the amino-bound form hinders isolation of crystalline product in the absence of excess ligand.

Relevance to B_{12} Chemistry and Biochemistry. Model studies reveal that steric interactions between bulky R groups and equatorial ligands weaken Co–C bonds as evidenced by longer[11] and weaker Co–C bonds.[3-6] Similarly, cobalamins with bulky R groups have less stable Co–C bonds.[2,30-32]

Comparisons of the structures of coenzyme B_{12} (5′-deoxyadenosylcobalamin) and MeB_{12} (methylcobalamin with each other and with models reveal no unusual structural features.[7,9,10] Indeed, Co–C bond cleavage in coenzyme B_{12} requires a conformational change induced by the enzyme.[1] A feasible change is a protein-induced distortion which increases steric repulsion between the corrin and the deoxyadenosyl and/or Co–C–C or N–Co–C bond angle deformations.[1,2,10,30-34]

The importance of such steric interactions has been clearly demonstrated for cobaloximes with trans P-donor ligands where the equatorial $Co(DH)_2$ system is distorted toward R.[11] However, from trans N-donor ligands, large distortions are not found with any regularity except for very bulky R where the distortion is toward the N donor.[11]

In cobalamins with bulky R, the "base off" forms (pendant 5,6-dimethylbenzimidazole, 5,6DMBz) are relatively stable but the "base on" forms are very unstable to Co–C bond cleavage.[31,32] Similarly, bulky R groups promote dissociation of 5,6DMBz and thus stabilize the "base off" form, which is believed to be five coordinate.[31,32] This information together could be taken to suggest that the 5,6DMBz distorts the corrin and thereby weakens the Co–C bond.[31]

However, there are some problems with such an interpretation. First, the bulky R groups studied are also good trans labilizers.[32] The "base off" form is favored by good trans labilizer ligands regardless of bulk.[32] Thus, the electronic and steric effects are not easily separated. Second, Co–C bond homolysis of such "base off" cobalamins would form an unstable four-coordinate cobalt(II) species (presumably through an incipient four-coordinate cobalt(II) activated complex).[33] Thus, the steric effect of the 5,6DMBz may be limited to maintaining the Co in the equatorial corrin N_4 plane.[32,33,35] Our observation, that the value of K (eq 4 and 8) is not dependent on the electronic properties of R (as judged by Co–N bond distances, ^{13}C shifts, etc.) but on the bulk of R, is the first clear evidence for a steric effect of R on N-donor binding in solution.

A picture which is emerging from the ongoing studies in several laboratories is that the 5,6DMBz's major role is to maintain Co in the corrin N_4 plane and to stabilize the cobalt(II) intermediate.[33] Additional distortions caused by the enzyme could include (a) Co–C–C and/or N–Co–C bond distortion, (b) corrin ring deformation, (c) Co–N (5,6DMBz) bond lengthening, or (d) a combination of (a) → (c). Although the most obvious corrin ring distortion would involve enhanced interaction with the 5′-deoxyadenosyl, it is conceivable that the Co–N(5,6DMBz) bond could also be lengthened.[9,12] Additional experimental and theoretical studies on models, cobalamins, and enzymic systems are clearly needed to help resolve these issues.

Acknowledgment. This work was supported by NIH Grant GM 29225 to L.G.M. and a grant from MPI (Rome) to L.R. L.G.M. thanks the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award. The NSF aided in the purchase of the 360-MHz NMR instrument.

Supplementary Material Available: Tables of elemental analyses, bond lengths, and bond angles, hydrogen atom coordinates, anisotropic thermal parameters, and calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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(35) A reviewer has pointed out that the 5,6-DMBz coordination causes folding of the corrin. A second reviewer questions the view that the "base off" species is five coordinate and suggests a six-coordinate aquo species as a more likely alternative. We agree that the nature of the "base off" cobalamin is presently not understood and that the spectral evidence for a five-coordinate species has alternative explanations. However, we also feel that there are good reasons, independent of the spectral evidence, for suggesting the existence of five-coordinate organo cobalamins. This issue clearly needs resolution.

A Flash Photolysis Investigation of Dihydrogen Elimination from Phosphine Complexes of Iridium(III) and Rhodium(III): $H_2IrCl(CO)(PPh_3)_2$, $H_2IrCl(PPh_3)_3$, and $H_2RhCl(PPh_3)_3$

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Abstract: Flash photolysis studies of the two iridium(III) dihydride complexes $H_2IrCl(L')(PPh_3)_2$ (L′ = CO or PPh_3) in deaerated benzene solution demonstrate the formation of a common intermediate $IrCl(PPh_3)_2$ for each case. This species reacts with CO and PPh_3 to form $IrCl(CO)(PPh_3)_2$ and $IrCl(PPh_3)_3$ with the respective rate constants 2.5×10^8 and 1.3×10^7 M^{-1} s^{-1}. A model is proposed by which the primary photoreaction in these cases is ligand dissociation to give the common five-coordinate intermediate $H_2IrCl(PPh_3)_2$ which undergoes rapid dihydrogen elimination to give $IrCl(PPh_3)_2$ in competition with back reaction with L′. Continuous photolysis in the presence of added L′ reduced quantum yields for dihydrogen loss in a manner consistent with this model. The dramatically enhanced rate of H_2 elimination from the pentacoordinate intermediate (relative to the hexacoordinate analogues) would be consistent with theoretical treatments of this process based on orbital topology changes. The rhodium(III) dihydride $H_2RhCl(PPh_3)_3$ undergoes a different photoreaction pathway, concerted dihydrogen elimination, to give the tetracoordinate species $RhCl(PPh_3)_3$ as the primary photoproduct. These results indicate the multiplicity of reaction channels available to the electronic excited states of such complexes.

