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Formation of Carboxylic Acid Halides by the Reactions of Halogens with Acetyl-, (Phenylacetyl)-, and Benzoylchlorobis(triphenylphosphine)platinum(II) and Acetyl-, (Phenylacetyl)-, and Benzoylchloro(triphenylphosphine)palladium(II) Complexes

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The reactions of the acylmetal complexes *trans*-[M(PPh$_3$)$_2$Cl(RCO)] where M is Pt or Pd and R is CH$_3$, C$_6$H$_5$CH$_2$, or C$_6$H$_5$ with the halogens (X$_2$) chlorine, bromine, or iodine yield the carboxylic acid halides RCOX. The carboxylic acid bromides and iodides subsequently undergo exchange to form the carboxylic acid chlorides. The addition of bromine to *trans*-[Pt(PPh$_3$)$_2$Cl(PhCO)] in the presence of (PPN)Cl gives benzoyl bromide. The reactions of bromine with [Pt(COD)Cl(PhCO)] and [Pt(dppe)Cl(PhCO)] give benzoyl bromide. The reaction of ICl with *trans*-[M(PPh$_3$)$_2$Cl(RCO)] gives the carboxylic acid chlorides. The reaction of ICN with *trans*-[Pd(PPh$_3$)$_2$Cl(PhCO)] gives PhCOCl. Mechanisms for the formation of carboxylic acid halides are discussed.

Introduction

Reactions of carbon monoxide that are catalyzed by transition-metal compounds typically proceed through a sequence of steps that include oxidative addition, formation of acyl–transition-metal compounds by migratory insertion of carbon monoxide into a metal–carbon bond, and reductive elimination.[1] The mechanism of the industrially important Monsanto rhodium iodide catalyzed carbonylation of methanol to form acetic acid includes the following reactions:[2]

$$\mathrm{CH_3OH + HI \rightarrow CH_3I + H_2O} \tag{1}$$

$$\mathrm{CH_3I + [Rh(CO)_2I_2]^- \rightarrow [RhI_3(CO)_2CH_3]^-} \tag{2}$$

$$\mathrm{[RhI_3(CO)_2CH_3]^- + CO \rightarrow [RhI_3(CO)_2(CH_3CO)]^-} \tag{3}$$

$$\mathrm{[RhI_3(CO)_2(CH_3CO)]^- \rightarrow [RhI_2(CO)_2]^- + CH_3COI} \tag{4}$$

$$\mathrm{CH_3COI + H_2O \rightarrow CH_3COOH + HI} \tag{5}$$

Oxidative addition reactions of methyl iodide (eq 2) and migratory insertion reactions (eq 3) have been intensively investigated,[1,3] but the reductive elimination of acetyl iodide (eq 4) appears not to have been previously investigated in depth. Reductive elimination of acetyl iodide is also important in two catalytic cycles proposed for the carbonylation of methanol with iridium compounds[4] and the rhodium iodide catalyzed synthesis of acetic anhydride.[5] Stoichiometric decarbonylation of carboxylic acid chlorides with Wilkinson's catalyst [Rh(PPh$_3$)$_3$Cl] proceeds by a mechanism which includes alkyl migration, CO loss, and reductive elimination of alkyl halide.[6] Studies of reductive elimination reactions resulting in the formation of carbon–halogen bonds are scarce, and reductive elimination of alkyl halide often leads to other products. Thermal decomposition of [Rh(PPh$_3$)$_2$(CO)(CH$_3$)Cl$_2$] does not lead to methyl chloride but instead gives methyltriphenylphosphonium chloride.[7]

Attempts to reductively eliminate carboxylic acid halides (RCOX) instead lead to alkyl migration, decarbonylation, and reductive elimination of alkyl halide (the reverse of reactions 3 and 2). Decarbonylation rather than RCOCl elimination occurs when solid *trans*-[Pt(PPh$_3$)$_2$(RCO)Cl] (R = C$_6$F$_5$, Ph, Me) is heated at 461–493 K.[8] The decarbonylation of these acyl complexes in benzene solution is promoted by the presence of SnCl$_2$.[9] Bromination and subsequent methanolysis of acylpalladium(II) compounds to form esters have been previously described by Stille and co-workers.[10] Since reductive elimination reactions of six-coordinate di- and trialkylplatinum(IV) complexes have been explored intensively,[11] we planned to synthesize the Pt(IV) compounds [Pt(PPh$_3$)$_2$ClX$_2$(RCO)] by the firmly established oxidative addition[12] of halogens X$_2$ to the Pt(II)

