in the presence and absence of oxygen, (2) uncertainties regarding the nature of axial bases (if any) supplied by the graphite surface, and (3) the competitive inhibition by water shown in the present work. However, the surprisingly high dioxygen affinity of **1** can give new insight into the factors that influence dioxygen binding to metal centers.

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Registry No. 1, 89906-36-5; $1 \cdot O_2$, 89906-37-6; 1·(*N*-MeIm), 99665-74-4; $1 \cdot (H_2O)$, 99665-75-5; O_2, 7782-44-7.

Photochemical Carbonylation of Benzene by Iridium(I) and Rhodium(I) Square-Planar Complexes

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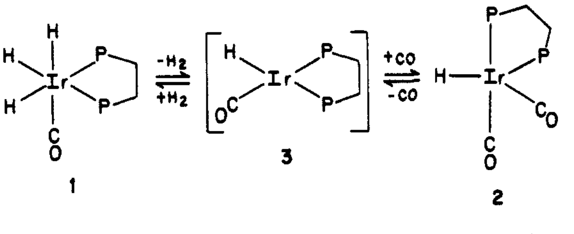
The photochemical behavior of d^8 square-planar complexes represents an area of current interest as evidenced by Ford's recent flash photolysis studies on $RhCl(CO)(PPh_3)_2$ and its well-known Ir analogue.[1-3] In these studies all intermediates and observed transients are thought to form via initial photodissociation of CO. In the absence of added substrate, the principal chemical reaction following the photolysis is recombination of $MCl(PPh_3)_2$ and CO, although for M = Rh, dimerization to $[MCl(PPh_3)_2]_2$ followed by slower carbonylation to starting complex is also noted. Flash photolysis of the Rh complex with either H_2 or C_2H_4 present gives spectral changes indicative of initial reaction of $RhCl(PPh_3)_2$ with substrate, but subsequent and rapid carbonylation leads to no net chemical change for the system. In this paper we report that photolysis of these complexes under long-term continuous irradiation leads to significant and new overall reaction chemistry. This chemistry, which is only observed upon photolysis, involves arene C–H functionalization and, in particular, the carbonylation of benzene to benzaldehyde. This observed C–H bond functionalization contrasts with the known oxidative carbonylation of arenes using Pd^{2+} in that no prior activation of the benzene ring is needed.[4] We are also able to show that the system is limited by the overall thermodynamics of the arene carbonylation reaction and not by the reactivity of the d^8 photocatalyst system.

The starting point for this work derives from a mechanistic proposal made previously in a report on benzene carbonylation using either $IrH_3(CO)(dppe)$ (**1**) or $IrH(CO)_2(dppe)$ (**2**) as the photocatalyst complex.[5] These coordinatively saturated complexes undergo exchange reaction (1) thermally or photochemically, presumably through the intermediacy of the four-coordinate species IrH(CO)(dppe) (**3**). Since benzene carbonylation was only observed upon photolysis, it was proposed that **3** was the photochemically active species for the system. A test of this proposal was performed based on the assumption that **3**, as a four-coordinate, 16-e^- species, would be yellow or orange and therefore absorb light at longer wavelengths than the two precursor complexes **1** and **2**. Two samples containing 6 mM solutions of



(1)

$IrH(CO)_2(dppe)$ (**2**) in benzene under 600 torr of CO were photolyzed through a 366-nm cut-off filter. Under these conditions, **2** is the only observable complex in solution, but it exhibits no significant absorptions at λ greater than 320 nm. The first sample, which was maintained at room temperature, showed no benzaldehyde formation after 48 h of photolysis. The second sample was heated during photolysis to 75 °C at which temperature dissociation of CO from **2** is known to occur.[4] After 6 h of photolysis the second sample was analyzed by gas chromatography and found to contain 1.1×10^{-3} mmol (1.8 mM) of benzaldehyde. This result provides strong support that **3** is the photochemically active species in the previously reported benzene carbonylation system.[5]

