

## Stoichiometric and Catalytic Oxygen Activation by Trimesityliridium(III)

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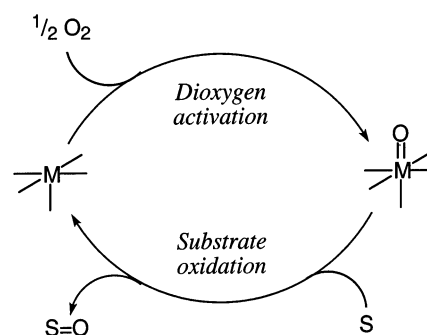
Trimesityliridium(III) (mesityl = 2,4,6-trimethylphenyl) reacts with  $O_2$  to form oxotrimesityliridium(V),  $(mes)_3Ir=O$ , in a reaction that is cleanly second order in iridium. In contrast to initial reports by Wilkinson, there is no evidence for substantial accumulation of an intermediate in this reaction. The oxo complex  $(mes)_3Ir=O$  oxidizes triphenylphosphine to triphenylphosphine oxide in a second-order reaction with  $\Delta H^\ddagger = 10.04 \pm 0.16$  kcal/mol and  $\Delta S^\ddagger = -21.6 \pm 0.5$  cal/(mol·K) in 1,2-dichloroethane. Triphenylarsine is also oxidized, though over an order of magnitude more slowly.  $Ir(mes)_3$  binds  $PPh_3$  reversibly ( $K_{assoc} = 84 \pm 3$  M<sup>-1</sup> in toluene at 20 °C) to form an unsymmetrical, sawhorse-shaped four-coordinate complex, whose temperature-dependent NMR spectra reveal a variety of dynamic processes. Oxygen atom transfer from  $(mes)_3Ir=O$  and dioxygen activation by  $(mes)_3Ir$  can be combined to allow catalytic aerobic oxidations of triphenylphosphine at room temperature and atmospheric pressure with overall activity (~60 turnovers/h) comparable to the fastest reported catalysts. A kinetic model that uses the rates measured for dioxygen activation, atom transfer, and phosphine binding describes the observed catalytic behavior well. Oxotrimesityliridium does not react with sulfides, sulfoxides, alcohols, or alkenes, apparently for kinetic reasons.

## Introduction

Molecular oxygen is an extremely desirable oxidant because of both its low monetary cost and its low environmental impact. While dioxygen is a thermodynamically potent oxidant, its reactions have an unfortunate combination of being both sluggish and unselective. Catalysis of the reactions of  $O_2$ , usually with transition metals, has been widely used to overcome these problems.<sup>1</sup>

One particularly simple and attractive mode of catalysis that can be envisioned involves formation of a terminal oxo moiety by reaction of  $O_2$  with a reduced metal center, followed by oxygen atom transfer<sup>2</sup> from the oxometal complex to a substrate (Scheme 1). While there are numerous well-characterized examples of both the former and the latter reactions individually, the number of cases of well-defined systems that can combine both reactions to achieve catalytic reactions at reasonable rates is still rather small. Both thermodynamic and kinetic considerations suggest that this combination will be challenging to achieve. Thermodynamically,

Scheme 1. Oxygen Atom Transfer-Based Strategy for Catalyzed Air Oxidations



cally, to allow both legs of the cycle to proceed, the strength of the metal–oxygen multiple bond is constrained to be strong enough to be formed exothermically from  $O_2$ , but not so strong that substrates cannot be oxidized. Kinetically, dioxygen is an electron-poor substance that reacts most favorably with electron-rich metal centers.<sup>3</sup> However, the reactivity of oxometal complexes in oxygen atom transfer reactions (with typical electron-rich substrates) is strongly

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dependent on the electrophilic character of the oxo complex.<sup>4,5</sup> Thus a catalyst acting by the mechanism of Scheme 1 must strike a balance between nucleophilic character in its reduced form and electrophilic character in its oxidized form and is unlikely to excel at both oxidative and reductive steps.

We were therefore struck by the report by Hay-Motherwell and Wilkinson that the homoleptic trimesityliridium(III)<sup>6</sup> reacts with O<sub>2</sub> to form oxotrimesityliridium(V), a unique example of a terminal oxo complex of iridium.<sup>7,8</sup> We reasoned that this high-valent iridium complex would have a high propensity for reduction to iridium(III), and thus a relatively weak metal–oxygen bond. We therefore hoped it would readily oxidize a variety of substrates by oxygen atom transfer, allowing it to act as a catalyst for air oxidations. Here we report the scope and mechanism of the stoichiometric and catalytic oxidation reactions of (mes)<sub>3</sub>Ir=O. We also describe the complex fluxional behavior of sawhorse-shaped four-coordinate (mes)<sub>3</sub>Ir(PPh<sub>3</sub>), which is present during oxidation reactions of PPh<sub>3</sub> catalyzed by (mes)<sub>3</sub>Ir=O.

## Experimental Section

**Materials and Methods.** Unless otherwise noted, all procedures were carried out on the benchtop. Dichloromethane and dichloroethane used in the kinetics studies were dried over 4 Å molecular sieves, followed by CaH<sub>2</sub>, and stored in an inert-atmosphere glovebox before use. All other reagents were commercially available and used without further purification. NMR spectra were measured on a General Electric GN-300 or a Varian VXR-300 or –500 FT-NMR spectrometer.

Oxotrimesityliridium(V) was prepared by a variation on the literature procedure.<sup>7</sup> A crude solution of trimesityliridium(III) in hexane was generated according to the literature procedure.<sup>6</sup> This brown solution was then exposed to the air and stirred vigorously overnight, turning green. The green solution was gravity-filtered, stripped to dryness on the rotary evaporator, and purified by repeated chromatography on silica gel, eluting with 5% Et<sub>2</sub>O/hexane. The pure fractions (as judged by TLC) were collected and the material crystallized from acetone/water or acetonitrile/water, and the purity of the recrystallized material was confirmed by NMR. Yields of this modified procedure are typically 5%, which is lower than that reported by Wilkinson<sup>6,7</sup> but similar to the yields obtained in our hands on repeating the literature procedure.

**Kinetics.** UV–visible data were collected on a Beckman DU-7500 diode-array spectrophotometer equipped with a multicell transport block. The temperature was regulated by a circulating water/ethylene glycol mixture and was measured by a thermocouple inserted in the cell block. Solutions were prepared in the drybox in 1-cm quartz cells fitted with septum caps. Reactions were monitored

by following the absorbance at 620 or 630 nm ( $\lambda_{\text{max}}$  for (mes)<sub>3</sub>Ir=O is 620 nm,  $\epsilon = 2000 \text{ M}^{-1} \text{ cm}^{-1}$ ).