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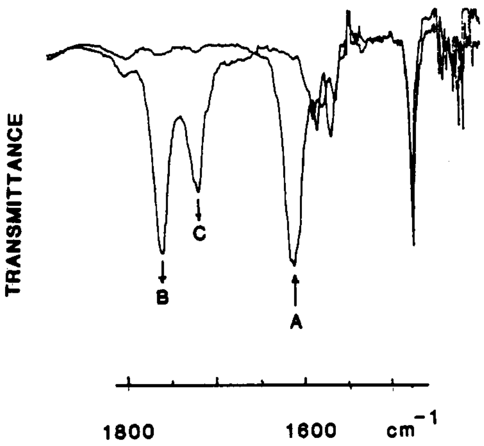

Figure 1. Changes in the IR spectra for the reaction of chlorine with *trans*-[Pt(PPh$_3$)$_2$(PhCO)Br] in CH$_2$Cl$_2$: A, 1620 cm^{-1}; B, 1772 cm^{-1}; C, 1728 cm^{-1}.

compounds [Pt(PPh$_3$)$_2$Cl(RCO)] and to investigate the elimination of RCOCl or RCOX. The formation of Pd(IV) compounds by the reaction of chlorine with Pd(II) compounds has also been widely reported.[13] The halogenation reactions instead gave the carboxylic acid halides directly and led us to conduct detailed studies of the halogen-induced formation of RCOX from the platinum and palladium acyl complexes *trans*-[M(PPh$_3$)$_2$Cl(RCO)] and [Pt(LL)Cl(PhCO)] (LL = COD, dppe).

Results

The addition of a dichloromethane solution of chlorine to *trans*-[Pt(PPh$_3$)$_2$(CH$_3$CO)Cl] gave a rapid reaction which resulted in the disappearance of the IR ν(CO) absorption band of the acetyl complex at 1639 cm^{-1} with formation of a very intense band at 1801 cm^{-1}. This latter band was demonstrated to be due to acetyl chloride by comparison with an authentic sample and also by conversion of the acetyl chloride to acetic acid (1756, 1709 cm^{-1}). The addition of dichloromethane solutions of bromine and iodine to the acetyl complex gave similar results, namely, the formation of acetyl bromide and acetyl iodide as shown by intense bands at 1808 and 1797 cm^{-1}. Hydrolysis of these acetyl halides with formation of acetic acid was indicated by the decay of the acetyl halide bands and growth of IR bands at 1756 and 1709 cm^{-1} due to acetic acid.

Investigations of the reactions of the halogens with the benzoylplatinum complexes provided more convincing evidence for new insights on the reaction pathways leading to the formation of the carboxylic acid halides from the acylplatinum complexes. The IR spectral changes resulting from the addition of a dichloromethane solution containing chlorine to the bromo benzoyl complex *trans*-[Pt(PPh$_3$)$_2$Br(PhCO)] are shown in Figure 1. The IR band at 1620 cm^{-1} (A) of the benzoyl platinum complex was immediately replaced by the IR bands at 1772 (B) and 1728 cm^{-1} (C). The doublet (B and C) bands are observed in the IR spectrum of an authentic sample of benzoyl chloride. Fortuitously, the latter band at 1728 cm^{-1} in the spectrum of benzoyl chloride, which is not present in the spectra of benzoyl bromide and benzoyl iodide, permits the positive identification of the benzoyl halide formed in the reaction. The doublet for PhCOCl was noted very early, but its origin has not been fully explained.[14]