The photochemical excitation of transition metal di- and polyhydrides generally is accompanied by the reductive elimination of dihydrogen to give a coordinatively unsaturated metal-containing product, e.g.,

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$$H_2ML_x \rightarrow H_2 + ML_x \quad (1)$$

There has long been considerable interest in the quantitative aspects of these reactions as studied by continuous photolysis techniques.[1-2] However, the recent use of such reactions to generate species capable of the activation of carbon–hydrogen bonds, even of saturated hydrocarbons,[3-6] adds further relevance to understanding the key reaction mechanisms. Of particular importance would be to understand the factors governing the photodissociation pathways and the reaction dynamics of transient intermediates generated in the course of these processes. Described here is an investigation of such photoreductive elimination of H_2 from the complexes $H_2IrCl(CO)L_2$, H_2IrClL_3, and H_2RhClL_3 (L = PPh_3) using "conventional" flash photolysis techniques. The results of these studies lead to the conclusion that there are at least two mechanisms operable for this reaction, one being the previously proposed concerted loss of H_2 from the initial complex, the other being prior dissociation of another ligand to give a pentacoordinate complex which undergoes rapid elimination of H_2.

Experimental Section

Benzene used as a solvent for the preparation of all reaction solutions was "spectra grade" (Mallinckrodt) and further purified by drying over $LiAlH_4$ then distilling under N_2. The gases carbon monoxide, dihydrogen, and dinitrogen (Linde) were CP grade and used without further purification. The phosphine complexes $RhCl(PPh_3)_3$, $IrCl(PPh_3)_3$; and $IrCl(CO)(PPh_3)_2$ were prepared by literature procedures.[7-9] The iridium(III) dihydrogen adducts $H_2IrCl(CO)(PPh_3)_2$ and $H_2IrCl(PPh_3)_3$ were prepared as described[8,10] from the corresponding iridium(I) complex and isolated as solids. The rhodium(III) dihydrogen adduct $H_2RhCl(PPh_3)_3$ was prepared in situ by dissolving the Rh^I species $RhCl(PPh_3)_3$ in H_2 saturated benzene.[7]

Flash photolysis experiments were carried out by using a "conventional" xenon flash apparatus described previously.[11,12] The "dead" time with this apparatus is about 20 μs. Wavelength selection for the flash experiments was effected by using concentrically jacketted cells with aqueous salt solutions in the outer jacket serving as cutoff filters. These were 0.5 M $NaNO_3$ ($\lambda_{irr} > 320$ nm) and 0.5 M $Na_2S_2O_3$ ($\lambda_{irr} > 295$ nm). (The actual cutoff of sodium thiosulfate is 254 nm; however, the benzene in the reaction solution serves as an internal filter of wavelengths less than 295 nm). Flash photolysis solutions were prepared by first deaerating the predried benzene solvent by four freeze-pump-thaw cycles on a vacuum manifold ($P < 10^{-4}$ torr) then distilling this solvent in vacuo from a Na/K amalgam into a preevacuated photolysis cell containing the solid materials. The resulting solution was then equilibrated with the appropriate gas mixtures (approximately 10 min), and the cell was transferred to the flash apparatus. All flash experiments were carried out at ambient temperature 23 ± 1 °C.

All continuous photolysis experiments were carried out by using the optical trains described previously using interference filters for wavelength selection.[13] Quantitative light intensities were measured by using the Heterocoerdianthron actinometer described by Brauer and Schmidt[14] and a YSI Kettering Model 65A radiometer was used to ensure that light fluxes were constant during an experiment. Photolysis solutions were prepared from predried benzene and transferred to photolysis cells under the appropriate gas by using Zwickel flask techniques.[15] Photosolution optical density changes were monitored using a Cary 118 UV–vis spectrophotometer. Incremental quantum yields were extrapolated to zero time to correct for inner filter effects from absorbing products.[13]

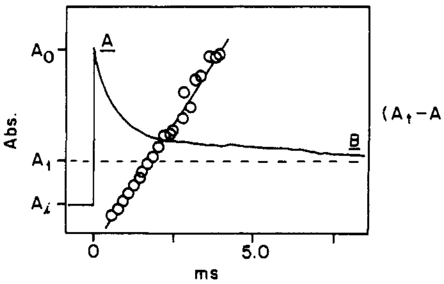

Figure 1. Flash photolysis trace (curve) following excitation of $H_2IrCl(CO)(PPh_3)_2$ in H_2 saturated benzene and $(A_t - A_l)^{-1}$ vs. *t* second-order plot (line) for the decay of transient A to $IrCl(CO)(PPh_3)_2$.

