

at 678 (ϵ 202) and 313 nm (ϵ 342) and a shoulder at ca. 418 nm (ϵ ca. 154) in 2 M HPTS (Figure 1). General features of these absorption spectra are similar to those of the corresponding molybdenum species: $[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$ (peaks at 508 (ϵ 64) and 304 nm (ϵ 270))^{12b} and $\text{Mo}_3^{\text{III,III,IV}}(\text{aq})$ (peaks at 1050 (ϵ 100) and 398 nm (ϵ 230), and a shoulder at 495 nm (ϵ ca. 115)).²⁰ All the absorption bands of the tungsten species are shifted to shorter wavelength.

Cyclic voltammogram of the orange aqua ion in 2 M HPTS showed an irreversible reduction wave at ca. -0.5 V vs. SCE at 25 °C, which is more negative than $E_{1/2}$ (-0.341 V vs. SCE) of the molybdenum(IV) aqua ion. There is no other inflection in the CV curve between $+1$ and -1 V. Oxidation of the trimer to W(V) is difficult since the tungsten(V) aqua ion appears to be dimeric.⁷

The tungsten(IV) aqua ion is slowly converted to $[\text{W}_3\text{O}_4(\text{NCS})_9]^{5-}$ (λ_{max} at 532 nm with ϵ ca. $280 \text{ M}^{-1} \text{ cm}^{-1}$ per W) in 1.3 M NH_4NCS and 1.0 M HPTS. The change in absorption spectrum occurred in roughly two steps: first step finished within a few minutes at 25 °C with more than 70% of the absorbance change (300–700 nm) and second step took ca. 2 h. Neither of the two steps showed good exponential absorbance change. The two-step change was observed also for the reaction of $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ with NCS^- .^{9b}

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(19) The absorption spectrum strictly obeyed Beer's law in the concentration range of 0.001–0.008 M (per W).

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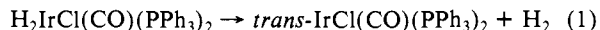
Common Intermediates in the Flash Photolysis of Vaska's Compound $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and Its Dihydride Adduct $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. Implications with Regard to Reductive Elimination Mechanisms

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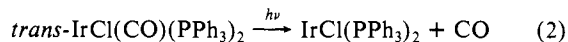
Phosphine complexes of low-valent metal complexes have a long history in the chemistry of homogeneous catalytic activation of small molecules.¹ In the investigation of such reactivities, Vaska's complex $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ has served as an important model for mechanistic investigation of catalytically relevant reactions such as oxidative addition of the small molecules O_2 and H_2 and the corresponding reductive eliminations to reform Vaska's complex, e.g.,



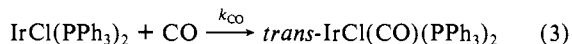
The dihydrogen elimination depicted in eq 1 has been shown to

occur slowly in thermally activated processes ($k_1 = 3.8 \times 10^{-5} \text{ s}^{-1}$ in 25 °C benzene solution²) but quite readily when the dihydride complex is photolyzed with 366-nm light.³ In the course of investigating reactive intermediates in the chemistry of rhodium(I) and iridium(I) phosphine complexes, we have observed that a common transient is produced in the flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ and of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. This result suggests that the mechanism of the photoinduced version of eq 1 occurs by a stepwise mechanism involving CO dissociation as the primary photoreaction of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. The resulting pentacoordinated Ir(III) intermediate appears to be dramatically activated toward H_2 elimination as predicted in theoretical treatments.⁴ Preliminary experiments with the orthometalated species $\text{HIrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$ lead to similar conclusions.

Flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ in stringently deaerated benzene solution under argon ($\lambda_{\text{irr}} > 254 \text{ nm}$)⁵ resulted in the formation of a transient with strong absorption in the spectral region 390–550 nm. This species decayed to the initial base line via cleanly second-order kinetics. The return to the initial spectrum is consistent with the earlier report that continuous photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ leads to no net photoreactions.^{3a} When similar flash experiments were carried out under various pressures of CO, the transient decay kinetics were first order with the observed rate constants k_{obsd} linearly dependent on P_{CO} . This observation leads to the conclusions that the intermediate formed is the product of CO photodissociation

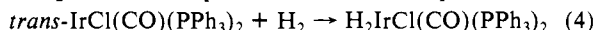


and that the decay process is



The second-order rate constant $k_{\text{CO}} = (2.7 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was determined from the linear plot⁶ of k_{obsd} vs. $[\text{CO}]$. These results are very similar to the chemistry induced by the flash photolysis of the rhodium(I) analogue $\text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$,⁷ although k_{CO} is about 4-fold faster for the Ir(I) transient.

