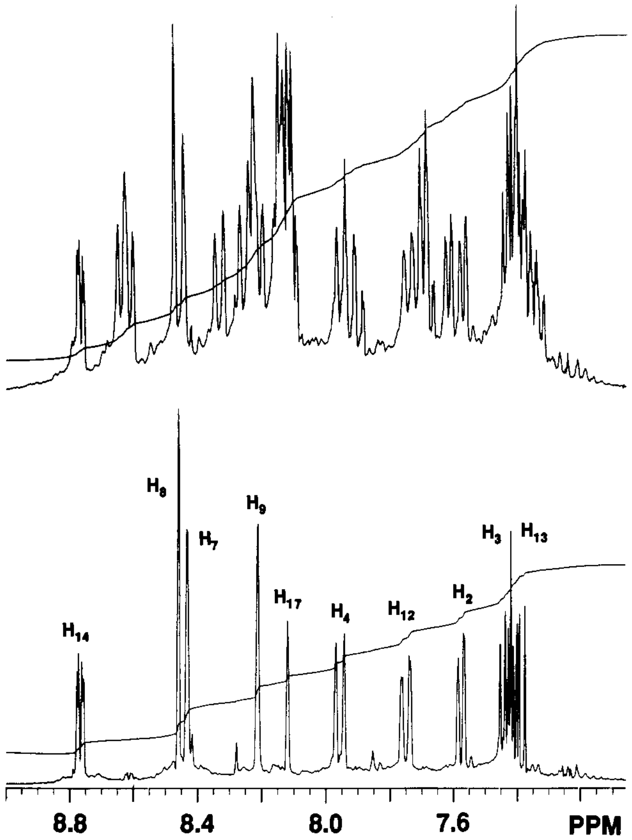
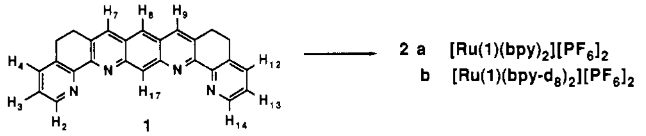


Figure 1. Downfield regions of the ^1H NMR spectra of $[Ru(1)(bpy)_2][PF_6]_2$ (top) and $[Ru(1)(bpy\text{-}d_8)_2][PF_6]_2$ (bottom) recorded at 300 MHz in CD_3CN.

1,1′-dioxide is treated twice successively with 0.73 g of sodium metal dissolved in 25 mL of D_2O (99.9 atom % D) followed by reduction of the perdeuterio di-*N*-oxide with PCl_3, 1.2 g (73%) of bpy-d_8 can be prepared. Mass spectral analysis indicated greater than 99% overall deuterium incorporation. The reaction of bpy-d_8 with $RuCl_3 \cdot 3H_2O$ according to a literature procedure[7] provided $Ru(bpy\text{-}d_8)_2Cl_2 \cdot 2H_2O$ in 63% yield.

To illustrate the utility of this new reagent, we have used it to prepare a mononuclear complex from a recently synthesized ligand with two equivalent bidentate sites: 5,6,10,11-tetrahydro-16,18-diazadipyrido[2,3-*a*:3′,2′-*n*]pentacene (**1**).[8] Figure 1 illustrates the ^1H NMR spectra of both the protio and deuterio analogues of this complex.



2 a $[Ru(1)(bpy)_2][PF_6]_2$
b $[Ru(1)(bpy\text{-}d_8)_2][PF_6]_2$

When the 16 signals due to the nonequivalent bpy protons are eliminated, the spectrum of the coordinated **1** becomes quite interpretable. By comparison with previously established chemical shift values for ruthenium(II) complexes with bridged derivatives of 2,2′-bipyridine[9] and 2,2′-biquinoline,[10] nearly unambiguous assignments of the 10 remaining signals can be made. If we assume that ruthenium binds to N_2 and N_{18}, we note that H_2 occurs at 1.2 ppm higher field than H_{14} due to a local shielding effect while H_3 and H_{13} are nearly identical. Due to charge depletion resulting from coordination, H_4 shifts downfield by 0.2 ppm compared with H_{12}. A similar shift is also observed for H_7 relative to H_9. In the free ligand, H_{17} is observed at 9.45 ppm, while in the complex, it is strongly shielded and shifted upfield by 1.35 ppm. The diminished intensity of this signal, due to the long relaxation time of H_{17}, is also observed in the spectrum of the free ligand and assisted in its chemical shift assignment.