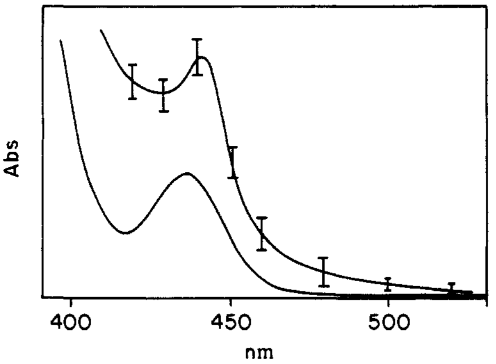

Figure 2. Transient spectrum recorded 100 μs after flash photolysis of $H_2IrCl(CO)(PPh_3)_2$ in benzene.

Thermal reaction kinetics were investigated by using a Durram–Gibson model D110 stopped flow spectrophotometer modified for use with deaerated solutions and for digital data collection and manipulation as described previously.[16] All reaction solutions were prepared under stringently deareated conditions. Some slower reactions were followed by using a Cary 118 spectrophotometer equipped with a constant temperature cell compartment.

Results

Photolysis of $H_2IrCl(CO)(PPh_3)_2$. The continuous photolysis of this compound has been previously demonstrated to lead to photoreductive elimination of H_2 (eq 2).[17] A quantitative study of this reaction was carried out by using optical density changes at 385 nm to monitor concentration changes (the *trans*-$IrCl(CO)(PPh_3)_2$ product, "Vaska's compound" is more strongly absorbing). For 313-nm irradiation, the quantum yield for di-

$$H_2IrCl(CO)(PPh_3)_2 \xrightarrow{h\nu} H_2 + trans\text{-}IrCl(CO)(PPh_3)_2 \quad (2)$$

hydrogen elimination ϕ_e was determined to be 0.56 ± 0.02 mol/einstein (23 ± 1 °C) under a dinitrogen atmosphere. In solutions equilibrated with air, the quantum yield for disappearance of the dihydride was the same, within experimental uncertainty. However, a significantly smaller value of ϕ_e (0.36 ± 0.03) was measured under 1.0 atm CO.

The flash photolysis ($\lambda_{irr} > 295$ nm) of $H_2IrCl(CO)(PPh_3)_2$ in H_2 saturated benzene (1.0 atm; 0.0028 M)[18] led to immediate absorbance changes to give a new species A followed by second-order decay to another species B (Figure 1). Over a much longer time span the absorbances due to B decayed via a first-order pathway ($k_{obsd} = 1.7 \times 10^{-3}$ s^{-1}) to regenerate the starting spectrum of the solution. The spectrum of B over the spectral region 390–530 nm (Figure 2) was found to be the same as that of *trans*-$IrCl(CO)(PPh_3)_2$.[17] Furthermore, the first-order rate

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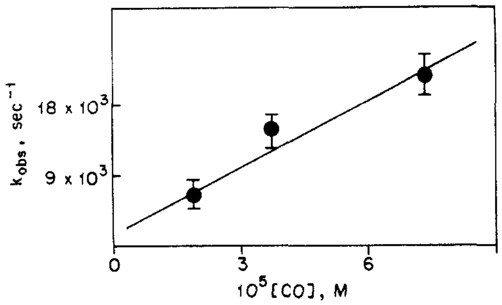

Figure 3. Plot of k_{obsd} vs. [CO] for the decay of transient A seen in the flash photolysis of $H_2IrCl(CO)(PPh_3)_2$.

constant for the reaction of B with H_2 to reform $H_2IrCl(CO)(PPh_3)_2$ proved consistent with that expected for the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ with H_2 (eq 3). If, in analogy to earlier

$$trans\text{-}IrCl(CO)(PPh_3)_2 + H_2 \xrightarrow{k_3} H_2IrCl(CO)(PPh_3)_2 \quad (3)$$

studies,[19] a second-order rate-limiting step is assumed, the value of k_3 would be 0.6 M^{-1} s^{-1} under these conditions as compared to the value 1.2 M^{-1} s^{-1} measured previously in 30 °C chlorobenzene.[19] Thus, it can be concluded that B is *trans*-$IrCl(CO)(PPh_3)_2$, the product of continuous photolysis (eq 2).

The spectrum of transient A (Figure 2) is within experimental uncertainty the same as that observed as the result of the flash photolysis of *trans*-$IrCl(CO)(PPh_3)_2$ and concluded to result from CO dissociation to give the tricoordinate complex $IrCl(PPh_3)_2$ or its solvated analogue (eq 4).[20] The second-order decay of A is

$$trans\text{-}IrCl(CO)(PPh_3)_2 \xrightarrow{h\nu} CO + IrCl(PPh_3)_2 \quad (4)$$

also consistent with eq 5, which has been demonstrated[20] to have

$$IrCl(PPh_3)_2 + CO \xrightarrow{k_5} IrCl(CO)(PPh_3)_2 \quad (5)$$

the second-order rate constant $k_5 = 2.6 \times 10^8$ M^{-1} s^{-1}. When the flash photolysis of $H_2IrCl(CO)(PPh_3)_2$ was carried out under various H_2/CO gas mixtures, the decay of A to give $IrCl(CO)(PPh_3)_2$ was accelerated and displayed first-order kinetics with rates linearly dependent on [CO] but independent of [H_2]. A plot of the resulting k_{obsd} values vs. [CO] was linear with a slope of (2.5 ± 0.6) × 10^8 M^{-1} s^{-1} (Figure 3). This confirmed that A is indeed $IrCl(PPh_3)_2$ formed by the photoinduced loss of both H_2 and CO from the hexacoordinate Ir^{III} dihydride.