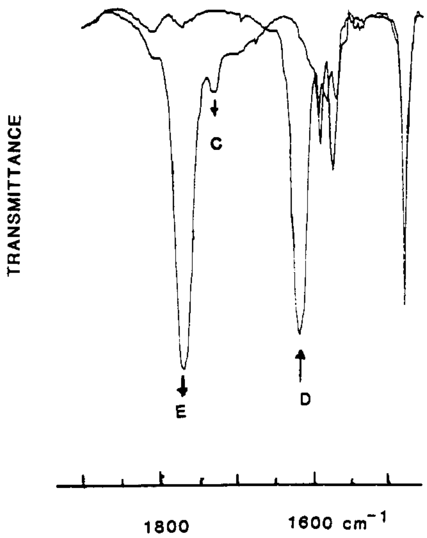

Figure 2. Changes in the IR spectra for the reaction of bromine with *trans*-[Pt(PPh$_3$)$_2$(PhCO)Cl] in CH$_2$Cl$_2$: D, 1618 cm^{-1}; E, 1772 cm^{-1}.

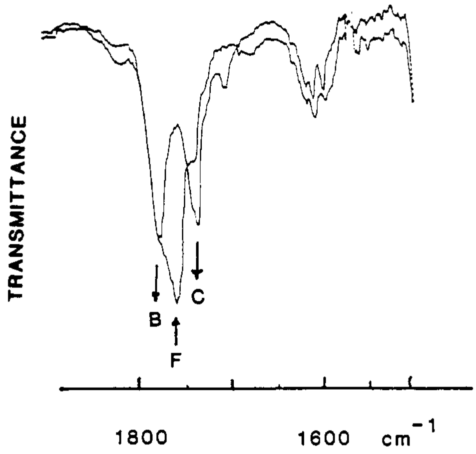

Figure 3. Changes in the IR spectra of the product formed in the reaction of iodine with *trans*-[Pt(PPh$_3$)$_2$(PhCO)Cl]: F, 1758 cm^{-1}; B, 1772 cm^{-1}; C, 1729 cm^{-1}.

Spectra for the addition of dichloromethane solutions of bromine to *trans*-[Pt(PPh$_3$)$_2$(PhCO)Cl] are shown in Figure 2. The CO absorption of the chloro benzoyl complex (D) at 1618 cm^{-1} immediately disappeared upon the addition of bromine to give a band (E) at 1772 cm^{-1}. The assignment of this band to benzoyl bromide was established by comparison with the spectrum of an authentic sample of benzoyl bromide. Within a minute after recording the spectrum shown in Figure 2, the conversion of the benzoyl bromide to benzoyl chloride was indicated by the increasing intensity of the weak band at 1728 cm^{-1} (C). In the presence of trace amounts of water, the IR band at 1772 cm^{-1} was found to decay with concomitant formation of bands at 1728 cm^{-1} and 1690 cm^{-1} due to benzoic acid.

The addition of a solution of bromine in dichloromethane to the bromobenzoylplatinum complex *trans*-[Pt(PPh$_3$)$_2$(PhCO)Br] gave an IR spectrum with a band at 1772 cm^{-1} which is characteristic of benzoyl bromide. Addition of iodine to *trans*-[Pt(PPh$_3$)$_2$(PhCO)Br] initially

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Table I. Infrared Absorption Data for the Addition of Halogen (X_2) to Acylplatinum Complexes in Dichloromethane Solution