Reactions involving deoxygenation of (mes)<sub>3</sub>Ir=O were initiated by injecting a small volume of a deoxygenated solution of the oxo complex into 2 mL of a solution of known concentration of the reducing agent (triarylphosphine or -arsine). Final concentrations of (mes)<sub>3</sub>Ir=O were between  $2 \times 10^{-4}$  and  $5 \times 10^{-4}$  M. These reactions were performed under pseudo-first-order conditions, with reductant in at least 10-fold molar excess over iridium. Rate constants were obtained by least-squares fits to the equation  $\ln|A_f - A| = -kt + \ln|A_f - A_0|$ , which were linear for at least four half-lives. Activation parameters were determined from plots of  $\ln(k/T)$  vs  $(1/T)$ .<sup>9</sup>

For the oxygenation experiments, solutions of trimesityliridium(III) were generated by treating (mes)<sub>3</sub>Ir=O in the drybox with a slightly substoichiometric amount of triphenylphosphine (usually 0.9 equiv) and allowing the deoxygenation to go to completion (at least 2 h at room temperature). NMR analysis of such solutions shows that the only phenyl resonances are those due to free triphenylphosphine oxide, indicating that this procedure generates free (mes)<sub>3</sub>Ir. Oxygenation was initiated by injecting a small volume of this stock solution into septum-capped cuvettes containing 2 mL of dichloromethane that had been saturated with either air or pure dioxygen by bubbling of the gas for at least 10 min. Given the reported solubilities of dioxygen in chlorinated solvents (8–10 mM at 1 atm of O<sub>2</sub>)<sup>10</sup> and  $[\text{Ir}] < 5 \times 10^{-4} \text{ M}$ , these conditions ensure that the dissolved dioxygen concentration should change <15% during the reaction and so mass transport of O<sub>2</sub> into the liquid should not affect the measured rates. Second-order rate constants were determined by nonlinear least-squares fitting, using the program Kaleidagraph, of the absorbance data to the equation  $A = A_f + (A_0 - A_f)/(1 + (A_0 - A_f)(kt/\Delta\epsilon_{630}))$  ( $\Delta\epsilon_{630} = -1700 \text{ M}^{-1} \text{ cm}^{-1}$ ). Rate constants were found to be invariant with iridium concentration over a range of  $1.2 \times 10^{-4}$  to  $5.0 \times 10^{-4} \text{ M}$ .

**Generation and Characterization of (mes)<sub>3</sub>Ir(PPh<sub>3</sub>).** In a typical experiment, a solution of trimesityliridium(III) was generated in an NMR tube sealed to a ground glass joint by treating a solution of (mes)<sub>3</sub>Ir=O in CD<sub>2</sub>Cl<sub>2</sub> in the drybox with a stoichiometric amount of triphenylphosphine-*d*<sub>15</sub> (Aldrich) and allowing deoxygenation to go to completion. After deoxygenation, 1 equiv of triphenylphosphine was added to the brown-red solution of trimesityliridium(III). The NMR tube was then affixed to a glass joint with a Teflon valve, taken out of the drybox, cooled to –78 °C, and flame sealed under reduced pressure. The tube was stored at –20 °C when not being analyzed, since the phosphine adduct decomposes over the course of about a day at room temperature. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, –98 °C; *a* refers to the phenyl or mesityl group in the mirror plane established at higher temperatures; *b* and *b'* refer to the phenyl or mesityl groups related by that mirror plane):  $\delta$  0.552 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>b</sub>); 0.998 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>a</sub>); 1.730 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>a</sub>); 1.828 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>b'</sub>); 1.965 (s, 3H, *p*-CH<sub>3</sub>, mes<sub>b</sub>); 2.006 (s, 3H, *p*-CH<sub>3</sub>, mes<sub>b'</sub>); 2.040 (s, 3H, *p*-CH<sub>3</sub>, mes<sub>a</sub>); 2.174 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>b</sub>); 2.390 (s, 3H, *o*-CH<sub>3</sub>, mes<sub>b'</sub>); 4.851 (s, 1H, ArH, mes<sub>b</sub>); 5.517 (t, 7.5 Hz, 1H, *o*-Ph<sub>b</sub>); 6.087 (s, 1H, ArH, mes<sub>a</sub>); 6.216 (s, 1H, ArH, mes<sub>b'</sub>); 6.267 (s, 1H, ArH, mes<sub>b</sub>); 6.379 (t, 7.5 Hz, 1H, *m*-Ph<sub>b</sub>); 6.443 (s, 1H, ArH, mes<sub>b'</sub>); 6.552 (s, 1H, ArH, mes<sub>a</sub>); 6.955 (t, 7.5 Hz, 1H, *p*-Ph<sub>b</sub>); 7.017 (t, 7.5 Hz, 1H, *m*-Ph<sub>b</sub>); 7.156 (br, 2H, *m*-Ph<sub>b'</sub>); 7.189 (t, 7.5 Hz, 1H, *o*-Ph<sub>b</sub>); 7.214 (br, 1H, *o*-Ph<sub>a</sub>); 7.401 (t, 7.5 Hz, 1H, *p*-Ph<sub>b'</sub>); ~7.5

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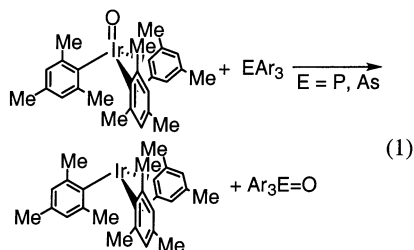
## Catalytic Oxygen Activation by Trimesityliridium(III)

(v br, 2H, *m*-Ph<sub>a</sub>); 7.504 (t, 7.5 Hz, 1H, *p*-Ph<sub>a</sub>); 7.604 (br, 2H, *o*-Ph<sub>b</sub>); 8.620 (br, 1H, *o*-Ph<sub>a</sub>).

**Catalytic Air Oxidation of PPh<sub>3</sub>.** In a typical run, triphenylphosphine (130.1 mg, 0.496 mmol) in 2.5 mL of toluene was added to a dark blue-green solution of (mes)<sub>3</sub>Ir=O (5.5 mg, 0.0096 mmol, 2 mol %) in 2.5 mL of toluene in a 15-mL two-necked round-bottom flask. Oxygen gas, which was presaturated with toluene by passing it through a gas dispersion tube in a 100-mL two-necked flask filled with toluene, was admitted to the reaction vessel through a needle. Oxygen was bubbled through the reaction mixture at a moderate rate and vented through a water bubbler. After addition of the triphenylphosphine, 0.2 mL of the reaction mixture was syringed out and added to a mixture of CDCl<sub>3</sub> (0.3 mL) mixed with 50 μL of concentrated aqueous HCl (to decompose the trimesityliridium) in an NMR tube. Aliquots were taken and quenched analogously throughout the course of the reaction, and each aliquot was then analyzed by <sup>31</sup>P{<sup>1</sup>H} NMR. Kinetic simulations were performed by numerical integration (Runge–Kutta) of the coupled differential equations with Microsoft Excel.