The photolability of *trans*-$IrCl(CO)(PPh_3)_2$ combined with the relative length of the flash pulse raises the question of whether the formation of $IrCl(PPh_3)_2$ was the consequence of a sequential, two photon process, namely, initial photodissociation of H_2 from $H_2IrCl(CO)(PPh_3)_2$ followed by photodissociation of CO from $IrCl(CO)(PPh_3)_2$. This possibility is made very unlikely by the observation that the light intensities required to produce comparable concentrations of A from $H_2IrCl(CO)(PPh_3)_2$ and from *trans*-$IrCl(CO)(PPh_3)_2$ was about a factor of five larger for the latter system under otherwise comparable conditions. Thus, formation of A appears to be the direct result of photoexcitation of $H_2IrCl(CO)(PPh_3)_2$.

Photolysis of $H_2IrCl(PPh_3)_3$. The continuous photolysis of $H_2IrCl(PPh_3)_3$ has also been studied previously, and it was demonstrated that dihydrogen photoelimination occurred with a substantial quantum efficiency (eq 6).[2] A reinvestigation of this

$$H_2IrCl(PPh_3)_3 \xrightarrow{h\nu} H_2 + IrCl(PPh_3)_3 \quad (6)$$

reaction using 334-nm continuous irradiation under a dinitrogen atmosphere confirmed this observation, and a quantum yield of 0.75 ± 0.07 mol/einstein was determined from the spectral changes at 450 nm recorded immediately at the conclusion of photolysis. (Immediate analysis proved necessary owing to the thermal back reaction of H_2 with $IrCl(PPh_3)_3$, see below.)

Table I. Quantum Yields (ϕ_e) for Photoelimination of H_2 from Continuous Photolysis Studies of $H_2IrCl(CO)(PPh_3)_2$ and $H_2IrCl(PPh_3)_3$ in Ambient Benzene Solution[a]

compound	conditions	ϕ_e
$H_2IrCl(CO)(PPh_3)_2$	*b*	0.56 ± 0.02
$H_2IrCl(CO)(PPh_3)_2$	P_{co} = 1.0 atm	0.36 ± 0.04
$H_2IrCl(PPh_3)_3$	[PPh_3] = 0.0 M	0.75 ± 0.02
$H_2IrCl(PPh_3)_3$	[PPh_3] = 0.010 M	0.66 ± 0.02
$H_2IrCl(PPh_3)_3$	[PPh_3] = 0.025 M	0.50 ± 0.05
$H_2IrCl(PPh_3)_3$	[PPh_3] = 0.050 M	0.34 ± 0.01

[a] λ_{irr} = 313 nm, 23 °C. [b] 1.0 atm N_2 except where noted.

Quantum yields for eq 6 were also determined in the presence of added PPh_3 at various concentrations, and it was noted that ϕ_e was substantially smaller at higher [PPh_3] (Table I).

Flash photolysis (λ_{irr} > 320 nm) of $H_2IrCl(PPh_3)_3$ in H_2 saturated benzene resulted in the immediate formation of a transient C with substantially increased absorbance over the wavelength range 390–530 nm. These spectral characteristics are, within experimental uncertainty, the same as those described above for the tricoordinate Ir^I intermediate $IrCl(PPh_3)_2$ (Figure 2).[20] The intermediate C decayed by second-order kinetics to a new species D with the spectral characteristics over the same range (λ_{max} 450 nm) the same as those reported for the tetracoordinate complex $IrCl(PPh_3)_3$.[2] Lastly D decayed by first-order kinetics to the original base line with a k_{obsd} value consistent with that found in thermal reaction studies of eq 7.[21]

$$IrCl(PPh_3)_3 + H_2 \xrightarrow{k_7} H_2IrCl(PPh_3)_3 \quad (7)$$

The second-order decay of C suggests the scenario where this transient reacts with a ligand (presumably PPh_3) formed in the same concentration by some prelabilization process. To test this proposal, the flash photolysis of $H_2IrCl(PPh_3)_3$ was carried out in H_2 saturated benzene with various small concentrations of added PPh_3. The lifetime of D was not affected, but there was a shortening of C's lifetime and transformation of the decay kinetics for this species to first-order behavior. Ratios of the resulting k_{obsd} values to [PPh_3] (2–4 × 10^{-4} M) were roughly constant with the average value (1.5 ± 0.7) × 10^7 M^{-1} s^{-1}. Thus, it was concluded that the decay process is eq 8.