To verify that the use of bpy-d_8 would not cause an isotope effect on the ^1H chemical shifts, we compared $Ru(bpy\text{-}d_8)_2(bpy)^{2+}$ with $Ru(bpy)_3^{2+}$. Both compounds gave virtually identical ^1H NMR spectra at 300 MHz in CD_3CN.

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Photoelimination of Benzoyl Chloride from Benzoylchlorobis(triphenylphosphine)palladium(II) and -platinum(II)

The reductive elimination of acetyl iodide from a rhodium(III) intermediate is one of the basic steps of the Monsanto acetic acid synthesis,[1] but in comparison to oxidative-addition and migratory insertion reactions, very little is known about the reductive elimination of carboxylic acid halides.[2] We report in this paper the photoinduced reductive elimination of carboxylic acid chlorides, RCOCl, from *trans*-$[M(PPh_3)_2Cl(RCO)]$ (M = Pd, Pt) and $[Pt(LL)Cl(PhCO)]$ (LL = COD, dppe) in the presence of PPh_3 and CS_2. The photoelimination of RCOCl is unique because the photolysis of acylmetal complexes typically results in the loss of a ligand and subsequent migration of CO to the metal.[3] Substitution of CO by PPh_3 rather than migration takes place when $[Fe(C_5H_5)(CO)_2(CH_3CO)]$ is photolyzed in the presence of PPh_3.[4] While the photocleavage of metal–carbon bonds in metal alkyl complexes is well established,[5] the photocleavage of the metal–acyl carbon bond has not been previously demonstrated.

The acyl complexes *trans*-$[M(PPh_3)_2Cl(RCO)]$ are decarbonylated when heated at high temperatures.[6] A solution of *trans*-$[Pd(PPh_3)_2Cl(PhCO)]$ (**1**) and PPh_3 in dichloromethane that was stirred for 88 h gave no indication of reaction. The infrared spectra of a solution of **1** and PPh_3 in dichloromethane that was irradiated (450-W Ace-Hanovia medium-pressure ultraviolet lamp fitted with a quartz sleeve) are shown in Figure 1. The reaction proceeds with decay of the band at 1620 cm^{-1} due to **1** and concomitant growth of bands at 1772 and 1729 cm^{-1}, which are due to benzoyl chloride. The characteristic doublet band for benzoyl chloride, which was previously noted by Bellamy, was attributed to Fermi resonance.[7] The photoelimination of acetyl

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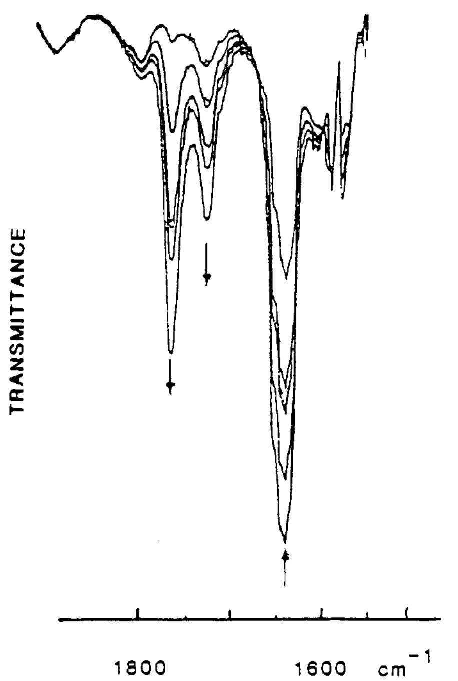
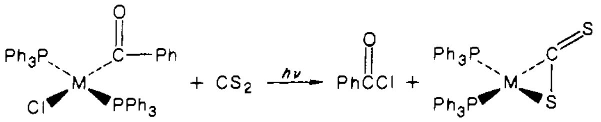


Figure 1. Infrared spectra during the course of photolysis of a solution of 17.4 mM *trans*-[Pd$(PPh_3)_2$Cl(PhCO)] and 39.6 mM PPh_3 in CH_2Cl_2 at 0, 2, 4, 5, and 10 min.

