

its higher pK_a (6.6 vs. 5.3) would suggest a stronger σ bond relative to pyridine.

In a previous work, Boucher⁷ proposed that the relative stability of Mn(III) porphyrin complexes could be predicted by the relative positions of band V in the electronic absorption spectra. Specifically, the complex that was most stable would have the peak maxima of band V occurring at the highest energy. Applying this rule to the ligands in Table V, one would predict pyridine to form the weakest complex (band V occurs at 480 nm), followed by imidazole (472 nm) and then by Me₂SO, which forms the strongest complex (464 nm). One can see that the validity of this rule is in question when applied to ligands containing different donor atoms, although it may be valid for ligands containing the same donor atom.

In contrast to the Mn(III) complexes, the Mn(II) complexes are all of roughly equal stability. The higher electron density on Mn(II) reduces the importance of σ donation from the axial ligand. Mn(II) has been shown to lie significantly farther out of the porphyrin plane and provides much less steric interactions with axial ligands than does Mn(III). In addition, the Mn d orbitals, which are involved in π bonding to the porphyrin in Mn(III), are available to interact with the axial ligand. Although Mn(II) complexes with pyridine and imidazole are thought to involve pure σ bonding,³⁴ π bonding may contribute to the Me₂SO complex and account for its higher stability relative to that of the Mn(III) complex.

It should be pointed out that the measured $\log K_1 = 4.55$, for pyridine addition to Mn(II), is almost 2 orders of magnitude larger than that previously reported for addition of pyridine to Mn(II) when the starting complex was (TPP)MnCl ($\log K_1 = 2.70$).¹¹ This increase in stability constant is consistent with the lack of binding of a ClO₄⁻ anion to Mn(II), as was postulated when the starting material contained a Cl⁻ counterion. Likewise, the difference between the values of Mn(III) ligand addition when the starting materials were (TPP)MnClO₄ ($\log K_1 = 4.08$) and (TPP)MnCl ($\log K_1 = 1.10$)¹¹ is also consistent with the difference in binding

strengths between (TPP)Mn⁺ and the halide or the perchlorate counterion. No comparable values have been published for addition of Me₂SO or imidazole to (TPP)MnCl.

In summary, we have observed that manganese porphyrins are greatly influenced by the strong interaction between the porphyrin π ring and the Mn(III) center. The influence of counterions and solvent upon metal-centered reductions is greatly reduced relative to iron and cobalt porphyrins.³¹ For solvents of low coordinating ability ($DN < 25$), the counterion is associated, while more strongly coordinating solvents displace the counterion, in qualitative agreement with other studies. The coordinating ability of Mn(III) toward σ donors is nearly equal to that of Mn(II) and explains the relatively small potential dependence upon solvents of widely varying donorities.

Finally, the work has provided the first measured stepwise stability constants for the addition of axial ligands to a Mn(III) porphyrin in nonaqueous media. Moreover, the data analysis has revealed the spectrum of an intermediate five-coordinate Mn(III) porphyrin complex with axial ligands. When combined with electrochemical measurements of stability constant ratios, values of $\log K_1$ may also be obtained for addition of the same ligands to Mn(II). The values measured for addition of Me₂SO, pyridine, and imidazole to (TPP)Mn (generated from (TPP)MnClO₄) are consistent with those previously presented in the literature.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE-7921536) is gratefully acknowledged. We also acknowledge the help of Dr. David Leggett in analyzing the spectrophotometric data via SQUAD.

Registry No. (TPP)MnClO₄, 67161-73-3; (TPP)MnI, 55290-33-0; (TPP)MnSCN, 82613-97-6; (TPP)MnBr, 55290-32-9; (TPP)MnCl, 32195-55-4; (TPP)MnN₃, 56413-47-9; CH₂Cl₂, 75-09-2; ClCH₂C-H₂Cl, 107-06-2; CH₃NO₂, 75-52-5; PhCN, 100-47-0; CH₃CN, 75-05-8; PrCN, 107-12-0; (CH₃)₂CO, 67-64-1; THF, 109-99-9; DMF, 68-12-2; DMA, 127-19-5; Me₂SO, 67-68-5; py, 110-86-1; [(TPP)Mn(Im)₂]⁺, 82613-98-7; [(TPP)Mn(py)₂]⁺, 82613-99-8; [(TPP)Mn(Me₂SO)₂]⁺, 82614-00-4; (TPP)Mn, 31004-82-7.