$$IrCl(PPh_3)_2 + PPh_3 \xrightarrow{k_8} IrCl(PPh_3)_3 \quad (8)$$

The conclusion that the common intermediate $IrCl(PPh_3)_2$ is formed in the photolysis of both $H_2IrCl(CO)(PPh_3)_2$ and $H_2IrCl(PPh_3)_3$ can be probed by examining the flash photolysis properties of each of these species in the presence of both added PPh_3 and CO. For example, given that the 470-nm extinction coefficient for $IrCl(PPh_3)_3$ (500 M^{-1} cm^{-1}) is substantially larger than that for $IrCl(CO)(PPh_3)_2$ (20 M^{-1} cm^{-1}), the relative amounts of $IrCl(CO)(PPh_3)_2$ and $IrCl(PPh_3)_2$ produced initially by competitive reactions of the tricoordinate intermediate with PPh_3 or CO can be determined from the absorbance changes at this wavelength. In one series of experiments, the flash photolysis (>295 nm) of $H_2IrCl(PPh_3)_3$ was carried out in H_2 saturated benzene with a constant concentration of PPh_3 (1.5 × 10^{-3} M), but concentrations of CO varied from 0 to 6 × 10^{-5} M. The 470-nm absorbance was monitored 10 ms after the flash. At [CO]

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(21) The high intensity of the analyzing lamp for the flash photolysis kinetic spectrophotometer appeared to have some influence on the relatively slow reaction of D with H_2 (eq 7), although a first-order rate constant of about 10^{-2} was measured under these conditions. Therefore, in order to check this reaction rate under more favorable conditions, a solution of $H_2IrCl(PPh_3)_3$ (3 × 10^{-5} M) in benzene under 10% H_2/90% N_2 at 1 atm ([H_2] = 2.8 × 10^{-4} M) was flashed and then quickly transferred to a Cary 118 spectrophotometer. The decay of absorbances at 450 nm due to D demonstrated first-order kinetics with k_{obsd} 0.009 5 ± 0.000 5 s^{-1}. This k_{obsd} value was unchanged when the analogous flash experiment was carried out with added PPh_3 (0.015 M). In comparison, the thermal reaction studied on the Cary 118 by rapidly dissolving $IrCl(PPh_3)_3$ in H_2 saturated benzene under identical conditions gave a k_{obsd} = 0.0100 ± 0.000 5 s^{-1}. If a second-order rate law, as observed for the analogous reaction of $IrCl(CO)(PPh_3)_2$, is assumed, then k_7 is 36 M^{-1} s^{-1}, about 60-fold greater than k_3.

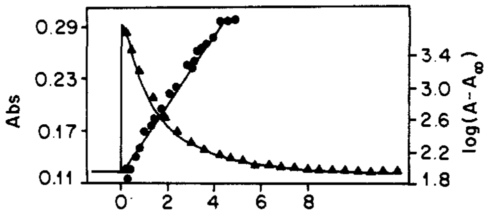


Figure 4. Decay of transient produced in the flash photolysis of $H_2RhCl(PPh_3)_3$ in H_2 saturated benzene. Line represents the $\ln(A_t - A_\infty)$ vs. t first-order kinetics plot.

= 3.5×10^{-5} M, the 10-ms absorbance indicated that the $[IrCl(CO)(PPh_3)_2]/[IrCl(PPh_3)_3]$ ratio was 0.33 ± 0.06. From this ratio, the concentrations of CO and PPh_3 and the value 1.5×10^7 M^{-1} s^{-1} for k_8, one can calculate a k_5 value of $(3.2 \pm 0.6) \times 10^8$ M^{-1} s^{-1}, within experimental uncertainty of the value (2.6×10^8 M^{-1} s^{-1}) measured in the flash photolysis of $H_2IrCl(CO)(PPh_3)_2$ in the previous section. Alternatively, when the flash photolysis (>295 nm) of $H_2IrCl(CO)(PPh_3)_2$ was carried out in the presence of a large excess of added PPh_3 ($2-4 \times 10^{-4}$ M) in H_2 saturated benzene, the resulting transient A underwent first-order decay to give a transient spectrum identical with that of D. The ratio of the resulting k_{obsd} values to $[PPh_3]$ was shown to be constant, $(1.3 \pm 0.4) \times 10^7$ M^{-1} s^{-1}, in good agreement with the k_8 value calculated above. Thus, the initial transients observed in the flash photolysis of either $H_2IrCl(CO)(PPh_3)_2$ or $H_2IrCl(PPh_3)_3$ have identical spectral and kinetics characteristics.[22]