acyl complex [ν(CO), cm^{-1}]	halogen	ν(CO), cm^{-1}	acid halide
[Pt(PPh_3)$_2$(CH_3CO)Cl] (1639)	Cl_2	1801	CH_3COCl
	Br_2	1808	CH_3COBr
	I_2	1797	CH_3COI
[Pt(PPh_3)$_2$(PhCO)Cl] (1620)	Cl_2	1772, 1729	PhCOCl
	Br_2	1772	PhCOBr
	I_2	1758	PhCOI
	ICl	1772, 1729	PhCOCl
[Pt(PPh_3)$_2$(PhCO)Br] (1620)	Cl_2	1772, 1728	PhCOCl
	Br_2	1772	PhCOBr
	I_2	1757	PhCOI
[Pt(PPh_3)$_2$($PhCH_2CO$)Cl] (1647)	Cl_2	1797	$PhCH_2COCl$
	Br_2	1801	$PhCH_2COBr$
	I_2	1785	$PhCH_2COI$
	ICl	1796	$PhCH_2COCl$
[Pt(COD)(PhCO)Cl] (1637)	Br_2	1772	PhCOBr
[Pt(dppe)(PhCO)Cl] (1607)	Br_2	1772	PhCOBr
[Pd(PPh_3)$_2$(CH_3CO)Cl] (1676)	Cl_2	1800	CH_3COCl
	Br_2	1807	CH_3COBr
	I_2	1795	CH_3COI
[Pd(PPh_3)$_2$($PhCH_2CO$)Cl] (1669)	Cl_2	1798	$PhCH_2COCl$
	Br_2	1800	$PhCH_2COBr$
	I_2	1784	$PhCH_2COI$
[Pd(PPh_3)$_2$(PhCO)Cl] (1640)	Cl_2	1771, 1729	PhCOCl
	Br_2	1770	PhCOBr
	I_2	1756	PhCOI

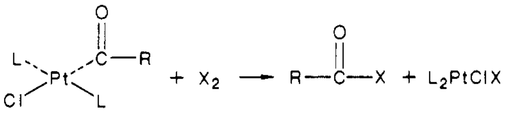
gave a spectrum with the IR band at 1757 cm^{-1} characteristic of benzoyl iodide. This band was replaced within 15 min by a band at 1769 cm^{-1} due to benzoyl bromide. Addition of iodine to *trans*-[Pt(PPh_3)$_2$(PhCO)Cl] immediately gave a band (F) at 1758 cm^{-1} due to benzoyl iodide. As shown in Figure 3, band F was replaced within 2 min by bands B and C at 1772 and 1729 cm^{-1}, respectively due to benzoyl chloride. The addition of iodine to *trans*-[Pt(PPh_3)$_2$Cl($PhCH_2CO$)] first gave a band at 1785 cm^{-1} due to phenylacetyl iodide, which was rapidly converted to phenylacetyl chloride (shown by a band at 1797 cm^{-1}). The addition of bromine to [Pt(COD)Cl(PhCO)] and [Pt(dppe)ClPhCO)] immediately gave the singlet band at 1772 cm^{-1} characteristic of benzoyl bromide before giving the doublet at 1772 and 1728 cm^{-1} of benzoyl chloride. In the presence of small amounts of water, the bands due to RCOX were replaced by bands at 1728 and 1690 cm^{-1} due to benzoic acid. These data thus indicate that substitution of iodide and bromide from the first formed RCOX by the chloride from the platinum complexes is relatively rapid. Since the reactions of excess halogen with the platinum(II) complexes are extremely rapid, the final product in the reaction of chlorine with *trans*-[Pt(PPh_3)$_2$Cl($PhCH_2CO$)] was found to be [Pt(PPh_3)$_2$$Cl_4$]. Careful stoichiometric addition of a dilute solution of iodine in dichloromethane to a solution of *trans*-[Pt(PPh_3)$_2$Cl(PhCO)] resulted in the isolation of a product which had the approximate analysis for [Pt(PPh_3)$_2$$I_2$]. Infrared data for the addition of dichloromethane solutions of halogens to other platinum acyl complexes are given in Table I.

Data for the halogenation reactions of the analogous palladium complexes *trans*-[Pd(PPh_3)$_2$Cl(RCO)] where R is Me, Ph, or $PhCH_2$ which are shown in Table I indicate that the acylpalladium compounds follow the same reactivity pattern for formation of RCOX. The data provided in Figures 1, 2, and 3 and Table I clearly demonstrate that the halogen atom of the carboxylic acid halides originates from the halogen molecule which is added to the platinum and palladium acyl complexes. The rates of the RCOX-forming reactions like other halogenation reactions of Pt(II) compounds[15] were too rapid for kinetic studies by standard spectral techniques. Infrared spectral examination of the reaction solution conducted at 183 K showed the presence of the reactant acyl complexes and the RCOX product but did not reveal the presence of intermediates.