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Transition-Metal-Catalyzed Oxidation of Carbon Monoxide by Dichlorine To Produce Phosgene

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Halometal carbonyls of gold, palladium, and platinum catalyze the formation of COCl₂ from carbon monoxide and dichlorine at atmospheric pressure and room temperature under exclusion of light. Semiquantitative data show that the catalytic efficiency in this homogeneous process is Au > Pd > Pt. Attack at the carbonyl carbon of soluble halo-carbonyl complexes by coordinated chloride or by dichlorine to give unstable M-C(O)-Cl groupings is believed to be operative in these processes.

Although the formation of COCl₂ from carbon monoxide and dichlorine is a highly exothermic reaction,¹ the kinetics of the reaction are such that thermal activation on active coal or light promotion is required.² Although trisubstituted phosphine oxides have been used³ for the catalytic combination

of carbon monoxide at superatmospheric pressure with dichlorine at room temperature, we are not aware of any report on transition-metal-catalyzed formation of phosgene at room temperature.

We had already noted^{4,5} that phosgene is frequently the only observable product of the reduction of some late-transition-metal halides (Au(III), Pt(IV)) by carbon monoxide. Thus,

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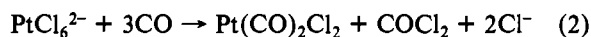
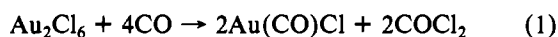
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for example, Au_2Cl_6 and hexachloroplatinic acid are reduced under anhydrous conditions to the corresponding halo-carbonyl complexes according to the stoichiometries given in eq 1 and 2.



Besides describing some new experimental observations and rationalizing some of the earlier ones, we report what we believe to be the first well-authenticated case of transition-metal-catalyzed formation of phosgene from carbon monoxide and dichlorine under mild conditions.

Experimental Section

Solvents were dried prior to use by conventional methods. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen under careful exclusion of light by aluminum foil protection of the reaction flask. Anhydrous gold(III) chloride was prepared from commercially available tetrachloroauric acid as previously described.⁴

Treatment of $\text{Au}(\text{CO})\text{Cl}$ with Organic and Inorganic Halides. No visual and spectroscopic changes were observed upon treatment of $\text{Au}(\text{CO})\text{Cl}$ with the following substances at room temperature: (a) neat CH_3I ; (b) neat CH_3COCl ; (c) SnCl_4 in CH_2Cl_2 ; (d) titanium tetrachloride in dichloromethane and heptane; (e) anhydrous iron(III) chloride in dichloromethane; (f) tungsten hexachloride in dichloromethane; (g) aluminum bromide in benzene.

On the contrary, $\text{Au}(\text{CO})\text{Cl}$ (0.399 g, 1.53 mmol) and Al_2Br_6 (0.389 g, 0.729 mmol) in heptane (20 cm^3) readily gave a shift of the carbonyl stretching band from 2150 to 2176 cm^{-1} .

Halometal Carbonyls and Dihalogens at Room Temperature. No reaction was observed between dichlorine and $\text{Pt}(\text{CO})_2\text{Cl}_2$ in dichloromethane.

A colorless solution of $\text{Au}(\text{CO})\text{Cl}$ (0.320 g, 1.23 mmol) in thionyl chloride (30 cm^3) was treated with dichlorine (1.9 g, 26.8 mmol). After a few minutes precipitation of the slightly soluble Au_2Cl_6 was observed and phosgene was detected spectroscopically ($\bar{\nu}_{\text{CO}} = 1804 \text{ cm}^{-1}$; 1.0 mmol) in solution. Similar results were obtained with CCl_4 as solvent.

No reaction occurred in the dark between dichlorine and thionyl chloride and between CO and dichlorine with thionyl chloride as solvent.

A solution of $[\text{Pd}(\text{CO})\text{Cl}_3]^-$ obtained by treatment of $\text{Pd}_2(\text{CO})_2\text{Cl}_4^6$ (0.202 g, 0.98 mmol of palladium) with the equivalent amount of $\text{NH}_2\text{Et}_2\text{Cl}$ in thionyl chloride (25 cm^3 ; carbonyl stretching band at 2144 cm^{-1}) was treated with dichlorine (19.3 mmol). After about 2 h, the solution showed no phosgene while the intensity of the 2144- cm^{-1} band had remained substantially unchanged.