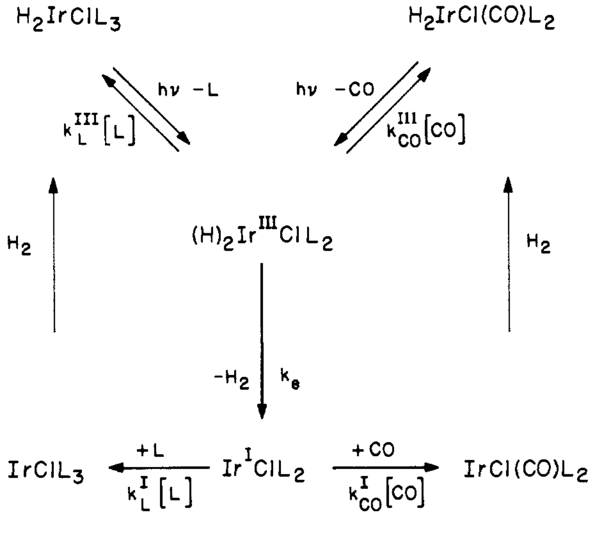
Photolysis of $H_2RhCl(PPh_3)_3$. The transient chemistry resulting from the flash photolysis (either >295 nm or >320 nm) of $H_2RhCl(PPh_3)_3$ in H_2 saturated benzene was considerably different from that seen for the two iridium(III) complexes noted above. Flash photolysis resulted in the formation of a single transient displaying a spectrum with absorbance characteristics in the range 390–570 nm the same as that of the tetracoordinate complex $RhCl(PPh_3)_3$ (i.e., "Wilkinson's catalyst") and considerably different from those reported for the tricoordinate $RhCl(PPh_3)_2$ complex analogous to A.[12] This transient decayed exponentially to reform the starting material (Figure 4) and the resulting k_{obsd} (0.51 ± 0.1 s^{-1} at 22 °C) values proved to be independent of dihydrogen pressure over the range 0.25–1.00 atm. However, substantially slower relaxation rates were observed in the presence of added PPh_3. This behavior is consistent with the earlier kinetics investigation of the hydrogenation of Wilkinson's catalyst to reform $H_2RhCl(PPh_3)_3$ and has been explained by Halpern[23] in terms of rate limiting, prior dissociation of PPh_3, (eq 9) followed by rapid sequential reactions with dihydrogen and then PPh_3 (eq 10). The 0.51 s^{-1} (22 °C) relaxation rate constant noted

$$RhCl(PPh_3)_3 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} RhCl(PPh_3)_2 + PPh_3 \qquad (9)$$

$$RhCl(PPh_3)_2 \xrightarrow[k_{10}]{+H_2} H_2RhCl(PPh_3)_2 \xrightarrow{+PPh_3} H_2RhCl(PPh_3)_3 \qquad (10)$$

in the flash photolysis is in reasonable agreement with the 0.68 s^{-1} value (25 °C) measured for k_9 under slightly different conditions.[23] The inhibition by PPh_3 is readily explained by the trapping of the tricoordinate intermediate in competition with addition of dihydrogen ($k_{-9} = 3.0 \times 10^6$ M^{-1} s^{-1}; $k_{10} = 1 \times 10^5$ M^{-1} s^{-1}).[12]

Scheme I



Discussion

A key observation here is that flash photolysis of either $H_2IrCl(CO)(PPh_3)_2$ or $H_2IrCl(PPh_3)_3$ leads to formation of the common intermediate $IrCl(PPh_3)_2$ and that this intermediate is not the result of the secondary photolysis of the expected square planar Ir^I products. These results indicate that photoreductive elimination of dihydrogen from the iridium(III) complexes is a more complicated mechanism than previously inferred from continuous photolysis experiments. A likely explanation of these data would be that the hexacoordinate Ir^{III} dihydrides $H_2IrCl(L')(PPh_3)_2$ undergo initial photodissociation of the ligand L′ (CO or PPh_3, respectively) to give first a common pentacoordinate intermediate I which undergoes elimination of H_2 to give the common tricoordinate intermediate A (Scheme I). The latter pathway, i.e., the k_e step, must be complete within the lifetime of the flash itself (20 μs), thus a lower limit for k_e would be about 5×10^4 s^{-1}, dramatically larger than the H_2 elimination rate constants from the hexacoordinate starting materials (3.8×10^{-5} s^{-1} in 25 °C benzene[19] for $H_2IrCl(CO)(PPh_3)_2$ and much smaller for $H_2IrCl(PPh_3)_3$).

Alternative proposals would be that loss of the three ligands in going from the starting hexacoordinate complexes to the tricoordinate intermediate occurs in an unprecedented concerted process or that H_2 elimination occurs from a vibrationally excited pentacoordinate intermediate immediately subsequent to photodissociation of one ligand. However, such a mechanism would be inconsistent with the observation that the photoelimination quantum yields ϕ_e are significantly smaller when carried out in the presence of added CO (for $H_2IrCl(CO)(PPh_3)_2$) or added PPh_3 (for $H_2IrCl(PPh_3)_3$). These results are best interpreted (see below) in terms of the trapping of I by the added ligand in competition with H_2 elimination via the k_e step. Such a species would be sufficiently long-lived to undergo vibrational relaxation. A third (also unprecedented) alternative that I is a long-lived, thermally equilibrated, pentacoordinate electronic excited state cannot be unequivocally rejected given the present information.