Consistent with the earlier report,³ we found that $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ undergoes facile photoelimination of H_2 (eq 1). The quantum yield was 0.56 mol/einstein for continuous photolysis at 313 nm, a value close to that reported^{3b} for the similar complex $\text{H}_2\text{IrCl}(\text{PPh}_3)_3$ (0.55). Flash photolysis of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in benzene under 1.0 atm of H_2 ($\lambda_{\text{irr}} > 254 \text{ nm}$) resulted in transient absorbance in the spectral region 400–550 nm qualitatively the same as that seen for the flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$. This transient decayed via second-order kinetics to give Vaska's compound. Over a period of 10 min, the latter underwent subsequent reaction with H_2 to reform the starting complex according to eq 4 ($k_{\text{obsd}} = 1.2 \text{ M}^{-1} \text{ s}^{-1}$).² The identical kinetics behavior was found for the flash photolysis under 0.25 atm of H_2 with the exception that the rate of eq 4 was a factor



of 4 slower. Flash photolysis of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ under H_2/CO mixtures gave decay rates linearly dependent on P_{CO} . Plots of k_{obsd} vs. $[\text{CO}]$, as above, gave the second-order rate constant

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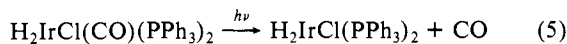
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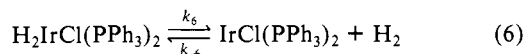
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$(2.6 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ within experimental uncertainty of the k_{co} reported for eq 3.

These results indicate that $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ first undergoes photodissociation of CO (eq 5) followed by elimination of H_2 from



the resulting pentacoordinated intermediate (eq 6) to give the



" $\text{IrCl}(\text{PPh}_3)_2$ " transient formed directly via flash photolysis of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. This view⁸ contrasts to the proposal⁹ that the dihydride photoelimination occurs by a single concerted step but is consistent with theoretical arguments⁴ and several experimental observations^{10,11} that reductive elimination from d^6 complexes often occurs much more readily after ligand dissociation from the original hexacoordinate species to give a pentacoordinate intermediate. Given that formation of $\text{IrCl}(\text{PPh}_3)_2$ was complete within the lifetime of the flash (20 μs), a lower limit for k_6 can be estimated as $5 \times 10^4 \text{ s}^{-1}$. Thus, we conclude that dissociation of CO accelerates dihydrogen elimination by at least 9 orders of magnitude. Notably, this rate acceleration occurs despite the dissociation of the π -acid CO which would be expected to favor the lower oxidation state of the metal center. Another notable feature is that the equilibrium indicated by eq 6 apparently lies largely to the right in contrast to the observation that under similar conditions the equilibrium for the Rh(I) analogue must lie to the left.⁷

Preliminary investigations of the Ir(III) species $\text{H}^+\text{IrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2$,¹² the orthometalated isomer of Vaska's compound, as well as of the dinitrogen Ir(I) complex *trans*- $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$,¹³ demonstrate that flash photolysis leads in both cases to immediate appearance of a transient spectrum qualitatively the same as that attributed to " $\text{IrCl}(\text{PPh}_3)_2$ ". In the former case the transient decays by a second-order pathway (P_{CO} dependent, i.e., eq 3) to form *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ as the photoproduct. Again it appears that the starting complex has undergone CO photodissociation to give a pentacoordinate intermediate followed by H/aryl elimination to form $\text{IrCl}(\text{PPh}_3)_2$ within the 20- μs lifetime of the flash. Thus, reductive elimination from this pentacoordinate intermediate must be at least 8 orders of magnitude faster than the rate of about $3 \times 10^{-4} \text{ s}^{-1}$ (70 °C) we have measured for the thermal reaction of $\text{H}^+\text{IrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2$ to give *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$.¹⁴ For $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$, photolabilization of N_2 to give $\text{IrCl}(\text{PPh}_3)_2$ is irreversible and, in the absence of the other reactants, this reactive intermediate apparently undergoes internal orthometalation of a triphenylphosphine. This is accompanied by slow absorbance decreases in the 340–550-nm range with isosbestic points at 460 and 334 nm consistent with formation of Ir(III) products. The

proton NMR spectrum of the product solutions from the continuous photolysis of $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ in C_6D_6 under otherwise analogous conditions displays a -22.5 ppm resonance indicating formation of an iridium hydride.¹⁵ These investigations will be described in detail in subsequent publications.

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Diagonal Peak Suppression in 2D-NOE Spectra

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The 2D correlation NMR experiments COSY¹ and NOESY² are standard techniques for study of molecular structure in solution. COSY, which is based on coherence transfer via the J coupling, has been the progenitor of a myriad of other pulse sequences for specific applications.³⁻⁵ Particularly useful have been filtered COSY pulse sequences,⁶ which are conceptually derived from multiple-quantum selective-excitation experiments.^{7,8} Double-quantum filtered COSY especially is frequently employed to suppress single-quantum peaks, improving the dynamic range and the resolution close to the diagonal.⁹ NOESY, which detects through-space magnetization-transfer via direct dipolar relaxation, frequently suffers from a more severe dynamic range problem than COSY. While use has recently been made of coherence transfer via the J coupling to selectively observe certain resonances in NOESY spectra,¹⁰ until now there has not been a general method for removing the diagonal. Thus, cross-peaks between nuclei with similar chemical shifts, which fall close to the diagonal, are obscured. Furthermore, the spectra are also often marred by strong solvent lines and t_1 noise. In this paper we describe a magneti-

(8) The following observation argues against a sequential two-photon process involving initial H_2 photolabilization to generate $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ followed by secondary photolysis of this product to give " $\text{IrCl}(\text{PPh}_3)_2$ ". The relative pulse intensity required to generate the same concentration of the latter transient was 5 times larger when the initial substrate was *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (under argon) than when $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (under H_2) was the initial substrate. An alternative mechanism should be considered, namely, the possibility that both CO and H_2 are dissociated from the excited state of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. At present such a mechanism, although unprecedented, cannot be differentiated from the stepwise pathway proposed in eq 5 and 6.

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