## Results

**Reactivity of Oxotrimesityliridium(V).** Oxotrimesityliridium(V) ((mes)<sub>3</sub>Ir=O; mes = 2,4,6-trimethylphenyl) is quantitatively reduced by triphenylarsine and by a variety of triarylphosphines to give homoleptic trimesityliridium(III) and the corresponding arsine or phosphine oxide (eq 1). The rates of these reactions may be conveniently



measured by monitoring the decrease in absorbance at 620 nm as the blue-green iridium(V) is converted to yellow iridium(III). In all cases, isosbestic points are observed and the pseudo-first-order rate constants measured in the presence of excess reducing agent are proportional to the concentration of the phosphine or arsine reagent. In some cases, the reducing agents form detectable amounts of adducts with (mes)<sub>3</sub>Ir (see below). However, since the ligands are present in substantial excess and binding rates are invariably much faster than rates of reduction, adduct formation does not interfere with kinetic measurements. Oxidation of phosphines and arsines by (mes)<sub>3</sub>Ir=O is irreversible.

These observations are consistent with atom transfer taking place in a reaction that is first order in both iridium and substrate and which proceeds without observable intermediates. An analysis of the temperature dependence of *k*<sub>ox</sub> for the deoxygenation of (mes)<sub>3</sub>Ir=O by PPh<sub>3</sub> in 1,2-dichloroethane from 15 to 55 °C gives activation parameters for this reaction of Δ*H*<sup>‡</sup> = 10.04 ± 0.16 kcal/mol and Δ*S*<sup>‡</sup> = -21.6 ± 0.5 cal/(mol·K) (Figure S1, Supporting Information). Second-order rate constants for the reactions of various triarylphosphines and of triphenylarsine with (mes)<sub>3</sub>Ir=O, measured at ambient temperature in dichloromethane, are

**Table 1.** Rate of Oxygen Atom Transfer from (mes)<sub>3</sub>Ir=O to Phosphines and Arsines (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C)

substrate	<i>k</i> <sub>atom transfer</sub> (M <sup>-1</sup> s <sup>-1</sup> )
PPh <sub>3</sub>	3.95 (5)
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub>	3.76 (6)
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>3</sub>	6.33 (12)
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>3</sub>	10.88 (14)
P( <i>o</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	0.058 (2)
AsPh <sub>3</sub>	0.111 (17)

<sup>a</sup> Measured at 21.9 °C.

listed in Table 1. Electron-donating substituents on the triarylphosphine increase the rate of oxidation, but only slightly. The modest Hammett ρ value of -0.29 ± 0.10 (Figure S2, Supporting Information) has the same sign but is smaller in magnitude than is typically observed for oxygen atom transfer to triarylphosphines by metal–oxo complexes (compare, for example, atom transfer from TpReOCl<sub>2</sub>, ρ = -0.47<sup>4</sup>). Bulky triarylphosphines such as tri-*ortho*-tolylphosphine react much more slowly than their unhindered counterparts. Triphenylarsine reacts substantially more slowly than triphenylphosphine, as is expected given the smaller driving force for triphenylarsine oxidation.<sup>11</sup> The rate difference of a factor of 36 is similar to the 61-fold faster oxidation of PPh<sub>3</sub> over AsPh<sub>3</sub> by (tetramesitylporphyrinato)dioxoruthenium(VI),<sup>12</sup> while much smaller differences are seen in peroxo-metal oxidations.<sup>13</sup>

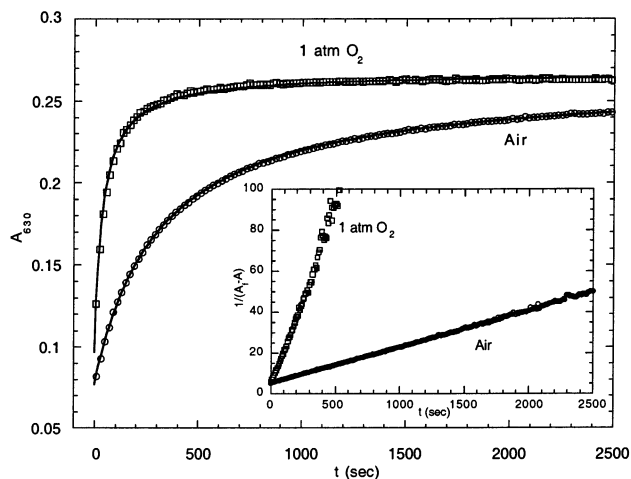
In contrast to its ready oxidation of phosphines and arsines, (mes)<sub>3</sub>Ir=O is inert to all commonly occurring organic functional groups. Thus, dimethyl sulfide, dimethyl sulfoxide, styrene, norbornene, 2,3-dihydrofuran, allyl alcohol, and benzaldehyde do not react with (mes)<sub>3</sub>Ir=O over a period of one week at room temperature. In certain cases, the ability of the reduced (mes)<sub>3</sub>Ir species to deoxygenate organic substrates has been tested, and it too is found to be unreactive to substrates such as styrene oxide and Me<sub>2</sub>SO. However, the more strongly oxidizing trimethylamine-*N*-oxide has been reported to convert (mes)<sub>3</sub>Ir to (mes)<sub>3</sub>Ir=O.<sup>7</sup>

**Reaction of Trimesityliridium(III) with Dioxygen.** Trimesityliridium is very air-sensitive, being oxidized rapidly to (mes)<sub>3</sub>Ir=O by O<sub>2</sub>.<sup>7</sup> The kinetics of this oxygen uptake process may be monitored spectrophotometrically by measuring the growth of the absorbance of the iridium(V) complex at 630 nm. The kinetics observed in this manner show a clean *second-order* dependence on iridium(III) concentration (Figure 1). Individual kinetic runs fit extremely well to second-order kinetics, and the rate constants obtained in this manner are independent of the total iridium concentration (1.2 × 10<sup>-4</sup> to 5.0 × 10<sup>-4</sup> M). In air, the observed second-order rate constant is 31 ± 2 M<sup>-1</sup> s<sup>-1</sup>. The reaction performed under 1 atm of pure O<sub>2</sub> is much faster (Figure 1), with a corresponding rate constant of 240 ± 60 M<sup>-1</sup> s<sup>-1</sup>. This rate acceleration under 1 atm of O<sub>2</sub> of 7.7 ± 2.0 is reasonably close to the factor of 5 difference in oxygen partial pressure between air and pure O<sub>2</sub>, strongly suggesting that the reaction is first order in dioxygen.

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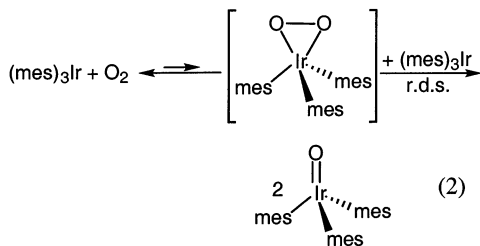
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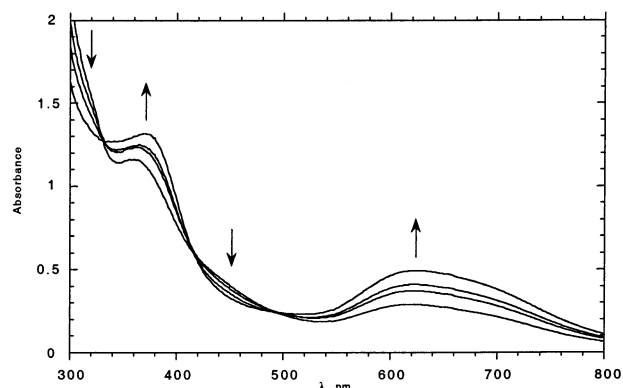


**Figure 1.** Reaction of  $(\text{mes})_3\text{Ir}$  with  $\text{O}_2$  in air (open circles) or under 1 atm of  $\text{O}_2$  (open squares). The solid line is the fit to second-order kinetics. The iridium concentration is  $1.2 \times 10^{-4}$  M. Inset: Plots of  $1/(A - A_\infty)$  for the same two kinetic runs.