There have been previous indications that ligands other than hydrides may be photolabile for the Ir^{III} hydrides. For example, Strohmeier and co-workers have demonstrated photocatalytic behavior of $IrCl(CO)(PPh_3)_2$ in the hydrogenation of substrates such as alkenes.[24,25] These results have been interpreted by Moggi

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(22) Another complication in flash photolysis studies with both CO and PPh_3 present is the reaction of $IrCl(PPh_3)_3$ with CO to give $IrCl(CO)(PPh_3)_2$. The kinetics of this reaction was therefore briefly examined by stopped-flow kinetics experiments in 25 °C benzene. Equal portions of $IrCl(PPh_3)_3$ solution (4×10^{-4} M, deaerated with N_2) and CO solution at 0.006 M or 0.0006 M (prepared by equilibrating benzene with 100% CO or 10% CO/90% N_2 at 1.0 atm, respectively) were mixed in the stopped-flow spectrophotometer, and absorbance decreases at 460 nm were recorded. The $\ln(A_t - A_\infty)$ vs. time plots were linear indicating the reaction to be first order in the limiting reagent $IrCl(PPh_3)_3$ and giving the respective k_{obsd} values: 275 ± 5 and 21 ± 1 s^{-1}. Calculated from these is the second-order rate constant $(8 \pm 1) \times 10^4$ M^{-1} s^{-1} for the reaction $IrCl(PPh_3)_3 + CO \rightarrow IrCl(CO)(PPh_3)_2 + PPh_3$. Thus, this reaction is sufficiently sluggish not to interfere with analysis of $IrCl(PPh_3)_3/IrCl(CO)(PPh_3)_2$ ratios (observed within 10 ms) from which the relative rates of PPh_3 and CO trapping of the intermediate $IrCl(PPh_3)_2$ were calculated.

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(24) (a) Strohmeier, W.; Steiger, H.; Wiegelt, L. *J. Organomet. Chem.* **1977**, *129*, 243–248. (b) Strohmeier, H.; Steigerwald, W. *J. Organomet. Chem.* **1977**, *125*, C37–39. (c) Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1977**, *129*, C47–53.

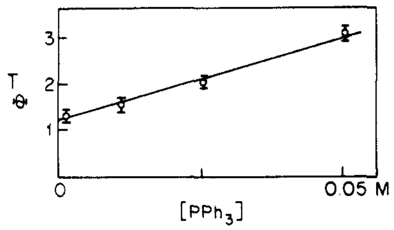

Figure 5. Plot of ϕ_e^{-1} vs. [PPh$_3$] for the CW photolysis of $H_2IrCl(PPh_3)_3$.

et al.[25] in terms of a mechanism proceeding via photodissociation of one ligand (CO or PPh$_3$) from the predominant species present in this system, i.e., $H_2IrCl(CO)(PPh_3)_2$ to give a coordinatively unsaturated dihydride such as I. Ligand photolability is also indicated by the observation[2] that when the photolysis of $H_3Ir(PPh_3)_3$ was carried out under H_2, the pentahydride $H_5Ir(PPh_3)_2$ was formed. This presumably was one result of primary photodissociation of phosphine.

The model described in Scheme I demonstrates how adding CO or PPh$_3$ to $H_2IrCl(CO)(PPh_3)_2$ or $H_2IrCl(PPh_3)_3$ would serve to decrease the quantum yields for formation of the square planar complexes $IrCl(CO)(PPh_3)_2$ or $IrCl(PPh_3)_3$, respectively. The relationship between ϕ_e and the concentration of added L′ is defined in terms of this model as

$$\phi_e = \phi_i\left(\frac{k_e}{k_e + k_{L'}^{III}[L']}\right) \qquad (11)$$

and the reciprocal of ϕ_e equals

$$(\phi_e)^{-1} = (\phi_i)^{-1}\,(1 + k_{L'}^{III}[L']/k_e) \qquad (12)$$

Equation 12 predicts a linear relationship between the reciprocal of ϕ_e and [L′] as seen in Figure 5 for the photolysis of $H_2IrCl(PPh_3)_3$ in the presence of added PPh$_3$ (data in Table I). Thus, this behavior is quantitatively consistent with the model described in Scheme I. The slope to intercept ratio of this plot is equal to $k_{L'}^{III}/k_e$, the value 28 ± 4 M^{-1} being derived from these data for L′ = PPh$_3$.

Equation 12 can also be used to calculate a $k_{L'}^{III}/k_e$ ratio of 92 ± 10 M^{-1} for L′ = CO from the ϕ_e values measured for $H_2IrCl(CO)(PPh_3)_2$ at P_{co} = 0.0 atm and 1.0 atm, respectively, and assuming $\phi_i = \phi_e$ in the former case. The quotient of these two ratios leads to calculation of the ratio $k_{co}^{III}/k_{PPh_3}^{III} = 3.3 \pm 0.9$, which suggests that the intermediate I is only moderately selective in its reactions with the ligands CO or PPh$_3$. In comparison, the ratio of the competing rate constants for reaction of L′ with the tricoordinate intermediate (k_5 and k_8 for CO or PPh$_3$, respectively) equals 17 ± 7, thus, the unsaturated iridium(I) species is somewhat more selective. The lower selectivity of I may be a reflection of the greater phosphine affinity of the Ir^{III} center relative to that of the Ir^{I} center or simply of the greater reactivity of the former species with two-electron donors.

