,21]

[a] KBr. [b] Benzene. [c] H_2O.

Table 3. ^{31}P Resonances (in ppm from H_3PO_4) for TPPMS Complexes in Comparison to PPh_3 Complexes

complex	L = TPPMS	L = PPh_3
trans-$Ir(CO)(Cl)L_2$	25.6[a]	23.7[b]
trans-$Ir(CO)(OH)L_2$	27.7[c]	27.9[b]
$Ir(CO)_3L_2^+$	−2.2[a]	−2.4[a]
$Ir(CO)(H)L_3$	15.6[c]	16.5[b]

[a] DMSO. [b] $CDCl_3$. [c] D_2O.

Results and Discussion

Synthesis and Characterization. Complexes of iridium(I) with TPPMS can be prepared by exchange of TPPMS for PPh_3 in THF.

$$\begin{aligned} &trans\text{-}Ir(CO)X(PPh_3)_2 + TPPMS \xrightarrow{THF} \\ &\qquad trans\text{-}Ir(CO)X(TPPMS)_2\,(\downarrow) + PPh_3 \quad (1) \end{aligned}$$

The reactions were accomplished with a slight molar deficiency of TPPMS such that the precipitate was pure complex; *trans*-$Ir(CO)(X)(PPh_3)_2$ and PPh_3 remained in the THF solution. From the carbonyl stretching frequencies (Table 2) and ^{31}P resonances (Table 3), it is apparent that the TPPMS complexes are very similar to the PPh_3 analogues, but with altered solubility. The TPPMS complexes of iridium(I) are not soluble in Et_2O, THF, or other organic solvents; they are quite soluble in DMSO and have some solubility in H_2O. The chloro complex, *trans*-$Ir(CO)(Cl)(TPPMS)_2$, is only slightly soluble in H_2O ($\sim 2 \times 10^{-5}$ M, sufficient for infrared and kinetic studies, but not for routine NMR characterization), while the hydroxo analogue, *trans*-$Ir(CO)(OH)(TPPMS)_2$, has excellent solubility in water.

Structure of TPPMS. The TPPMS ligand has been known for years, and a number of complexes have been prepared with this ligand, but the structure has not, to our knowledge, been reported. We obtained good crystals as the $NEt_3(CH_2C_6H_5)^+$ salt and determined the structure. This compound consists of an ordered array of $[NBzEt_3^+]$ cations, $[PPh_2(m\text{-}C_6H_4SO_3)^-]$ anions, and water of solvation in a 1:1:1 ratio. The Supporting Information contains a figure which shows a view of the $[PPh_2(m\text{-}C_6H_4SO_3)^-]$ anion, while Figure 1 shows the entire crystallographic asymmetric unit, including the hydrogen-bonding scheme between the water molecule and the sulfonate anion. Interatomic distances and angles are collected in Table 4.

The phosphorus atom is in the expected trigonal pyramidal environment, and the P−C distances are essentially equivalent, with P(1)−C(11) = 1.830(6) Å, P(1)−C(21) = 1.828(6) Å, and P(1)−C(31) = 1.819(7) Å. The C−P−C angles are C(11)−P(1)−C(21) = 104.0(3)°, C(11)−P(1)−C(31) = 101.1(3)°, and C(21)−P(1)−C(31) = 102.5(3)°. The mean P−C distance is 1.826 Å, and the mean C−P−C angle is 102.5°; these results are insignificantly different from the values of 1.828 ± 0.005 Å and 103.0 ± 0.8° reported by Daly for the structure of PPh_3.[26] The geometry around phosphorus in $P(p\text{-}C_6H_4SO_3K)_3 \cdot KCl \cdot 0.5H_2O$ is also nearly identical with that in PPh_3.[27] The sulfur atom associated with the SO_3^- group has a tetrahedral environment, with the O−S−C angles averaging 105.5° and the O−S−O angles averaging 113.1°. The S(1)−C(13) distance of 1.781(6) Å is indicative of a sulfur−carbon single bond, while the mean S−O bond distance of 1.442 Å is consistent with a sulfur−oxygen bond order between 1.5 and 2.0 and may be compared with the mean S−O distance of 1.473 ± 0.013 Å observed for the SO_4^{2-} anion.[28]