A solution of $\text{NH}_2\text{Et}_2[\text{Pt}(\text{CO})\text{Cl}_3]$ (0.349 g, 0.86 mmol) in thionyl chloride (20 cm^3) characterized by a carbonyl stretching vibration at 2109 cm^{-1} was treated with dichlorine (18.4 mmol). Immediately after addition of the halogen, a single band at 2191 cm^{-1} was observed, while the band at 2109 cm^{-1} had disappeared. The intensity remained substantially unchanged for about 2 h and decreased to about half within 20 h.

Transition-Metal-Catalyzed Formation of Phosgene at Room Temperature and Atmospheric Pressure. $\text{Au}(\text{CO})\text{Cl}$ (0.070 g, 0.27 mmol of gold) in thionyl chloride (70 cm^3) was treated with dichlorine (1.9 g, 26.8 mmol) and carbon monoxide at the total pressure of 1 atm. By IR spectroscopy the following quantities (mmol) of phosgene were found to be present in solution at the indicated times (h): 1.7 mmol (2.5 h); 3.0 (3.75); 5.4 (5.8); 8.3 (8.4); 14.4 (14); 15.1 (25); 16.0 (30.7). The final value corresponds to a $\text{COCl}_2:\text{Au}$ molar ratio of 59.2.

A solution of $\text{Pd}_2(\text{CO})_2\text{Cl}_4$ (0.040 g, 0.195 mmol of palladium) in thionyl chloride (20 cm^3) was treated with dichlorine (26.1 mmol) and CO at the total pressure of 1 atm. By IR spectroscopy the following amounts of COCl_2 were detected in solution at the indicated times: 0 mmol (0.7 h); 0.3 (18.3); 1.3 (46); 2.9 (172).

The solution of $[\text{Pd}(\text{CO})\text{Cl}_3]^-$ (0.98 mmol) in thionyl chloride (25 cm^3) prepared as described above was treated with dichlorine (10.8 mmol) and CO at the total pressure of 1 atm. By IR spectroscopy

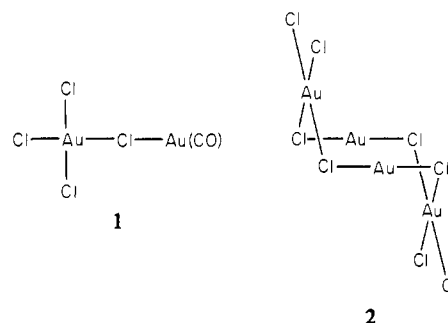
the following amounts of phosgene were detected: 2.9 mmol (47.3 h); 4.9 (77).

A solution of $\text{NH}_2\text{Et}_2[\text{Pt}(\text{CO})\text{Cl}_3]$ (0.349 g, 0.86 mmol) in thionyl chloride (20 cm^3) was treated with dichlorine (10.2 mmol) and CO at the total pressure of 1 atm. The following amounts of phosgene were detected by IR spectroscopy: 0.2 mmol (47 h); 0.3 (144).

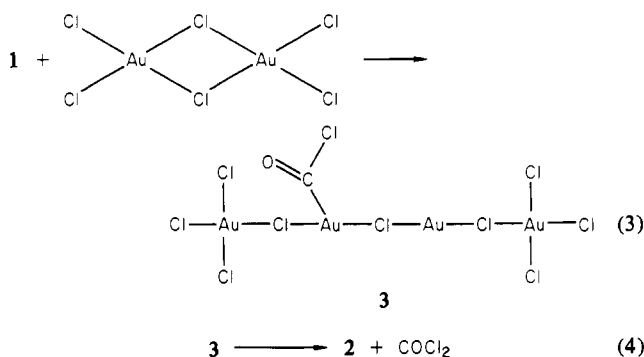
Silver chloride and the chlorides of copper(I), copper(II), and iron(III) were found to be inactive under similar conditions.

Results and Discussion

(A) Reductive Carbonylation of Gold(III) Chloride. Two products have been observed that are related to the reductive carbonylation of gold(III) chloride to give $\text{Au}(\text{CO})\text{Cl}$, namely, the $\text{AuCl}_3\text{-Au}(\text{CO})\text{Cl}$ 1:1 adduct⁵ **1** and the tetranuclear mixed-valence $\text{Au}(\text{III})\text{-Au}(\text{I})$ chloride shown⁷ to have structure **2**.