The dramatic enhancement of H_2 elimination for I relative to either hexacoordinate Ir^{III} complex is consistent with theoretical arguments[26] based on orbital topology considerations that reductive elimination from d^6 complexes should occur much more readily after ligand dissociation. Indications of such rate enhancements from analogous mechanisms have appeared previously in several thermal C–H eliminations from rhodium(III) and iridium(III) complexes[27] and are implied in the analysis[23,28] of the reactivities of the rhodium homologue $H_2RhCl(PPh_3)_2$.[29]

We have no ready explanation for the failure of the rhodium(III) complex $H_2RhCl(PPh_3)_3$ to follow an analogous mechanism for the photoreductive elimination of H_2. The perversity of this system in not adhering to a mechanism common to the iridium homologue illustrates the multiplicity of reaction channels available to such electronically excited complexes. It is likely that a perturbation such as the change in the central metal ion may lead to a different excited state energy ordering. Thus, for iridium(III), low energy ligand field states may be the precursors of ligand dissociation, while, for $H_2RhCl(PPh_3)_3$, states which are derived from transitions involving more intimately the M–H bonding and antibonding orbitals such as described by Geoffroy and co-workers[1] may be responsible. Such a mechanism would be the likely explanation for the observation from low-temperature matrix studies that photolysis of $H_2Fe(CO)_4$ leads to formation of the tetracarbonyl $Fe(CO)_4$.[30] However, it is noteworthy that there has also been a report[31] of CO photodissociation from the osmium homologue $H_2Os(CO)_4$ providing another example of a change in the primary photoreaction pathway as the consequence of a change in the central metal atom of dihydride complex.

Acknowledgment. This research was supported by grants from the National Science Foundation. We thank Johnson-Matthey, Inc. for a loan of the rhodium and iridium.

Registry No. $H_2IrCl(CO)(PPh_3)_2$, 17000-11-2; $H_2IrCl(PPh_3)_3$, 17035-59-5; $H_2RhCl(PPh_3)_3$, 17949-78-9; $IrCl(PPh_3)_2$, 31690-54-7; $RhCl(PPh_3)_3$, 14694-95-2; H_2, 1333-74-0.

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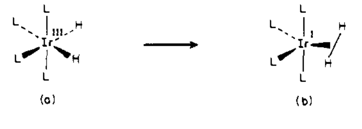
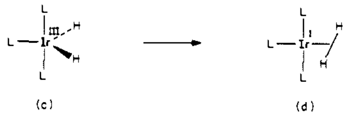
[29] (a) The same prediction is the result of simplistic crystal field or orbital angular overlap arguments. The transition state of H_2 elimination from a d^6 dihydride Ir^{III} complex of coordination number *n* may be viewed as structurally similar to a d^8 Ir^{I} complex having a coordination number *n*–1 with one ligand in the latter species being the sidewise coordinated ("agostic") H_2, e.g., eq x or y. If identical crystal field strengths for H_2, H$^-$, and L and



(x)



(y)

regular geometries (octahedral, trigonal bipyramidal, or square planar) were assumed, the crystal field stabilization energies (CFSE) of $H_2Ir^{III}L_4$ (a), $Ir^{I}(H_2)L_4$ (b), $H_2Ir^{III}L_3$ (c), and $Ir^{I}(H_2)L_3$ (d) would be 24, 12.5, 12.5, and 24.6 Dq, respectively (ref 29b). Thus, the substantial decrease in CFSE for the transformation a → b would add significantly to the activation energy for eq x while the increase in CFSE for the transformation c → d would serve to decrease E_a for eq y. Alternatively one can use angular scaling factors (ref 29c) and the additive ligand parameters σ_i and π_i (where the subscript i denotes the ligand L, H$^-$, or H_2) to estimate changes in the destabilization energies of the ligand field orbitals as the results of such transformations. Such a treatment gives a change in the ligand field orbital contribution to the complexes' energy of $\Delta E_{aao} = 3\sigma_L + 1.5\sigma_{H2} + 4\pi_{H2}$ for eq x. Given that σ_L should be a large positive number, σ_{H2} should be a smaller positive number, and π_{H2} should be a small negative number (agostic H_2 would be expected to be a weak σ donor but a weak π acceptor as well); ΔE_{aao} in this case should make a substantial positive contribution to E_a for this reaction. The ΔE_{aao} for eq y would similarly be calculated to be $1.5\sigma_L + 0.5\sigma_{H2} + 4\pi_{H2} - 1.5\sigma_{H^-}$. Given the strong σ donor character of the hydride ligand (i.e. $\sigma_{H^-} > \sigma_L$) it is probable that ΔE_{aao} in this case makes a negative contribution to E_a for eq y. Thus, according to either treatment, H_2 elimination from the pentacoordinate intermediate c should be much more facile than from the hexacoordinate species a. As a referee has pointed out, the d^6 pentacoordinate intermediate $H_2Ir^{III}L_3$ may be square pyramidal instead of trigonal bipyramidal. However, similar treatment of eq y using either the CFSE or AO approaches but assuming c to be square pyramidal leads to the same qualitative conclusion, namely, that the CFSE or ΔE_{aao} contribution to the E_a for eq y will be much more favorable than for eq x. (b) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; Chapter 3. (c) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; Chapter 9.

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