The observed rate law (rate =  $k[\text{Ir(III)}]^2[\text{O}_2]$ ) is consistent with a reaction mechanism involving weak preequilibrium complexation of  $\text{O}_2$  by one iridium center, followed by rate-determining reduction of this complex by another molecule of  $(\text{mes})_3\text{Ir}$  to give 2 equiv of  $(\text{mes})_3\text{Ir}=\text{O}$  (eq 2). (A direct



termolecular reaction is consistent with the kinetics but is chemically implausible.) While we have no structural information about the intermediate, an  $\eta^2$  complex seems more likely, given the extensive precedent for this mode of coordination to iridium.<sup>14</sup> The mechanism proposed in eq 2 is essentially identical with that suggested by Hay-Motherwell, Wilkinson, and co-workers.<sup>7</sup> The previous study also reported the observation of new NMR signals on treatment of  $(\text{mes})_3\text{Ir}$  with  $\text{O}_2$ , which were assigned to a labile intermediate iridium peroxide. In fact, any intermediates present in this reaction do *not* accumulate to a significant extent, as demonstrated by the scrupulous adherence to second-order kinetics throughout the course of the reaction and by the presence of tight isosbestic points at 492, 415, and 330 nm (Figure 2). The new NMR signals seen at intermediate stages of the reaction by Wilkinson may be plausibly explained by the surprising observation that degenerate intermetal oxygen atom transfer between  $(\text{mes})_3\text{Ir}$  and  $(\text{mes})_3\text{Ir}=\text{O}$  is fast on the NMR time scale. For example, anaerobic titration of  $(\text{mes})_3\text{Ir}=\text{O}$  with  $\text{PPh}_3$  in  $\text{CDCl}_3$



**Figure 2.** Spectral evolution of the reaction between  $(\text{mes})_3\text{Ir}$  (initial concentration  $2.5 \times 10^{-4}$  M) and  $\text{O}_2$  in air-saturated  $\text{CH}_2\text{Cl}_2$ . Spectra were taken at 0, 120, 600, and 2200 s; arrows show the direction of absorbance change.

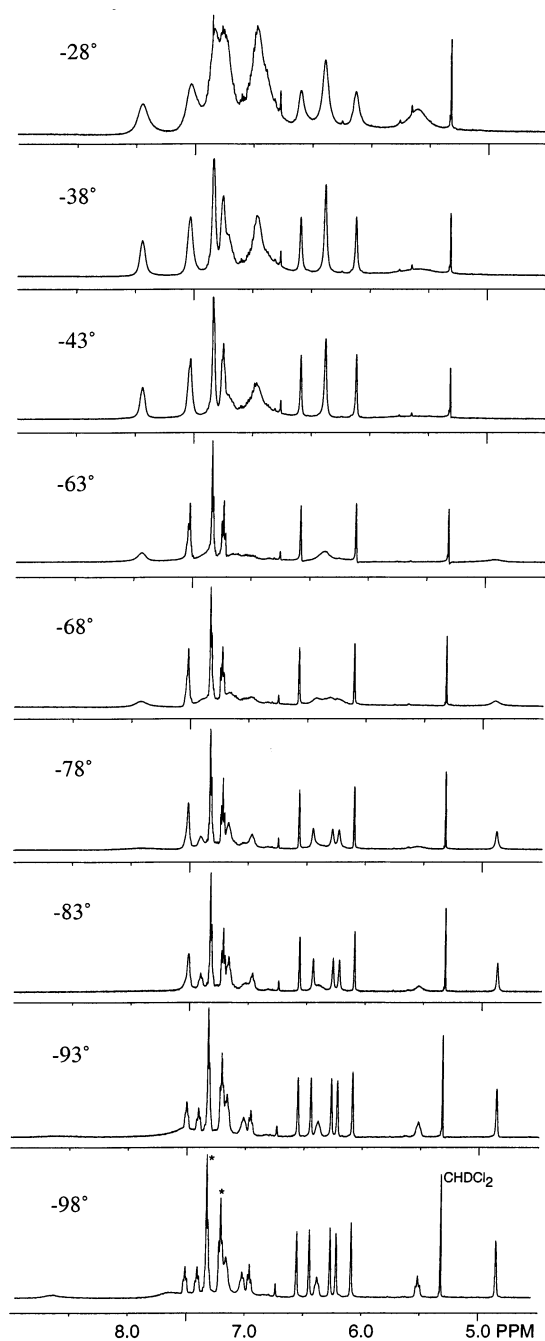
(conditions where formation of a peroxo species is most unlikely) results in  $^1\text{H}$  NMR resonances due to free  $\text{OPPh}_3$  and mesityl resonances at the population-weighted average positions for iridium(III) and iridium(V) (Figure S3, Supporting Information). Apparently new NMR signals therefore appear in incompletely oxygenated solutions of  $(\text{mes})_3\text{Ir}$  as a result of this exchange phenomenon rather than because an intermediate is present. Details of this unprecedentedly fast oxygen atom exchange will be discussed elsewhere.<sup>15</sup>

**Binding of Triphenylphosphine to Trimesityliridium(III).** Solutions of  $(\text{mes})_3\text{Ir}$  in  $\text{CH}_2\text{Cl}_2$  containing an excess of  $\text{PPh}_3$  at room temperature show a single, slightly broadened resonance in the  $^{31}\text{P}\{^1\text{H}\}$  NMR. That the broadening is due to weak, reversible binding of  $\text{PPh}_3$  to the iridium center is made evident upon cooling the solution, whereupon the  $^{31}\text{P}$  resonance broadens further, decoalesces, and splits into resonances at  $\delta -6.2$  ppm for free  $\text{PPh}_3$  and  $\delta 2.7$  ppm for  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  (Figure S4, Supporting Information), with phosphine exchange becoming slow on the NMR time scale below about  $-30$  °C. One equivalent of  $\text{OPPh}_3$  is also observed by  $^{31}\text{P}$  and  $^1\text{H}$  NMR, as the complex is generated by addition of excess  $\text{PPh}_3$  to  $(\text{mes})_3\text{Ir}=\text{O}$ . The weak binding of phosphine and the moderate thermal instability of the complex (it decomposes in solution over the course of about a day at room temperature) have prevented us from isolating a pure solid sample of the adduct, and all studies were carried out on samples generated in situ.

