

Hydrolysis of an iridium–methyl bond, formation of *trans*-[Ir(CO)(OH)L₂] from *trans*-[Ir(CO)MeL₂] [L = PPh₂(*m*-C₆H₄SO₃Na), PPh₂(*m*-C₆H₄SO₃K) or P(C₆H₄SO₃Na)₃] upon dissolving in water

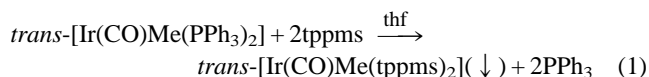
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The synthesis, characterization and rapid hydrolysis of *trans*-[Ir(CO)MeL₂] (L = a water-soluble phosphine) to *trans*-[Ir(CO)(OH)L₂] and CH₄ are reported.

There have been increasing reports on use of water-soluble organometallic complexes as catalysts for hydroformylation and hydrogenation of alkenes.^{1,2} Such catalytic reactions involve, of necessity, formation of metal alkyls. Several alkyl complexes of Cr^{III}, Co^{III} and Pt^{III} have been studied in aqueous solution^{2,3} with both homolytic and heterolytic decomposition pathways identified. However, alkyl complexes of lower valent organometallic centres have not been reported. In this manuscript we report the synthesis of the sodium and potassium salts of *trans*-[Ir(CO)Me(tppms)₂] [tppms = PPh₂(*m*-C₆H₄SO₃⁻)], the attempted synthesis of *trans*-[Ir(CO)Me(tppts)₂] [tppts = P(*m*-C₆H₄SO₃Na)₃] and the rapid hydrolysis of the Ir–Me bond in water.

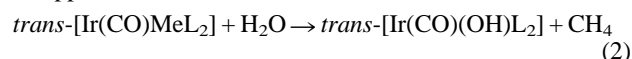
The methyl complexes of tppms were prepared by ligand exchange on *trans*-[Ir(CO)Me(PPh₃)₂] [eqn. (1)].^{4†}



Both the Na⁺ and K⁺ salts precipitate from thf. The characterization data shown in Table 1 confirm the formulation as do the microanalytical data.[‡]

Dissolving *trans*-[Ir(CO)Me(tppmsNa)₂] in H₂O (or D₂O) results in *trans*-[Ir(CO)(OH)(tppmsNa)₂][§] and CH₄ in seconds. The *trans*-[Ir(CO)(OH)(tppmsNa)₂] was indicated by the ³¹P resonance at δ 28.4(s)[§] and the CH₄ by a sharp singlet at δ -0.07(s) in the ¹H NMR. No other resonances were observed in the ³¹P or the ¹H NMR to higher field than δ 6.0. The NMR tube was opened and an IR spectrum recorded (ν_{CO} = 1953 cm⁻¹). To complete characterization of the iridium product the water was removed by vacuum and the residue dissolved in (CD₃)₂SO and combined with 10 mg of *trans*-[Ir(CO)(CH₃)(tppmsNa)₂]

for NMR characterization. The ¹H and ³¹P NMR spectra clearly showed equal quantities of *trans*-[Ir(CO)(OH)(tppmsNa)₂] {³¹P NMR [(CD₃)₂SO], δ 26.9(s); ¹H NMR [(CD₃)₂SO], δ 0.2 (t, J_{PH} 6.5 Hz) and the methyl complex. Thus a rapid hydrolysis of the iridium–methyl bond occurred in water [eqn. (2), L = tppmsNa].



The reaction was sufficiently rapid that the methyl complex could not be observed in H₂O by NMR.

Attempts to prepare *trans*-[Ir(CO)Me(tppts)₂] by biphasic exchange of tppts for PPh₃ always resulted in formation of *trans*-[Ir(CO)(OH)(tppts)₂][§] in a similar hydrolysis reaction.

The very rapid hydrolysis of iridium methyl complexes provides a caution for increasing use of water-soluble organometallic compounds as catalysts. Such hydrolyses, coupled with facile water–gas shift reactions, offer different mechanistic possibilities for organometallic complexes in water.

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Footnotes and References

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† In a glove box, ca. 100 mg of *trans*-[Ir(CO)(CH₃)(PPh₃)₂]⁴ was dissolved in 20 ml of thf and 90 mg of tppms added. The solution was stirred overnight and the canary yellow precipitate collected and washed with thf and with benzene. The yield of the K⁺ salt was 87% (103 mg) and the yield of the Na⁺ salt was 46% (54 mg).

‡ [Ir(CO)(CH₃)(tppmsK)₂]. Found: C, 45.8; H, 3.7; P, 6.2; S, 6.3. Calc. C, 45.8; H, 3.1; P, 6.2; S, 6.4%. [Ir(CO)(CH₃)(tppmsNa·H₂O)₂]. Found: C, 46.5; H, 3.7; S, 6.6. Calc.: C, 45.6; H, 3.5; S, 6.4%.

§ ν_{CO}(H₂O) = 1961; ³¹P(D₂O) δ 28; ¹H [(CD₃)₂SO] δ 0.01 (t, J_{PH} 7.6 Hz).

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Table 1 IR and NMR characterization data for iridium complexes

Complex	ν _{CO} (Me ₂ SO)	δ _P [(CD ₃) ₂ SO]	δ _H [(CD ₃) ₂ SO] (J _{PH} /Hz)
<i>trans</i> -[Ir(CO)Me(PPh ₃) ₂]	1935	31.2	-0.4(t) (8.5)
<i>trans</i> -[Ir(CO)Me(tppmsK) ₂]	1937	31.5	-0.4(t) (8.9)
<i>trans</i> -[Ir(CO)Me(tppmsNa) ₂]	1937	31.6	-0.4(t) (8.5)
<i>trans</i> -[Ir(CO)(OH)(tppmsNa) ₂]	1953	26.9	0.2(t) (6.5)