The addition of dichloromethane solutions of ICl to *trans*-[Pt(PPh_3)$_2$Cl(PhCO)] and the other acyl complexes gave the corresponding acid chlorides RCOCl. These results may reflect the greater reactivity of chlorine compared to iodine that is formed in the disproportionation of iodine monochloride.[16] Cyanogen bromide and cyanamide did not undergo reaction with *trans*-[Pt(PPh_3)$_2$Cl(PhCO)]. The reaction of cyanogen iodide with *trans*-[Pt(PPh_3)$_2$Cl(PhCO)] proceeded at a slower rate than the addition of iodine, and the only product observed was benzoyl chloride. This contrasts with the observation for the reaction with iodine, in which benzoyl iodide was first observed before its transformation to benzoyl chloride. The reaction of cyanogen iodide with *trans*-[Pd(PPh_3)$_2$Cl(PhCO)] proceeded with rapid disappearance of the band at 1620 cm^{-1} and appearance of an IR absorption band at 1666 cm^{-1} which decayed with concomitant growth of the bands at 1772 and 1729 cm^{-1} due to benzoyl chloride. The reaction of cyanogen bromide and *trans*-[Pd(PPh_3)$_2$Cl(MeCO)] similarly gave an intermediate with IR absorption at 1705 cm^{-1}, but efforts to isolate the Pd(IV) intermediates resulted in the formation of a mixture of decomposition products.

Discussion of Results

The addition of dichloromethane solutions of halogens X_2 to *trans*-[M(PPh_3)$_2$Cl(RCO)] (M = Pt, Pd; R = Ph, Me, $PhCH_2$) and to [Pt(LL)Cl(PhCO)] where LL is COD or dppe results in the rapid initial formation of carboxylic acid halide RCOX.



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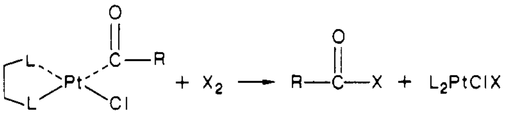

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In the presence of excess halogen the well-known rapid halogenation of the M(II) complexes to form M(IV) complexes takes place.[12,13] Special precautions including rapid addition of dry dichloromethane solutions of the halogen to the solid acyl complexes and immediate recording of the spectra were imperative for the detection of the highly reactive first formed RCOX, especially the iodide, which was subsequently rapidly substituted by the chloride ligand of the M(II) complexes.

Since it has been established that halogens undergo reactions with almost all Pd(II) and Pt(II) compounds[12,13] and that the oxidative addition of halogen X_2 to planar platinum(II) complexes to form octahedral complexes is known to proceed with trans addition of the halogen atoms,[12a–d] a reasonable mechanism for RCOX formation is the trans addition followed by the cis reductive elimination of RCOX (eq 8). Our inability to observe a platinum(IV)

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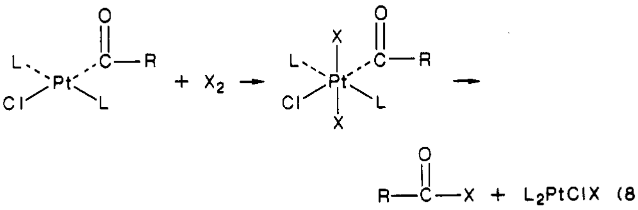
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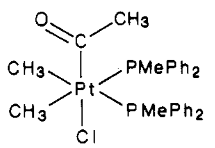
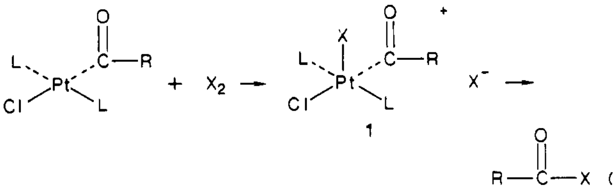
acyl intermediate in our experiments conducted at 183 K is surprising because platinum(IV) acyl complexes such as shown below are thermally stable.[17]