A system of hydrogen bonding links the $[PPh_2(m\text{-}C_6H_4SO_3)]^-$ anions through H_2O molecules of solvation. The O···O contact within this hydrogen bonding scheme is O(2)···O(1s) = 2.929(8) Å.

pH of the Complexes. The pH values measured for ~35 mg of iridium complex in 3.0 mL of H_2O ($\sim 1 \times 10^{-2}$ M) are given in Table 5. The hydroxo complex, *trans*-$Ir(CO)(OH)(TPPMS)_2$, is somewhat more basic than the chloro complex, but the pH of 8.7 is not sufficiently basic to indicate dissociation of OH^- as a strong electrolyte. The most interesting aspect of the pH values is that $Ir(CO)(H)(TPPMS)_3$ is quite basic. Usually late transition metal hydrides are acidic; pK_a values are known for many hydrides.[29] The pH value of 10.7 indicates that $Ir(CO)(H)(TPPMS)_3$ is sufficiently basic to be protonated in water. This is observed and is described in the following section. The conjugate acid, *cis,mer*-$Ir(CO)(H)_2(TPPMS)_3^+$, is a weak acid with a pH of 2.5.

Reactions with Water. In contrast to most organic solvents, water is not innocuous. Protonation, hydrogen exchange, and nucleophilic attack may be expected in aqueous solution.[30] Protonation reactions have been observed previously on iridium hydride complexes. For example, $Ir(CO)(H)(PPh_3)_3$ was protonated to $Ir(CO)(H)_2(PPh_3)_3^+$ by CF_3CO_2H[31] and $Ir(CO)_2(H)(P(p\text{-tolyl})_3)_2$ was protonated to $Ir(CO)_2(H)_2(P(p\text{-tolyl})_3)_2^+$ by HBF_4.[32,33] A similar protonation of $Ir(CO)(H)(TPPMS)_3$ with CF_3CO_2H led to the clean synthesis of $Ir(CO)(H)_2(TPPMS)_3^+$. The infrared spectrum, $\nu_{CO} = 2020$ (s) cm^{-1} and $\nu_{Ir-H} = 2118$ (m) cm^{-1}, agrees with that reported by Kong and Roundhill for $Ir(CO)(H)_2(PPh_3)_3^+$.[31] The NMR spectra are diagnostic for the geometry shown in Figure 2. H_a is a quartet (−10.5 ppm, $J_{P-H} = 16.7$ Hz) from the accidental degeneracy of the coupling from three *cis* TPPMS ligands. H_b is a doublet of triplets (−12.4 ppm, $J_{P-H(trans)} = 115.6$ Hz, $J_{P-H(cis)} = 18.1$ Hz). In DMSO-d_6 the TPPMS ligands show two resonances in a 1:2 integrated ratio at 0.66 (t) and 4.44 (d), $J_{P-P} = 14$ Hz. These spectroscopic data require the *cis,mer* geometry shown in Figure 2.

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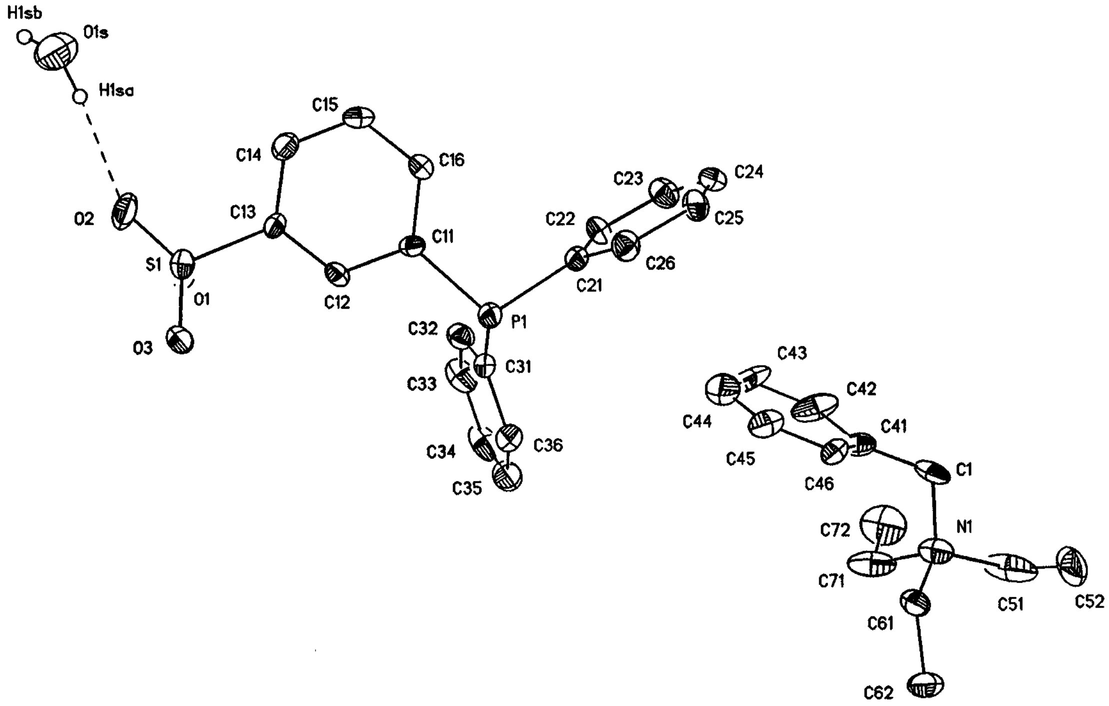