We assume that in reaction 3 there is a direct attack of



Au_2Cl_6 -coordinated chloride at the carbonyl carbon of $\text{Au}(\text{CO})\text{Cl}$. The resulting intermediate (**3**) would then be responsible for the two-electron transfer from coordinated carbon monoxide to gold(III). The latter mechanism proposed is similar to the inner-sphere mechanism⁸ suggested for electron transfers in coordination chemistry.

Bonds of the type $\text{M-C}(\text{O})\text{-X}$ are well-known⁹ for $\text{X} = \text{H}$, R , OH , OR , and so on, but no stable transition-metal complexes for $\text{X} = \text{halogen}$ have been reported as yet. However, Hieber and Bader¹⁰ have reported that $\text{Fe}(\text{CO})_5$ reacts with dihalogens to give $\text{Fe}(\text{CO})_4\text{X}_2$ through the intermediate formation of thermally unstable pentacarbonyl adducts formulated as $\text{Fe}(\text{CO})_5\text{X}_2$. Examination of the dibromine reaction in $\text{CH}_2\text{Cl}_2\text{-CHCl}_3$ mixtures¹¹ led to the conclusion that an unstable $\text{BrCO-Fe}(\text{CO})_4\text{Br}$ species could be present in solution at low temperature.

The postulated attack of coordinated chloride on coordinated carbon monoxide, as in reaction 3, is certainly favored by the increased positive character of the carbonyl carbon (the ν_{CO}

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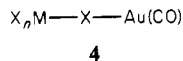
(9) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299-311.

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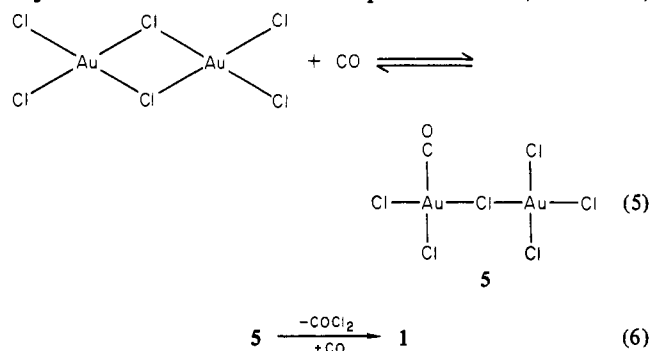
of adduct **1** is 2180 cm^{-1} in thionyl chloride, which represents a 18-cm^{-1} increase with respect to $\text{Au}(\text{CO})\text{Cl}$.¹²

We have found that only Al_2Br_6 , besides Au_2Cl_6 , among the metal halides tested, forms 1:1 adducts with $\text{Au}(\text{CO})\text{Cl}$; in the aluminum derivative the carbonyl stretching vibration with heptane as solvent is at 2176 cm^{-1} . It is likely that other 1:1 adducts of the general type **4** can be prepared. It can be noted



that only dimeric halogen-bridged metal halides M_2X_n , such as Au_2Cl_6 and Al_2Br_6 can give adducts **4** without increase of the coordination number of the central metal atom. Also, the formation of the Al_2Br_6 adduct is prevented with benzene as solvent, presumably due to the competitive basicity of the solvent.

The formation of $\text{Au}(\text{CO})\text{Cl}$ from Au_2Cl_6 and CO^5 is believed to require precoordination of CO to gold(III), followed by COCl_2 elimination, addition of CO, and formation of **1**. A kinetic accumulation of **1** has been observed by appropriate adjustment of the reactants. Equilibrium **5** is, of course,



largely shifted to its left, and we have no direct evidence of the gold(III)-CO adduct. However, some examples of CO coordination to transition-metal complexes in relatively high oxidation states are now known such as zirconium(IV)¹³ and platinum(IV).¹⁴

This suggests that for some transition-metal complexes π back-bonding can be very weak, if it exists at all, and σ donation from carbon monoxide can be revealed by the conventional methods. It is to be noted also that the B-C bond energy for borane carbonyl¹⁵ has been reported to be between 19 and 34 kcal, a value that is close to that¹⁶ typical of several terminal CO-transition-metal bonds, for which both σ and π components are operative.

Manchot and Lehmann have reported¹⁷ that some chlorides of transition metals can be reduced by carbon monoxide to give phosgene: ruthenium and platinum chlorides gave COCl_2 by treatment at 270 and 140 °C, respectively. Gold(III) chloride gave COCl_2 and Cl_2 at 95 °C, while AuCl gave the same products at 75 °C.