Only 1 equiv of  $\text{PPh}_3$  binds to  $(\text{mes})_3\text{Ir}$ , even at  $-98$  °C. Rates of phosphine exchange are independent of  $[\text{PPh}_3]$ , suggesting that phosphine exchange is dissociative, with  $k_{\text{diss}} = 1.5 \times 10^4 \text{ s}^{-1}$  at 23 °C. Analysis of the temperature dependence of the NMR line shape from 235 to 295 K (Figure S5) gives  $\Delta H^\ddagger = 15.41(\pm 0.24) \text{ kcal/mol}$  and  $\Delta S^\ddagger = +12.4(\pm 0.9) \text{ cal/(mol}\cdot\text{K)}$  for phosphine dissociation. From the amounts of free and bound phosphine that are observed at higher temperatures (as judged from the position of the averaged  $^{31}\text{P}$  NMR signal), one can estimate thermodynamic parameters for phosphine binding (Figure S6) as  $\Delta H^\circ = -15.7(\pm 0.9) \text{ kcal/mol}$  and  $\Delta S^\circ = -44(\pm 3) \text{ cal/(mol}\cdot\text{K)}$ ;

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**Figure 3.**  $^1\text{H}$  NMR spectra (500 MHz) (aryl region) of  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  in  $\text{CD}_2\text{Cl}_2$  from  $-28$  to  $-98$   $^\circ\text{C}$ . Peaks due to excess  $\text{PPh}_3$  are marked with an asterisk.

at 295 K,  $K_{\text{eq}}$  for binding is  $97(\pm 7) \text{ M}^{-1}$ . UV–visible titration data in toluene at 293 K (Figure S7) give similar values ( $K_{\text{eq}} = 84 \pm 3 \text{ M}^{-1}$ ).

Although the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  is invariant below about  $-30$   $^\circ\text{C}$ , the  $^1\text{H}$  NMR undergoes substantial changes as the temperature is lowered to  $-98$   $^\circ\text{C}$  (aryl region, Figure 3; methyl region, Figure S8). In the low-temperature spectra, the presence of six inequivalent aromatic protons and nine inequivalent methyl groups indicates that all mesityl groups are inequivalent and that  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  is therefore completely unsymmetrical ( $C_1$  symmetric). However, as the temperature is raised, two pairs of aromatic hydrogens ( $\delta$  4.85 and 6.22,  $\delta$  6.27 and 6.44)

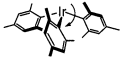
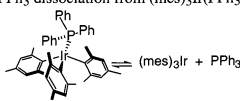
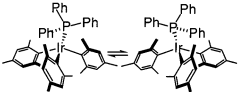
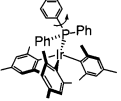
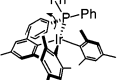
and three pairs of methyl groups ( $\delta$  0.56 and 1.83,  $\delta$  1.97 and 2.01, and  $\delta$  2.17 and 2.39) undergo pairwise exchange. All five pairwise exchanges occur at the same rate, indicating that they are due to a common chemical process. Two aromatic hydrogens ( $\delta$  6.09, 6.56) and three methyl groups ( $\delta$  1.00, 1.74, 2.04) are unaffected by the exchange process and remain sharp until the onset of phosphine dissociation at ca.  $-30$   $^\circ\text{C}$ . This pattern of exchange indicates that some motion introduces a mirror plane on the NMR time scale, rendering two mesityl groups equivalent, although top and bottom remain inequivalent and do not exchange. Line shape analysis of this “rocking” motion gives activation parameters of  $\Delta H^\ddagger = 11.19(\pm 0.25) \text{ kcal/mol}$  and  $\Delta S^\ddagger = +6.0(\pm 1.1) \text{ cal/(mol}\cdot\text{K)}$  (Figure S9).

At low temperature, all three phenyl groups of the  $\text{PPh}_3$  ligand are inequivalent, and further changes in the spectra can be attributed to slowing of rotation rates about the three P–C bonds, with one phenyl group showing effectively stopped rotation at  $-98$   $^\circ\text{C}$ , one showing a moderate rotation rate ( $k_{175\text{K}} = 170 \text{ s}^{-1}$ ), and one still rotating rather rapidly (decoalescence is not observed even at 175 K). Curiously, it is the unique phenyl group whose environment is not affected by the rocking motion of the mesityls that shows the middle rotation rate. It is also apparent that this phenyl group does not exchange with the other two phenyl groups up to the onset of  $\text{PPh}_3$  dissociation (note for example that the coalesced resonance due to the two *ortho* protons of this phenyl group at  $\delta$  7.94 ppm are still distinct from the other four *ortho* protons at  $\delta_{\text{av}} = 6.9$  ppm even at  $-28$   $^\circ\text{C}$ ). Thus, rotation about the Ir–P bond, which would interconvert all three phenyl groups, must be slower than phosphine dissociation. The rates and activation parameters of the observed fluxional processes in  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  are summarized in Table 2.

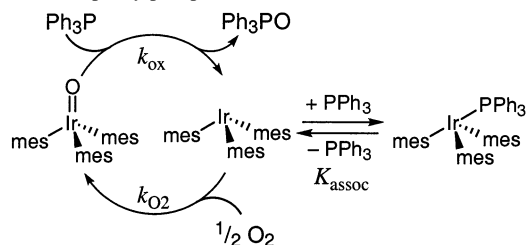
Triphenylarsine forms a similar unsymmetrical adduct  $(\text{mes})_3\text{Ir}(\text{AsPh}_3)$ , though it appears to bind more weakly than does triphenylphosphine. Tri-*o*-tolylphosphine does not bind to  $(\text{mes})_3\text{Ir}$ , even at  $-80$   $^\circ\text{C}$ , nor do the phosphine oxides  $\text{OPPh}_3$  or  $\text{OP}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$ .

**Catalysis of Air Oxidations by Oxotrimesityliridium-(V).** Since  $(\text{mes})_3\text{Ir}=\text{O}$  reacts with triphenylphosphine and triphenylarsine to form  $(\text{mes})_3\text{Ir}$ , and since  $(\text{mes})_3\text{Ir}$  reacts with  $\text{O}_2$  to regenerate  $(\text{mes})_3\text{Ir}=\text{O}$ , it is clear that  $(\text{mes})_3\text{Ir}=\text{O}$  should be a catalyst for the air oxidation of  $\text{Ph}_3\text{P}$  or  $\text{Ph}_3\text{As}$ , albeit with some potential inhibition due to ligand binding to  $(\text{mes})_3\text{Ir}$  (Scheme 2). Indeed, these substrates are converted quantitatively to the corresponding oxides in the presence of air or  $\text{O}_2$  and catalytic amounts of  $(\text{mes})_3\text{Ir}=\text{O}$ . Catalysis proceeds in a variety of solvents, but chlorinated solvents cause decomposition of the trimesityliridium. In chloroform, decomposition takes place quite rapidly, effectively halting catalysis after a few turnovers, but even in  $\text{CH}_2\text{Cl}_2$  or 1,2-dichlorobenzene there is noticeable decomposition after  $<20$  turnovers. In contrast, catalysis in benzene or toluene can proceed to  $>50$  turnovers without noticeable catalyst decomposition, as monitored by NMR integration against an internal standard. No phosphine oxidation is observed in the absence of catalyst. For phosphine oxidation, the resting state