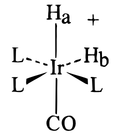
Figure 1. The crystallographic asymmetric unit for $[NBzEt_3^+][PPh_2(m\text{-}C_6H_4SO_3)^-]\cdot H_2O$. Organic hydrogen atoms are omitted for clarity.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[NBzEt_3^+][PPh_2(m\text{-}C_6H_4SO_3)^-]\cdot H_2O$

P(1)−C(11)	1.830 (6)	P(1)−C(21)	1.828 (6)
P(1)−C(31)	1.819 (7)	S(1)−O(1)	1.437 (6)
S(1)−O(2)	1.440 (5)	S(1)−O(3)	1.448 (5)
S(1)−C(13)	1.781 (6)	C(11)−C(12)	1.399 (9)
C(11)−C(16)	1.381 (8)	C(12)−C(13)	1.381 (8)
C(13)−C(14)	1.388 (8)	C(14)−C(15)	1.371 (11)
C(15)−C(16)	1.379 (9)	C(21)−C(22)	1.375 (10)
C(21)−C(26)	1.384 (10)	C(22)−C(23)	1.364 (10)
C(23)−C(24)	1.365 (12)	C(24)−C(25)	1.365 (13)
C(25)−C(26)	1.389 (11)	C(31)−C(32)	1.368 (11)
C(31)−C(36)	1.386 (10)	C(32)−C(33)	1.376 (12)
C(33)−C(34)	1.372 (16)	C(34)−C(35)	1.356 (20)
C(35)−C(36)	1.392 (14)	N(1)−C(1)	1.532 (8)
N(1)−C(51)	1.479 (13)	N(1)−C(61)	1.497 (9)
N(1)−C(71)	1.699 (11)	C(1)−C(41)	1.489 (10)
C(41)−C(42)	1.397 (13)	C(41)−C(46)	1.354 (11)
C(42)−C(43)	1.403 (16)	C(43)−C(44)	1.371 (18)
C(44)−C(45)	1.325 (17)	C(45)−C(46)	1.366 (12)
C(51)−C(52)	1.517 (17)	C(61)−C(62)	1.518 (9)
C(71)−C(72)	1.405 (15)		
C(11)−P(1)−C(21)	104.0(3)	C(11)−P(1)−C(31)	101.1(3)
C(21)−P(1)−C(31)	102.5(3)	O(1)−S(1)−O(2)	113.3(3)
O(1)−S(1)−O(3)	113.5(3)	O(2)−S(1)−O(3)	112.6(3)
O(1)−S(1)−C(13)	105.3(3)	O(2)−S(1)−C(13)	105.6(3)
O(3)−S(1)−C(13)	105.7(3)	P(1)−C(11)−C(12)	117.5(4)
P(1)−C(11)−C(16)	124.8(5)	P(1)−C(21)−C(22)	125.0(5)
P(1)−C(21)−C(26)	117.1(5)	P(1)−C(31)−C(32)	125.6(5)
P(1)−C(31)−C(36)	115.8(6)		

Table 5. Measured pH Values for TPPMS Complexes of Iridium(I) ($\sim 1.0 \times 10^{-2}$ M) in H_2O

complex	pH
trans-Ir(CO)(Cl)$(TPPMS)_2$	6.1
trans-Ir(CO)(OH)$(TPPMS)_2$	8.7
Ir(CO)(H)$(TPPMS)_3$	10.7
cis,mer-Ir(CO)$(H)_2(TPPMS)_3^+$	2.5



L = TPPMS

Figure 2. Structure of $Ir(CO)(H)_2(TPPMS)_3^+$.