The formation of benzaldehyde is also seen when benzene solutions of the chelated di(phosphine) complexes $IrH_3(CO)(dppp)$ (**4**) (dppp = 1,3-bis(diphenylphosphino)propane) and IrBr(CO)(dppe) (**5**) are irradiated under 600 torr of CO. Complex **4** is synthesized analogously to the procedure used for **1**[5] and, like **1**, undergoes thermal and photochemical exchange with CO and H_2, presumably through the 16-e^- species IrH(CO)(dppp). The four-coordinate complex **5** exists under CO in equilibrium with its five-coordinate carbonyl adduct $IrBr(CO)_2(dppe)$ and ν_{CO} for both species are observed in solution.[6]

The observation of benzene carbonylation promoted photochemically by four-coordinate species of general formula IrX(CO)($P\frown P$) prompted us to examine the photolysis of benzene solutions of Ir(I) and Rh(I) monodentate phosphine complexes under CO. We find that for $IrCl(CO)(PPh_3)_2$, $RhCl(CO)(PPh_3)_2$, and $RhH(CO)(PPh_3)_3$, PhCHO forms under long-tern continuous irradiation. The most extensively studied of these systems is $RhCl(CO)(PPh_3)_2$. In a typical experiment, a 7.2 mM solution of $RhCl(CO)(PPh_3)_2$ [3.0 mg of complex in 0.6 mL of benzene] was placed under 100 mm of CO and the tube was flame-sealed. The sample was irradiated at ambient temperature through Pyrex. Benzaldehyde was observed by ^1H NMR in a concentration of 0.15 mM after 2 h of photolysis.[7] The concentration continued to increase until it remained essentially constant at 15 mM after 40 h of photolysis. This final aldehyde concentration was further confirmed by GC analysis.[8]

In all runs the amounts of PhCHO formed are small, never exceeding 3 turnovers. This is consistent with the unfavorable thermodynamics for the reaction $C_6H_6 + CO = C_6H_5CHO$, for

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(6) (a) Infrared data in benzene solution for IrBr(CO)(dppe), ν_{CO}, 1980 cm^{-1}; $IrBr(CO)_2(dppe)$, ν_{CO} 2040 and 1940 cm^{-1}. (b) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

(7) (a) All proton spectra were recorded on a Bruker WH-400 400-MHz spectrometer. (b) Benzaldehyde (PhCHO) was observed by ^1H NMR by using a solvent peak suppression program. The reaction solvent was 20% C_6D_6 in C_6H_6, and the irradiated frequency was 7277.67 Hz.

(8) Benzaldehyde was detected on 10 ft of Apiezon L on Chromosorb W on a Hewlett-Packard 5730A GLC (FID) equipped with an HP 3380A automatic integrator. GLC conditions: injector port, 200 °C; oven, 150 °C; detector, 200 °C.

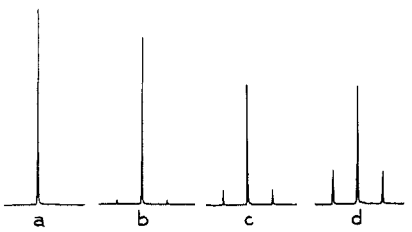

Figure 1. Aldehyde proton resonance (400 MHz) for $RhCl(CO)(PPh_3)_2$ + ^{13}CO + PhCHO in C_6D_6 showing successive incorporation of ^{13}C isotope into benzaldehyde. The resonance is at δ 9.63 ppm with $J(^{13}C\text{–}H)$ of 173 Hz. Irradiation times: (a) $t = 0$; (b) 1 day; (c) 5 days; (d) 10 days.

which we calculate $\Delta G°_{298} = +1.7$ kcal.[9] The reverse reaction, PhCHO decarbonylation, has been studed in detail by others.[10] As a catalytic reaction using $RhCl(CO)(PPh_3)_2$, it is found to require temperatures greater than 170 °C. In contrast, we find that $RhCl(CO)(PPh_3)_2$ is a photochemical decarbonylation catalyst at ambient temperature, as shown by photolysis of a 7.2 mM solution of $RhCl(CO)(PPh_3)_2$ (4 μmol) containing 20 μmol of PhCHO. After 24 h of photolysis, the amount of PhCHO had decreased to 12 μmol as determined by GC analysis. In an earlier report, Geoffroy et al. observed that treatment of photolyzed solutions of $RhCl(CO)(PPh_3)_2$ with PhCHO led to benzene formation, but they did not see direct photochemical decarbonylation using heptanal as substrate.[11]