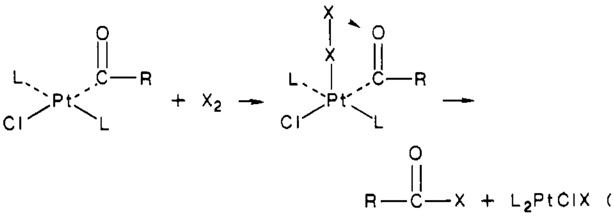


Pyrolysis of this acyl complex does not give reductive elimination of acetyl chloride but instead gives acetone and *trans*-$[PtClMe(PMe_2Ph)_2]$. The formation of acetone was shown to proceed by initial loss of a ligand,[18] and evidence for acceleration of reductive elimination from cationic platinum(IV) complexes has been provided by several investigators.[17,19] Treatment of the Pt(IV) compound with silver ion to abstract the chloride ligand to form a cationic intermediate led to formation of acetone at room temperature. Metal–chlorine stretching frequencies and bond lengths have been used to suggest that the trans labilizing power of the acetyl moiety is very high, decreasing as RCO > Me > PPh_3 > CO > Cl.[20] Thus the chlorine ligand trans to the acetyl ligand would be expected to be labilized to form a cation from which acetone rather than acetyl chloride is the elimination product.

Stop-flow kinetic studies of the addition reactions of chlorine and bromine with platinum(II) compounds showed that the oxidative addition reaction first forms a halogenated platinum(IV) intermediate cation that subsequently reacts with the halide anion.[15] Cationic intermediates were also detected in the oxidative addition of alkyl halides to platinum(II) compounds.[21] A reasonable mechanism for the rapid formation of RCOX observed in this study that is consistent with the previous studies of oxidative addition of halogens to Pt(II) complexes, and the favored reductive elimination from cationic Pt(IV) complexes would be the oxidative addition of halogen to form a cationic intermediate, followed by the unimolecular elimination of RCOX before addition of the halide anion (eq 9). The addition of cyanogen bromide to *trans*-[Pd$(PPh_3)_2Cl(RCO)$] (R = Me, Ph) gave intermediates with CO frequences at 1705 and 1666 cm^{-1} indicative of Pd(IV) species, but these intermediates decomposed before they could be fully characterized. The addition of bromine to [Pt(COD)Cl(PhCO)] or [Pt(dppe)Cl(PhCO)] was observed to yield benzoyl bromide instead of benzoyl chloride. These results indicate that even if the acyl and chloro ligands are cis in the Pt(IV) complex, the carboxylic acid halide product which is formed results from the halogen that is added.


(9)

An intermediate in the oxidative addition of iodine to $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}o,o\}]$ was shown to have a linear Pt–I–I bond with the I–I bond elongated from 2.715 Å in free iodine to 2.822 Å in the complex.[22] The formation of carboxylic acid halide may also proceed through an intermediate shown in eq 10. In support of this pathway is our observation of the RCOCl products in the reaction of ICl with *trans*-$[Pt(PPh_3)_2Cl(RCO))$ (R = Ph, CH_2). The carboxylic acid iodides would have been expected in the cis elimination route described in eq 9. The formation of RCOCl, as pointed out earlier, however, may be due to the presence of chlorine which is known to be present in ICl.[16]


(10)

An alternative mechanism in which the anion X^- attacks the carbonyl carbon atom of the cationic intermediate 1 does not appear to be likely for two reasons. (1) The addition of bromine to *trans*-$[Pt(PPh_3)_2Cl(PhCO)]$ in the presence of excess PPN chloride gave PhCOBr instead of PhCOCl which would be expected in the presence of high chloride concentration. (2) The formation of benzoyl iodide from the addition of iodine to *trans*-[Pt$(PPh_3)_2Cl(PhCO)$] is not likely to result from the attack of the cationic species 1 at the carbonyl carbon by iodide.