chloride from the acetyl complex *trans*-[Pd$(PPh_3)_2$Cl(MeCO)] in the presence of PPh_3 in dichloromethane was also observed.[8] In contrast to the photoreactions of the palladium complexes, PhCOCl was not observed when a dichloromethane solution of *trans*-[Pt$(PPh_3)_2$Cl(PhCO)] and PPh_3 was photolyzed. The photolyses of *trans*-[M$(PPh_3)_2$Cl(PhCO)] (M = Pd, Pt) in dichloromethane–carbon disulfide (3/2 v/v) solution gave benzoyl chloride and the carbon disulfide compounds[9] [M$(PPh_3)_2(CS_2)$] (ν(CS) = 1186 and 1142 cm^{-1} (CH_2Cl_2) for M = Pd, Pt):



(1)

In addition to the photoelimination of RCOCl from the *trans*-[M$(PPh_3)_2$Cl(RCO)] complexes, the photoelimination of PhCOCl was shown to occur in the presence of dppe, PPh_3, or CS_2 from [Pt(LL)Cl(PhCO)] complexes (LL = dppe, COD), which have the acyl RCO and chloro ligands in cis coordination positions. The photoelimination of benzoyl chloride was not inhibited by galvinoxyl[10] or promoted by AIBN. The photoelimination of PhCOCl from **1** in the presence of PPh_3 occurred at a slower rate by using the same lamp with a Pyrex filter.

The photoelimination of carboxylic acid chlorides RCOCl in the presence of PPh_3 contrasts with the previously reported photoreductive eliminations of alkanes from *cis*- or *trans*-[$PdEt_2L_2$] (L = PMe_2Ph, PEt_2Ph, PEt_3), which are retarded by the presence of phosphine.[11,12] The photoelimination of RCOCl from *trans*-[Pd$(PPh_3)_2$Cl(RCO)] (eq 1) is proposed to proceed from an excited state with a tetrahedral geometry analogous to that proposed for the photoinduced trans to cis isomerization and photoelimination of alkanes from [PdL_2R_2].[11] The trans to cis photoisomerization of [Pt$(PEt_3)_2$PhCl] was shown to proceed from a charge-transfer rather than ligand field state.[13] Since the thermal alkyl–aryl migration from CO to Pt is promoted by formation of vacant coordination sites in three-coordinate Pt(II) intermediates,[14] the elimination of RCOCl appears to proceed by a concerted rather than a stepwise dissociatve pathway. While the thermal reductive elimination of alkanes from [PdL_2R_2] proceeds by a dissociative mechanism,[15] evidence for concerted photochemical reductive elimination from [PdL_2R_2] has also been reported.[11]

We have shown that the elimination of acyl RCO and Cl ligands can proceed from trans as well as cis coordination sites of Pt(II) complexes. The photoeliminations of CO_2,[16-18] RCN,[19] and dioxygen[20] ligands from cis sites of Pt(II) complexes have been reported to form reactive bis(phosphine) PtL_2 intermediates. Our investigations indicate that the oxidatively reactive RCOCl reagent can be photoeliminated from Pt(II) and Pd(II) complexes in the presence of CS_2, which reacts with the reactive ML_2 intermediate to form [M$(PPh_3)_2(CS_2)$],[9] which inhibits the back-reaction of RCOCl and ML_2. Triphenylphosphine traps the [Pd$(PPh_3)_2$] intermediate as [Pd$(PPh_3)_4$],[21] but the back-reaction of [Pt$(PPh_3)_4$] and PhCOCl prevents the net formation of PhCOCl in the photolysis of *trans*-[Pt$(PPh_3)_2$Cl(PhCO)].[22] It is important to note that CS_2 and PPh_3, which serve as traps for the reactive [M$(PPh_3)_2$] intermediates, have low affinity for the starting Pd(II) and Pt(II) complexes. Photoreduction of Pt(II) and Pd(II) complexes is observed (i) when the eliminated ligands such as CO_2,[16-18] RCN,[19] and alkanes[11,12] have low oxidative reactivity,[23] (ii) when the eliminated ligands react to form species with low oxidative reactivity,[24] or (iii) when the reactive Pt(0) and Pd(0) intermediates are deactivated by formation of less reactive compounds such as [M$(PPh_3)_2$L], where L is PPh_3, CS_2, or alkynes.[19] Deposition of the metal as in the photoreduction of $[PtCl_4]^{2-}$ also prevents the back-reaction.[25]

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