In order to confirm that the low yields of PhCHO produced in the photolysis of benzene solutions of $RhCl(CO)(PPh_3)_2$ were indeed the result of thermodynamic limitations and not kinetic inactivity of the system, an experiment was performed using ^{13}CO. A benzene-d_6 solution containing 3.0 mg of $RhCl(CO)(PPh_3)_2$ (4.3 μmol) and 2.0 μL of PhCHO (19.6 μmol) was placed under 1.2 atm of ^{13}CO and irradiated at 22 °C through a Pyrex filter. Examination of the aldehyde resonance by ^1H NMR (δ 9.63, $J_{C\text{-}H} = 173$ Hz) revealed significant incorporation of ^{13}CO into benzaldehyde, confirming the occurrence of carbonylation/decarbonylation sequences. As shown in Figure 1, the ^{13}C satellites of the aldehyde proton showed a steady increase in intensity over 10 days at which time the extent of ^{13}CO incorporation into PhCHO amounted to 38%. During this period, the PhCHO concentration decreased from 36 mM (5 equiv) to 21 mM (2.9 equiv) as determined by GC analysis.[8]

While this demonstrates the reversibility of photochemical carbonylation, it raises the question of whether there is a common intermediate for both the forward and reverse reactions or a photostationary state resulting from two independent photoreactions. To test this, three identical samples were prepared (7.5 mM complex, 12 mM PhCHO, and 1.0 atm of CO) and irradiated through a Pyrex filter for 3 days. One tube was opened and GC analysis showed that the PhCHO concentration had decreased to 10.5 mM. The other two samples were placed at distances 4 and 16 cm from the light source and irradiated for another day. Analysis of these two samples showed each to be 10.1 mM in PhCHO, indicating that carbonylation and decarbonylation proceed through a common intermediate and result eventually in an equilibrium mixture of PhCHO, CO, and benzene.

To account for the incorporation of ^{13}CO into PhCHO under photolysis, equivalence of ^{12}CO and ^{13}CO is required at some point in the catalysis. This may be achieved via free CO in solution or a dicarbonyl intermediate. The pathways leading to photochemical carbonylation and decarbonylation involve the same initial step which we believe is loss of a ligand to generate a 14-e$^-$ intermediate. While Ford and Wink have demonstrated efficient photochemical dissociation of CO from $MCl(CO)(PPh_3)_2$, they see no net reaction chemistry under the conditions of their experiment.[1,2] The formation of benzaldehyde in the present study may result from either a relatively inefficient reaction of $MCl(PPh_3)_2$ with C_6H_6 leading to arene activation and carbonylation, or from a second photochemical process which occurs much less efficiently than CO photodissociation. This process could be phosphine dissociation to generate $MCl(CO)(PPh_3)$.

Support for the notion of ligand dissociation as the photochemical step is obtained from photolyses carried out under different CO pressures and in the presence of added phosphine. Two 7.5 mM benzene solutions of $RhCl(CO)(PPh_3)_2$ under 36 and 615 mm of CO were prepared. The samples were irradiated and monitored by ^1H NMR spectroscopy[7b] for 20 h. Analysis by GC showed the samples to be 4.1 and 1.8 mM, respectively, in benzaldehyde. Thus the efficiency of benzene carbonylation is reduced as CO pressure is increased. The addition of PPh_3 to a benzene solution of $RhCl(CO)(PPh_3)_2$ under CO causes rapid formation of $RhCl(PPh_3)_3$ upon irradiation in accord with the results of Ford[1] and inhibition of benzaldehyde formation.

While further mechanistic details remain to be elucidated, the key point of the present study is that Rh(I) and Ir(I) phosphine complexes do exhibit photochemical reactivity which leads to significant, new reaction chemistry. If the arene carbonylation reaction seen here can be driven to overcome its unfavorable thermodynamics such as by subsequent hydrogenation, this photochemical functionalization may prove useful as well as interesting.

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Sustained Epoxidation of Olefins by Oxygen Donors Catalyzed by Transition Metal Substituted Polyoxometalates, Oxidatively Resistant Inorganic Analogues of Metalloporphyrins

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The homogeneous catalytic oxygenation of saturated and unsaturated hydrocarbons has been one of the most active areas of chemical research in the last 5 years.[1-12] Numerous metallo-

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