While protonation of iridium hydride complexes with strong acids such as HBF_4 or CF_3CO_2H is precedented, the possibility of protonating Ir(CO)(H)$(TPPMS)_3$ by H_2O suggested by the pH values is unprecedented. Dissolving Ir(CO)(H)$(TPPMS)_3$ in water produces Ir(CO)$(H)_2(TPPMS)_3^+$ in equilibrium with the monohydride, indicating that the iridium center of Ir(CO)(H)$(TPPMS)_3$ is a stronger base than H_2O. This reactivity supports the measurement of the pH for Ir(CO)(H)$(TPPMS)_3$. When Ir(CO)(H)$(TPPMS)_3$ is placed in D_2O, the resonance for H_b is absent but H_a and the ^{31}P resonances are consistent with the formation of *cis,mer*-Ir(CO)(H)(D)$(TPPMS)_3^+$.

That the resonance labeled H_a is observed when Ir(CO)(H)$(TPPMS)_3$ is dissolved in D_2O indicates that H−D exchange is not always rapid. Preparation of Ir(CO)$(H)_2(TPPMS)_3^+$ in H_2O and then dissolution in D_2O shows that H_b loses intensity and coupling rapidly (minutes) while H_a exchanges for deuterium only over several days. These results provide the limits observed for hydrogen−deuterium exchange between iridium hydrides and D_2O. The other hydride prepared in this study, Ir(CO)$(H)_3(TPPMS)_2$, exchanged with D_2O only slowly (over a couple of days).

None of the iridium hydrides prepared in this study reacted with water to eliminate H_2.

Reactions. The complexes *trans*-Ir(CO)X$(TPPMS)_2$, X = Cl and OH, retain the reactivity typical for square-planar iridium(I) complexes. In DMSO, the chloro complex reacts with H_2 to give the dihydride, Ir(CO)(Cl)$(H)_2(TPPMS)_2$, with spectral properties very similar to those for the PPh_3 analogues as shown in Table 6. Using Crabtree's nomenclature, this corresponds to a parallel addition of H_2.[34] The reaction of *trans*-Ir(CO)(Cl)$(TPPMS)_2$ with H_2 in water was not studied by NMR

Table 6. Spectral Properties for $Ir(CO)(Cl)(H)_2L_2$, L = TPPMS, PPh_3

L	ν_{CO} (cm^{-1})	ν_{Ir-H} (cm^{-1})	^{31}P (ppm)	^{1}H (ppm)[a]
TPPMS	1990[b]	2093 (s), 2204 (vw)[b]	11.6[c]	-8.3 (td, $J_{P-H} = 17.6$, $J_{H-H} = 4.8$), -19.4 (td, $J_{P-H} = 14.0$, $J_{H-H} = 4.8$)
PPh_3	1988[d]	2092 (br), 2212 (vw)	7.6[e]	-7.3 (td, $J_{P-H} = 17.2$, $J_{H-H} = 4.4$) -18.6 (td, $J_{P-H} = 13.8$, $J_{H-H} = 4.4$)

[a] Coupling constants, *J*, reported in Hertz. [b] In DMSO, in H_2O the absorptions are $\nu_{CO} = 2012$ (br), $\nu_{Ir-H} = 2104$ (br). [c] In DMSO. [d] In DMSO, in toluene the absorptions are $\nu_{CO} = 1990$, $\nu_{Ir-H} = 2095$ (br), 2191(w). [e] In CD_2Cl_2 for the L = P(*p*-tolyl)$_3$ complex, the PPh_3 complex lacks solubility for good NMR characterization.