**Table 2.** Dynamics of (mes)<sub>3</sub>Ir and (mes)<sub>3</sub>Ir(PPh<sub>3</sub>) in CD<sub>2</sub>Cl<sub>2</sub>

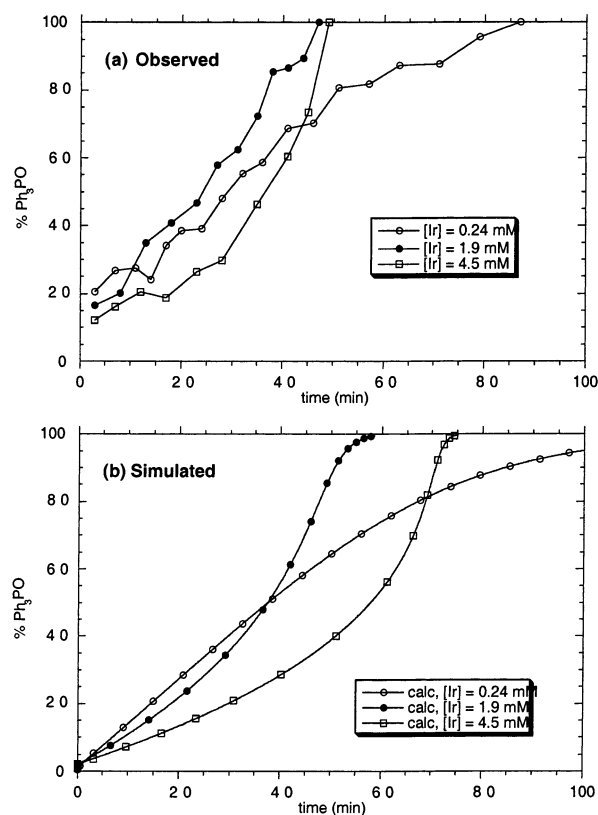
Dynamic Process	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (cal/mol·K)	$\Delta G^\ddagger$ (250 K) (kcal/mol)	$k_{250\text{ K}}$ (s <sup>-1</sup> )
Ir-C bond rotation in free (mes) <sub>3</sub> Ir <sup>a</sup> 	12.23 (16)	-4.5 (6)	13.4 (2)	1.0 × 10 <sup>1</sup> <sup>b</sup>
PPh <sub>3</sub> dissociation from (mes) <sub>3</sub> Ir(PPh <sub>3</sub> ) 	15.4 (2)	+12.4 (9)	12.3 (3)	9.2 × 10 <sup>1</sup>
“Rocking” motion (racemization) in (mes) <sub>3</sub> Ir(PPh <sub>3</sub> ) 	11.2 (3)	+6.0 (11)	9.7 (4)	1.7 × 10 <sup>4</sup>
P-C bond rotation, Ph <sub>b</sub> , (mes) <sub>3</sub> Ir(PPh <sub>3</sub> ) 	9.2 (7)	-1 (4)	9.4 (12)	3 × 10 <sup>4</sup> <sup>b</sup>
P-C bond rotation, Ph <sub>a</sub> , (mes) <sub>3</sub> Ir(PPh <sub>3</sub> ) 	9.76 (8)	+8.2 (4)	7.71 (13)	9.5 × 10 <sup>5</sup> <sup>b</sup>

<sup>a</sup> As measured for (mes)<sub>3</sub>Ir generated in situ from (mes)<sub>3</sub>Ir=O and excess P(*o*-tol); Wilkinson et al. report essentially identical values ( $\Delta G^\ddagger = 13.8$  kcal/mol at 287 K) for Ir(mes)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub> in the absence of P(*o*-tol)<sub>3</sub> and OP(*o*-tol)<sub>3</sub>.<sup>6</sup> <sup>b</sup> Extrapolated.

**Scheme 2.** Proposed Mechanism for (mes)<sub>3</sub>Ir=O-Catalyzed Aerobic Oxidation of Triphenylphosphine

of the catalyst is iridium(III), as judged by the yellow-orange color of the reacting solution, which reverts to blue-green on consumption of the triphenylphosphine.

Catalytic oxidation of PPh<sub>3</sub> with 2 mol % (mes)<sub>3</sub>Ir=O in toluene under 1 atm of O<sub>2</sub> at 20 °C was monitored over time by <sup>31</sup>P{<sup>1</sup>H} NMR at a variety of concentrations (Figure 4a). Dioxygen activation is rate-determining and is second order in iridium, so its rate slows at lower iridium concentrations. However, phosphine binding is stronger at higher phosphine concentrations, and thus phosphine inhibition is less important at lower phosphine concentrations. If the molar ratio of phosphorus:iridium is held constant but the overall concentration is varied, then these two effects oppose each other. The net result, at 2 mol % iridium with [Ir] in the range 0.24–4.5 mM, is that the initial turnover frequencies decrease slightly with increasing concentration, due to increased phosphine inhibition. However, turnover frequencies increase markedly at later times in the higher concentration runs as the phosphine inhibition is relieved. These phenomena are apparent in both the experimental runs and in kinetic



**Figure 4.** Air oxidation of PPh<sub>3</sub> catalyzed by (mes)<sub>3</sub>Ir=O. (a) Experimental data (toluene, 1 atm of O<sub>2</sub>, 20 °C). In each run the P:Ir ratio is 50:1; iridium concentrations range from 0.24 to 4.5 mM. (b) Kinetic simulations of the catalytic reaction using the model in Scheme 2 and the following rate and equilibrium constants:  $k_{\text{ox}} = 3.95 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{O}_2} = 155 \text{ M}^{-1} \text{ atm}^{-1} \text{ s}^{-1}$ , and  $K_{\text{assoc}} = 84 \text{ M}^{-1}$ .

simulations using the rate and equilibrium constants measured for the individual steps (Figure 4b;  $k_{\text{ox}} = 3.95 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{O}_2} = 155 \text{ M}^{-1} \text{ atm}^{-1} \text{ s}^{-1}$ , as measured in CH<sub>2</sub>Cl<sub>2</sub>, and  $K_{\text{assoc}} = 84 \text{ M}^{-1}$ , as measured in toluene). The balance between phosphine inhibition and oxygen uptake under these conditions means that the overall turnover frequency is relatively insensitive to total concentration in these experiments, and is about 60 h<sup>-1</sup>. The agreement of the experimental data with the predictions of the kinetic model based on independent measurements of the individual steps (which therefore has no adjustable parameters) is remarkably good, especially considering the differences one might expect based on the differing solvents (toluene vs dichloromethane). The only serious discrepancy is the consistent presence of a significantly elevated amount of phosphine oxidation in the first few minutes. The origin of this small initial burst of oxidation is unknown.