(B) Dichlorine Oxidation of $\text{Au}(\text{CO})\text{Cl}$ and Catalytic Cycle to Phosgene. *cis*-Dichlorodicyarbonylplatinum(II) does not react with dichlorine. On the other hand, we have confirmed the results by Crocker et al.¹⁴ and found ourselves that $[\text{Pt}(\text{CO})\text{Cl}_3]^-$ reacts with dichlorine in SOCl_2 to give a solution showing a carbonyl stretching band at 2191 cm^{-1} , which, in

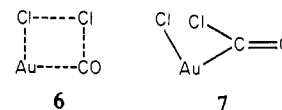
view of the exceedingly high wavenumber value, is attributed¹⁴ to a carbonyl species of platinum(IV), namely, $[\text{Pt}(\text{CO})\text{Cl}_5]^-$. We have found that the reaction takes place also in carbon tetrachloride, besides dichloromethane as originally reported,¹⁴ and that the life of this carbonyl species can be increased considerably with thionyl chloride as solvent, presumably due to lack of hydrolytic secondary reactions.¹⁸ On the other hand, under the same conditions, the corresponding anionic complex of palladium, $[\text{Pd}(\text{CO})\text{Cl}_3]^-$, is substantially unreactive toward dichlorine, a result that is in agreement with the lower accessibility of the oxidation state IV for palladium, as denoted, for example, by the nonexistence of neutral binary halo complexes of palladium(IV).¹⁹

We have also found that $\text{Au}(\text{CO})\text{Cl}$ is oxidized by dichlorine to give Au_2Cl_6 and phosgene. Reaction 7 suggests that no



dissociation of CO is required to form phosgene, since CO and dichlorine do not combine in the absence of gold at room temperature under exclusion of light. Reaction 7 has a precedent in the literature: Hieber and Romberg²⁰ reported that dichlorine oxidation of $\text{Cr}(\text{CO})_6$ at low temperature gave some COCl_2 in unspecified amounts, in addition to CO.

The attack of gold(I) by dichlorine may be visualized to occur via the four-center mechanism shown in **6**, which may



lead to the unstable carbonyl-chloro complex **7**. The latter, by COCl_2 elimination and further dichlorine attack, may give the observed product (Au_2Cl_6).

The observed high selectivity in COCl_2 for both the reductive carbonylation of Au_2Cl_6 and the dichlorine oxidation of $\text{Au}(\text{CO})\text{Cl}$ is an essential prerequisite for a catalytic cycle based on gold:



This has been verified, and although we have not made any attempt to optimize the yields, we have been able to convert up to about 60 mol of COCl_2 /mol of gold at atmospheric pressure and room temperature *in the dark*. Since $\text{Au}(\text{CO})\text{Cl}$ does not react with COCl_2 under the conditions of the experiment, there is no reason to doubt that an even higher catalytic efficiency could be obtained. The failure of $\text{Au}(\text{C}-\text{O})\text{Cl}$ to react with COCl_2 is in agreement with its inertness toward *neat* CH_3I and CH_3COCl .

Catalytic formation of phosgene at room temperature and atmospheric pressure was also observed with the anionic complexes $[\text{M}(\text{CO})\text{Cl}_3]^-$ ($\text{M} = \text{Pd}, \text{Pt}$), although much less efficiently than with gold. Our semiquantitative observations show that the catalytic efficiency decreases in the sequence $\text{Au}(\text{CO})\text{Cl} > [\text{Pd}(\text{CO})\text{Cl}_3]^- > [\text{Pt}(\text{CO})\text{Cl}_3]^-$. It is interesting to note that the ν_{CO} 's decrease in the same sequence, thus suggesting that the polarity of the metal-carbon bond is one of the determining factors in the reaction. However, we believe that a high-energy barrier in the oxidation from Pd(II) to Pd(IV) and the relative kinetic stability of the observed Pt(IV) carbonyl species may be at least partly responsible for the

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relative sequence of catalytic efficiency.