because of poor solubility of *trans*-$Ir(Cl)(CO)(TPPMS)_2$. However, the hydroxy complex has good water solubility and was studied. Reaction with H_2 produces $Ir(CO)(H)_3(TPPMS)_2$ (*fac* isomer only) and $HIr(CO)L_3$ (and the protonated form) in variable yields that depend on the amount of H_2 available (eq 2). When run in a Schlenk

$$trans\text{-}Ir(CO)(OH)(TPPMS)_2 \xrightarrow[-H_2O]{H_2} fac\text{-}Ir(CO)(H)_3(TPPMS)_2 + Ir(CO)(H)(TPPMS)_3 \quad (2)$$

flask under H_2, the trihydride dominates, but in an NMR tube, where the amount of H_2 is limited, the monohydride product dominates.[35] These products are consistent with the formation of *trans*-$Ir(CO)(H)(TPPMS)_2$ as an unstable intermediate by oxidative addition of H_2 and reductive elimination of H_2O. The square-planar hydride has not been observed for any phosphine ligands; for PPh_3, it reacts rapidly with any small molecule and in the absence of H_2, CO, etc., decomposes to $Ir(CO)(H)(PPh_3)_3$.[36] When H_2 is limited (as in the NMR tube reactions), $Ir(CO)(H)(TPPMS)_3$ dominates as a product of reaction 2. In DMSO, where the $[H_2]$ is nearly five times greater, the trihydrides (*fac* and *mer*) are the only products formed from reaction of H_2 with *trans*-$Ir(CO)(OH)(TPPMS)_2$.

An interesting facet of the reactions of *trans*-$Ir(CO)(OH)(TPPMS)_2$ with H_2 is the different isomer formation in DMSO (both *fac* and *mer* in ~1:1 ratio) and H_2O (only the *fac* isomer observed).[37] Since the ratio of *fac*- and *mer*-isomers in DMSO is very similar to the equilibrium ratio observed for $Ir(CO)(H)_3(PPh_3)_2$ in organic solvents,[36] we assume that the equilibrium is established in DMSO. In H_2O, only the facial isomer is observed. No change in the isomer ratio from toluene to DMSO with a dramatic change for the ratio in H_2O is a strong indication that hydrogen-bonding interactions hold the TPPMS ligands *cis* in the facial isomer. Hydrogen-bonding through H_2O was shown by the structure of $NEt_3(CH_2Ph)^+[PPh_2(m\text{-}C_6H_4SO_3)^-]\cdot H_2O$. Previously, strong intramolecular hydrogen-bonding interactions between TPPTS ligands were suggested to account for a lowered TPPTS lability in $Rh(CO)(H)(TPPTS)_3$ in comparison to $Rh(CO)(H)(PPh_3)_3$.[38] Such interactions may provide extra stability to the *cis*-TPPMS ligands in *fac*-$Ir(CO)(H)_3(TPPMS)_2$.

While we have not examined the kinetics of H_2 addition to *trans*-$Ir(CO)(OH)(TPPMS)_2$, in H_2O or DMSO, the reaction occurs over days, much slower than reaction of H_2 with the chloro analogue in these solvents. This is similar to the deactivation of the iridium(I) center of *trans*-$Ir(CO)(OH)(PPh_3)_2$ in toluene toward reaction with H_2.[39] A significant rate dependence for reaction of H_2 with *trans*-$Ir(CO)(X)(PPh_3)_2$ has been reported, where the more polarizable X reacts more rapidly.[40] The lack of reactivity for *trans*-$Ir(CO)(OH)L_2$ is consistent with that interpretation.

Reactions with carbon monoxide have also been examined for square-planar iridium complexes. In organic solvents, *trans*-$Ir(CO)(Cl)(PPh_3)_2$ reacts with CO to give the five-coordinate, dicarbonyl in an equilibrium

$$trans\text{-}Ir(CO)(Cl)(PPh_3)_2 + CO \rightleftharpoons Ir(CO)_2Cl(PPh_3)_2 \quad (3)$$

but reaction of *trans*-$Ir(CO)(Cl)(PMe_2Ph)_2$ with CO in CH_3OH gives $[Ir(CO)_3(PMe_2Ph)_2]Cl$.[41] Reaction of *trans*-$Ir(CO)(Cl)(TPPMS)_2$ in DMSO or H_2O produces $[Ir(CO)_3(TPPMS)_2]Cl$, also in an equilibrium.