## Discussion

**Structure and Dynamics of (mes)<sub>3</sub>Ir(PPh<sub>3</sub>).** Low-temperature NMR spectroscopy clearly shows that the iridium(III) phosphine adduct (mes)<sub>3</sub>Ir(PPh<sub>3</sub>) has an unsymmetrical (C<sub>1</sub>) structure (Figure 3). The triphenylarsine adduct shows similar spectral features. The low symmetry excludes a structure where the phosphine (or arsine) ligand binds on the 3-fold axis of (mes)<sub>3</sub>Ir, and instead is most consistent with a sawhorse geometry related to an octahedron by

removal of two cis ligands. This geometry appears to be universal in structurally characterized nominally four-coordinate  $d^6$  complexes such as  $\text{Pt}(\text{C}_6\text{Cl}_5)_4$ ,<sup>16</sup>  $\text{Rh}(\text{C}_6\text{Cl}_5)_3(\text{py})$ ,<sup>17</sup>  $[\text{Rh}(\text{C}_6\text{Cl}_5)_3\text{X}]^-$  ( $\text{X} = \text{Cl}, \text{C}_6\text{Cl}_5$ ) and  $[\text{Rh}(\text{COC}_6\text{Cl}_5)_2(\text{C}_6\text{Cl}_5)\text{Cl}]^-$ ,<sup>18</sup>  $[\text{IrH}_2(\text{P}^t\text{Bu}_2\text{Ph})_2]^+$  and  $[\text{IrH}(\eta^2\text{-C}_6\text{H}_4\text{P}^t\text{Bu}_2)(\text{P}^t\text{Bu}_2\text{Ph})]^+$ ,<sup>19</sup>  $[\text{Ru}(\text{R})(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2]^+$ ,<sup>20</sup> and  $\text{RuCl}_2(\text{PPh}_2)[2,6\text{-Me}_2\text{C}_6\text{H}_3]_2$ .<sup>21</sup> In these structurally characterized complexes, both vacant sites are generally occupied either by agostic C–H bonds or *o*-Cl atoms, with the exception of  $[\text{IrH}(\eta^2\text{-C}_6\text{H}_4\text{P}^t\text{Bu}_2)(\text{P}^t\text{Bu}_2\text{Ph})]^+$ , where only one agostic interaction can be achieved because of geometric constraints.<sup>19b</sup> However, calculations indicate that the sawhorse structure should still be preferred even in the absence of agostic interactions.<sup>19,22</sup>

Agostic interactions are likely present in  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  as well. Wilkinson and co-workers argued that agostic interactions are absent in  $(\text{mes})_3\text{Ir}$  and  $(\text{mes})_3\text{Rh}$  because they were unable to find any stigmata of their presence such as upfield shifts in the  $^1\text{H}$  NMR, reduced values of  $J_{\text{CH}}$ , or low-frequency C–H stretches in the IR, and indeed concluded that the trimesityls are planar in solution, in contrast to their pyramidal structures in the solid state.<sup>6,23</sup> The latter conclusion is clearly erroneous, since the appearance of two equal-intensity aromatic peaks and three equal-intensity methyl peaks in the low-temperature NMR spectra of the trimesityls is consistent only with a  $C_3$ -symmetric static structure and incompatible with any of the possible point groups of a planar trimesityl complex ( $D_{3h}$ ,  $D_3$ ,  $C_{2v}$ ,  $C_2$ , or  $C_1$ ). Pyramidalization at iridium does not in and of itself require the presence of agostic interactions with the *o*-methyl groups of the aryl ligands (for example, calculations support a pyramidal structure for nonagostic  $\text{RhH}_3$  in the gas phase<sup>24</sup>). However, the fact that there is a substantial barrier to Ir–C rotation in  $\text{Ir}(\text{mes})_3$ , with the ortho and aromatic resonances sharp and distinct below  $-20$  °C ( $\Delta G^\ddagger = 13.4$  kcal/mol at 250 K), while the corresponding resonances in four-coordinate  $\text{O}=\text{Ir}(\text{mes})_3$  are equivalent even at  $-80$  °C, is difficult to reconcile with a purely steric barrier to bond rotation and

suggests some energetic role for agostic methyl groups. Likewise, while we have no definitive evidence for agostic interactions in the phosphine adduct  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$ , the presence of upfield-shifted methyl groups in the  $^1\text{H}$  NMR ( $\delta$  0.55, 1.00) suggest that one or two of the *o*-methyl groups may be interacting with iridium. Unusually upfield resonances for one of the phenyl groups ( $\text{Ph}_b$ ,  $\delta$  5.52 and 6.38) suggest that some interaction between that phenyl ring and the iridium (agostic C–H or  $\eta^2$ -aryl) may also be possible. Such anomalous chemical shifts must be treated with extreme caution as possible indicators of direct interaction with a metal center; note for example the far upfield shift of one of the mesityl aromatic hydrogens ( $\delta$  4.85), which cannot be due to a direct interaction of the metal with the meta position of the ring and which instead is presumably a through-space effect of the ring current of one of the phosphine phenyl groups. Nonetheless, the presence of some interaction between  $\text{Ph}_b$  and the iridium would explain the otherwise puzzling observation that P–C bond rotation in that phenyl group is substantially slower than that in the two other groups, including the unique phenyl group that is presumably interdigitated between two of the mesityl groups.

Three independent dynamic processes can be observed in  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  by  $^1\text{H}$  NMR at temperatures below those required to promote phosphine dissociation (Table 2). Bond rotation around each of the three P–C bonds takes place at a different rate and two of these processes can be partially or fully frozen out at low temperatures. At higher temperatures, a “rocking” motion takes place that reverses the sense of the helical twist of the  $C_3$ -symmetric  $(\text{mes})_3\text{Ir}$  fragment and thus creates a time-averaged mirror plane. Equally interesting are two transformations that are *not* observed. Rotation about the Ir–P bond, which would interconvert the three phenyl groups, does not occur at a significant rate until the onset of phosphine dissociation. This “locking” of the phosphine substituents is not surprising, given the extreme crowding to be expected in  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$ . Also unobserved in  $(\text{mes})_3\text{Ir}(\text{PPh}_3)$  is formation of a pseudotetrahedral species, which would have the effect of causing exchange among all mesityl (and phenyl) groups. Since the tetrahedral adduct would presumably be favored sterically, this suggests a strong electronic preference for the sawhorse-shaped geometry. Since the aryl groups remain distinguishable until the onset of phosphine dissociation, one can conclude that the tetrahedral complex is disfavored by at least 12 kcal/mol relative to the sawhorse-shaped adduct.