The earlier literature²¹ reports a case of aluminum trichloride catalyzed formation of COCl_2 at 30–35 °C with chloroform as solvent. We have checked the experiment and found that only in the presence of light is phosgene formed under the specified conditions. The scope of the observed catalytic reaction is now under current investigation. Manchot and Lehmann¹⁷ report that RhCl_3 releases Cl_2 at 90 °C in the presence of CO. However, no COCl_2 was observed. $\text{Rh}_2(\text{C-O})_4\text{Cl}_2$ oxidatively adds dichlorine at room temperature with CCl_4 as solvent with no formation of phosgene.²² Thus,

rhodium does not appear to be an appropriate catalyst for the room-temperature combination of carbon monoxide with dichlorine to phosgene.

Acknowledgment. The authors wish to thank the National Research Council (CNR, Rome), Programma Finalizzato di Chimica Fine e Secondaria, for support of this work.

Registry No. Carbon monoxide, 630-08-0; dichlorine, 7782-50-5; $\text{Au}(\text{CO})\text{Cl}$, 50960-82-2; AuCl_3 , 13453-07-1; $[\text{Pd}(\text{CO})\text{Cl}_3]^-$, 44252-60-0; $\text{NH}_2\text{Et}_2[\text{Pt}(\text{CO})\text{Cl}_3]$, 82456-40-4; $\text{Pd}_2(\text{CO})_2\text{Cl}_4$, 43062-39-1.

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Photochemically Induced Reductive Elimination of Hydrogen from a Binuclear Platinum Hydride¹

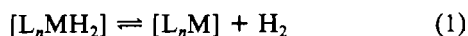
ROSS H. HILL, PAUL DE MAYO, and RICHARD J. PUDDEPHATT*

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Photolysis of $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6]$ (Ia), $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, using 362 ± 8 nm light occurs with quantum yields of 0.81 (MeCN solution) and 0.57 (pyridine solution) to give $[\text{Pt}_2\text{H}(\text{L})(\mu\text{-dppm})_2][\text{PF}_6]$ (Iic, L = MeCN; Iid, L = pyridine) and H_2 in quantitative yield. The primary isotopic effect on the quantum yields (from similar studies of $[\text{Pt}_2\text{D}_3(\mu\text{-dppm})_2][\text{PF}_6]$ (Ib)) is given by $\phi_{\text{H}}/\phi_{\text{D}} = 1.8$ and 1.6 in MeCN and pyridine solutions, respectively, and the reductive elimination is shown to be intramolecular (a mixture of Ia and Ib gives very largely H_2 and D_2 with little HD). The reaction can be sensitized with triphenylene but not by Michler's ketone, indicating that reaction is initiated from the singlet excited state.

Introduction

The thermally or photochemically induced reductive elimination of H_2 from mononuclear polyhydrido derivatives of transition metals has been studied in depth.²⁻⁵ The primary reaction, which may be reversible, is often described by the general equation (1) and involves a concerted intramolecular reductive elimination.²⁻⁷



In some cases, for example, with $[\text{IrH}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, both thermal and photochemical activation is possible, but in other cases, for example, with $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$, only photochemical activation is effective.⁷ The product $[\text{L}_n\text{M}]$ is necessarily coordinatively unsaturated and is often highly reactive; it may undergo self-reaction, typically by ortho metalation (e.g., when $[\text{L}_n\text{M}] = [\text{IrCl}(\text{PPh}_3)_3]^+$), or react with solvent (e.g., when

$[\text{L}_n\text{M}] = [(\eta^5\text{-C}_5\text{H}_5)_2\text{W}]^8$). The species $[\text{L}_n\text{M}]$ is expected to be an active catalyst in many cases although this area has not been developed. It may be possible to trap the primary product $[\text{L}_n\text{M}]$ with added ligand L^1 , but in the typical case where $[\text{L}_n\text{MH}_2]$ is an 18-electron complex, L^1 is not involved in the rate-determining reductive-elimination step.²⁻⁴

In contrast, although there are several examples of thermally induced reductive elimination of H_2 from binuclear and polynuclear transition-metal hydrides, very little is known about the mechanism of such reactions.⁹ Although almost all mononuclear polyhydrido derivatives of transition metals undergo photochemically induced reductive elimination of H_2 ,^{4,5,10} few examples of polynuclear transition-metal hydrides undergoing such a reaction have been reported.¹¹ For example $[\text{Re}_4\text{H}_4(\text{CO})_{12}]$ is emissive in hydrocarbon solutions but is not photochemically decomposed.¹²

We recently reported a very clean binuclear reductive elimination of H_2 from the cation¹³ $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$

(1) Publication No. 268 from the Photochemistry Unit, University of Western Ontario.

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