$$trans\text{-}Ir(CO)(Cl)(TPPMS)_2 + 2CO \rightleftharpoons [Ir(CO)_3(TPPMS)_2{}^+]Cl^- \quad (4)$$

The five-coordinate cation was characterized spectroscopically.[42] In DMSO, the neutral, dicarbonyl complex was an intermediate ($Ir(CO)_2(Cl)(TPPMS)_2$; $\nu_{CO} = 1978$ (s), 1926 (w) cm^{-1}; $^{31}P = 8.9$ ppm) but this species was not observed in H_2O. The back reaction (loss of CO) indicates considerable CO lability for $[(Ir(CO)_3(TPPMS)_2]Cl$. In DMSO, reactions of the PPh_3 and TPPMS complexes can be directly compared since $[Ir(CO)_3L_2{}^+]Cl^-$ is the product in each reaction. Approximate equilibrium constant calculations from infrared spectra show that the cation is favored by a factor of three for L = TPPMS over L = PPh_3. In neutral or basic H_2O, another product is observed with a ^{31}P resonance at -2.1 ppm and with a CO stretch at 2003 cm^{-1}. This product is minor, but is increased at short times or with less CO. We tentatively assign this product as $[Ir(CO)_2(TPPMS)_2{}^+]Cl$,[43] which may be an intermediate in the formation of $Ir(CO)_3(TPPMS)_2{}^+$ in aqueous solution.

Carbonylation of *trans*-$Ir(CO)(OH)(TPPMS)_2$ is considerably more complicated. The PPh_3 analogue is

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(34) Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034.

(35) In the NMR tube the mole ratio of H_2:Ir complex is 6:1, while in the Schlenk flask the mole ratio is 40:1.

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(37) *fac*-$Ir(CO)(H)_3(TPPMS)_2$: ^1H NMR (D_2O) -11.9 (second order), -10.5 (t) ppm; ^{31}P (D_2O): 5.9 (s) ppm. These are consistent with the characterization for *fac*-$Ir(CO)(H)_3(PPh_3)_2$.[32]

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(42) Infrared characterization of $[Ir(CO)_3L_2{}^+]$: L = PPh_3 in DMSO, $\nu_{CO} = 2074$ (w), 2014 (s), 2004 (s) cm^{-1}; L = TPPMS in DMSO, $\nu_{CO} = 2072$ (w), 2014 (s), 2003 (s) cm^{-1}; L = TPPMS in H_2O, $\nu_{CO} = 2078$ (w), 2022 (sh), 2007 (s) cm^{-1}; ^{31}P NMR (D_2O) = -2.4 ppm.

(43) Faraone, F.; Piraino, P.; Pietropaolo, R. *J. Chem. Soc. Dalton Trans.* **1973**, 1625.

unreactive toward 1 atm of CO.[44] Reaction of *trans*-Ir(CO)(OH)(TPPMS)$_2$ with CO in DMSO produces Ir(CO)$_3$L$_2^+$ and Ir(CO)$_2$(H)L$_2$ (L = TPPMS) in a 1:1 ratio. These are the expected products in a reaction that leads first to [Ir(CO)$_3$(TPPMS)$_2^+$][OH$^-$]; OH$^-$ then attacks at a carbon of CO producing CO$_2$ and Ir(CO)$_2$(H)(TPPMS)$_2$. The CO$_2$ produced would partly neutralize the OH$^-$, giving the two products in approximately equal amounts in DMSO. In H$_2$O, the same products are observed initially but further reactions leading to unidentified products occur with time.

Conclusion

The TPPMS complexes of iridium are very similar to their PPh$_3$ analogues. The spectral characterizations are nearly identical. The reactions of the TPPMS complexes in DMSO are almost the same as reactions of PPh$_3$ complexes in toluene, although a preference for ion formation in carbonylation was observed for the TPPMS complexes. However, the TPPMS complexes of iridium in water show weak acid/base equilibria and ionization processes not observed for iridium complexes in nonaqueous solvents.

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Supporting Information Available: Crystallographic details, tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms, and an ORTEP drawing of TPPMS (7 pages). Ordering information is given on any current masthead page.

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[44] Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179 and references therein.