**Oxygen Atom Transfer Reactivity of  $(\text{mes})_3\text{Ir}=\text{O}$ .** Given Wilkinson’s report that  $(\text{mes})_3\text{Ir}$  reacted rapidly with dioxygen to form  $(\text{mes})_3\text{Ir}=\text{O}$ ,<sup>7</sup> and given the high oxidation state of iridium in  $(\text{mes})_3\text{Ir}=\text{O}$ , we anticipated that  $(\text{mes})_3\text{Ir}=\text{O}$  would be an effective catalyst for the air oxidation of organic substrates. This potential is indeed realized for the oxidation of reactive substrates such as triphenylphosphine and triphenylarsine. Key mechanistic features of the catalytic air oxidation of triphenylphosphine are kinetically termolecular oxygen uptake (second order in  $\text{Ir}(\text{III})$ , first order in  $\text{O}_2$ ), bimolecular oxygen atom transfer from  $(\text{mes})_3\text{Ir}=\text{O}$  to  $\text{PPh}_3$ , and the inhibition of oxidation by phosphine binding

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to iridium(III) (Scheme 2). The reasonably good agreement between the observed catalytic rates and the behavior predicted from measurements of the individual steps indicates that this model effectively describes the principal pathway for oxidation. Other potential pathways, such as direct attack of PPh<sub>3</sub> on a transient iridium peroxide or air oxidation of the phosphine adduct (mes)<sub>3</sub>Ir(PPh<sub>3</sub>), may therefore be concluded to play little or no role in the reaction. Air oxidation of triphenylphosphine is a relatively easily catalyzed reaction, and many examples of oxidation catalysis both by oxometal species<sup>25</sup> and by other metal complexes<sup>26</sup> have been reported. It is worth noting that (mes)<sub>3</sub>Ir=O does appear to be among the most active catalysts reported to date among those catalysts with a significant lifetime.<sup>27</sup> For example, it is more active than the fastest oxo catalysts whose rates have been reported at or near room temperature (e.g., MoO<sub>2</sub>(S<sub>2</sub>CNPr<sub>2</sub>), ~15 turnovers/h at 40 °C<sup>25f</sup>) and similar to palladium- or platinum-based catalysts (for example, Pd(OAc)<sub>2</sub>/THF, ~55 turnovers/h at 30 °C<sup>26b</sup>).

But in general, (mes)<sub>3</sub>Ir=O displays surprisingly little reactivity toward organic reducing agents. The oxygen atom transfer reactivity of the complex is summarized in Table 3. Strong reducing agents such as PPh<sub>3</sub> and AsPh<sub>3</sub> (or aqueous dithionite<sup>7</sup>) will deoxygenate (mes)<sub>3</sub>Ir=O, and strong oxidizing agents such as Me<sub>3</sub>NO or O<sub>2</sub> will oxygenate (mes)<sub>3</sub>Ir.<sup>7</sup> One may use these reactions to bracket the strength of the iridium–oxygen bond above that of Me<sub>3</sub>NO and below that of Ph<sub>3</sub>AsO, giving a very approximate Ir=O bond dissociation energy of about 85 ± 15 kcal/mol. However, within this 30-kcal/mol gap, no reactivity is observed, and many other substrates whose oxidations are undoubtedly thermodynamically favorable (Me<sub>2</sub>SO, allyl alcohol) are also inert. Given the lack of reactivity in both oxidative and reductive directions, it must be concluded that the impediment is kinetic in origin.

Two factors may contribute to the sluggishness of (mes)<sub>3</sub>Ir=O as an oxidant. One is that the strongly donating mesityl groups may render the iridium center too electron-rich to be a kinetically effective oxidant. The importance of electrophilicity in oxidation of electron-rich substrates such as PPh<sub>3</sub> is well-established,<sup>4</sup> and the iridium shows only a modest

**Table 3.** Oxygen Atom Transfer Reactivity of (mes)<sub>3</sub>Ir=O and (mes)<sub>3</sub>Ir

X + (mes) <sub>3</sub> Ir=O $\xrightleftharpoons{?}$ XO + (mes) <sub>3</sub> Ir		XO	$\Delta H^\circ$ for XO (g) → X (g) + O (g) (kcal/mol) <sup>a</sup>
X	Observed reactivity		
Ph <sub>3</sub> P	→	Ph <sub>3</sub> PO	133
Me <sub>2</sub> SO	↔	Me <sub>2</sub> SO <sub>2</sub>	112
Ph <sub>3</sub> As	→	Ph <sub>3</sub> AsO	102
Me <sub>2</sub> S	↔	Me <sub>2</sub> SO	86
Ph	↔	Ph	~86 <sup>b</sup>
Me <sub>3</sub> N	← <sup>c</sup>	Me <sub>3</sub> NO	~67 <sup>d</sup>
—	←	1/2 O <sub>2</sub>	59

<sup>a</sup> Data from ref 11. <sup>b</sup> Value given is that for deoxygenation of propylene oxide. <sup>c</sup> Reference 7. <sup>d</sup> Value given is that for deoxygenation of PhCH=N-(O)<sup>t</sup>Bu.

degree of polarity in its reaction with phosphines ( $\rho = -0.29 \pm 0.10$  for reactions of substituted triarylphosphines). The electron-donating mesityl groups fit the iridium admirably for dioxygen activation, but are less suitable for encouraging subsequent oxygen atom transfer.

The geometric predilections of the iridium center may also play a role in retarding oxygen atom transfer. Oxygen atom transfer is an inner-sphere reaction, and the initial product is not the free oxidized substrate but its metal complex. For example, phosphine oxide complexes are universally invoked as initial products of the addition of phosphines to oxometal complexes, and can often be observed as the kinetic products of such reactions.<sup>4,28</sup> Typical d<sup>0</sup> or d<sup>2</sup> metal oxo complexes can readily accommodate a phosphine oxide in the site occupied by the oxo ligand prior to the oxygen atom transfer. Thus addition of phosphine to the oxo ligand can take place without substantial rearrangement of the coordination sphere. In contrast, deoxygenation of d<sup>4</sup> (mes)<sub>3</sub>IrO forms a d<sup>6</sup> (mes)<sub>3</sub>Ir fragment where the preferred binding site is not along the C<sub>3</sub> axis where the oxo ligand was located, but rather off to one side of the complex. The observed dynamic behavior of (mes)<sub>3</sub>Ir(PPh<sub>3</sub>) indicates that this geometric preference is sizable (> 12 kcal/mol). The transition state for oxygen atom transfer must exhibit a geometry unfavorable either to the oxo reagent or to the complexed phosphine oxide product; it cannot be optimal for both. This geometric mismatch can obviously be overcome in sufficiently exothermic reactions such as phosphine oxidation, but may contribute to the relatively poor oxygen atom transfer kinetics that prevent reactions with less easily oxidized substrates such as sulfides.

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## Conclusions

Trimesityliridium(III) reacts rapidly with dioxygen to form oxotrimesityliridium(V) in a process that is second order in iridium and first order in O<sub>2</sub>. When coupled with the ability of (mes)<sub>3</sub>Ir=O to oxidize substrates such as triphenylphosphine, this allows (mes)<sub>3</sub>Ir to catalyze the air oxidation of PPh<sub>3</sub> at 1 atm of pressure and room temperature at rates comparable to the fastest catalysts reported to date. The catalysis is significantly inhibited by binding of substrate to (mes)<sub>3</sub>Ir to form a sawhorse-shaped adduct, (mes)<sub>3</sub>Ir(PPh<sub>3</sub>), whose dynamic behavior has been probed by variable-temperature NMR. Despite its high formal oxidation state, (mes)<sub>3</sub>Ir=O oxidizes only the most reactive oxygen atom acceptors such as phosphines or arsines. The low kinetic reactivity of this late metal oxo complex may be due to its relative electron richness or to a geometric mismatch between

the pseudotetrahedral oxo complex and the sawhorse-shaped iridium(III) adduct that would be the immediate product of atom transfer.

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**Supporting Information Available:** Eyring, van't Hoff, and Hammett plots, NMR titration data, and variable-temperature <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H NMR spectra (Figures S1–S9). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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