The involvement of radicals in the formation of RCOX is not considered to be very likely, since PhCOCl formation was not observed when dichloromethane solutions of *trans*-$[Pt(PPh_3)_2Cl(PhCO)]$ and the radical initiator AIBN were heated. Cyclic voltammetric studies also indicated that the acyl platinum(II) compounds do not undergo facile outer-sphere electron-transfer reactions. Electrophilic attack by the halogen on the carbonyl of the acyl platinum(II) complexes is also not considered to be important because the halogens do not react rapidly with acyliridium(III) compounds such as $[Ir(CO)(RCO)Cl_2(PPh_3)_2]$. Electrophiles such as methyl iodide react with the oxygen atom of the acyl ligand to form carbene complexes.[23]

The oxidatively induced formation of carboxylic acid halides observed in the present study is consistent with the pathway involving a high-energy Pd(IV) or Pt(IV) intermediate and formation of stable $[Pt(PPh_3)_2ClX]$. These observations are consistent with Norton's conclusion that simple intramolecular reductive elimination becomes disfavored as the energy of the remaining metal fragment increases so that other elimination processes occur.[24] Formation of carboxylic acid halide is thus favored from a metal in a higher oxidation state such as from the d^6 Pt(IV) and Pd(IV) species in this study and Rh(III) in the Monsanto process.

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Experimental Section

Reagents. Dichloromethane was freshly distilled under nitrogen from calcium hydride before use. Cyanogen bromide, cyanogen iodide, and iodine monochloride were purchased from Aldrich and used without further purification. Literature methods were used to prepare $[PtCl_2(COD)]$,[25] $[PtClPh(COD)]$,[26] $[Pt(COD)Cl(PhCO)]$,[27] and $[Pt(dppe)Cl(PhCO)]$.[27] The acyl compounds *trans*-$[Pt(PPh_3)_2(RCO)X]$ were synthesized from the reactions of the corresponding acid halides RCOX and $[Pt(PPh_3)_2(C_2H_4)]$ as previously described.[9,28] The palladium acyl compounds were prepared from the reactions of the acyl halides and $[Pd(PPh_3)_4]$.[29] Anal. Calcd for $[Pd(CH_3CO)Cl(PPh_3)_2]$ ($C_{38}H_{33}OClP_2Pd$): C, 64.33; H, 4.69. Found: C, 64.23; H, 4.77. Anal. Calcd for $[Pd(PPh_3)_2Cl(PhCH_2CO)]$ ($C_{44}H_{37}OClP_2Pd$): C, 67.27; H, 4.75. Found: C, 67.30; H, 4.90. The purity of the acyl complexes was established by satisfactory elemental analysis as previously described, IR spectra data, and thin-layer chromatography on silica plates with elution with chloroform. Microanalyses were performed by the Galbraith Laboratories Inc., Knoxville, TN.

Isolation of Chlorinated Platinum Product. A suspension of 100 mg of *trans*-$[Pt(PPh_3)_2Cl(PhCH_2CO)]$ was treated with a stream of chlorine gas for 30 s. The yellow solution was stirred for 30 min, and the solvent was removed in vacuo. The yellow product was recrystallized from dichloromethane–ethanol (58 mg, 55%). Anal. Calcd for $[Pt(PPh_3)_2Cl_4]$ ($C_{36}H_{30}Cl_4P_2Pt$): C, 50.20; H, 3.50; Cl, 16.45. Found: C, 49.50; H, 3.51; Cl, 16.74.

IR Spectral Studies of the Halogenation Reactions. The IR spectrum of a stock solution of 70 mg of bromine in 10 mL of dichloromethane in a 0.5-mm sodium chloride cell was stored in the memory of a Perkin-Elmer 983 infrared spectrometer. This spectrum was subtracted from the spectrum of a solution prepared by the addition of 1 mL of the bromine stock solution to 5 mg of *trans*-$[Pt(PPh_3)_2(PhCO)Cl]$. The spectra such as shown in Figures 1 and 2 were recorded a few seconds after the addition of the solution containing the halogen. Similar data were obtained for solutions of chlorine, bromine, iodine, ICl, ICN, and BrCN added to the acylplatinum or -palladium complexes.

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A Metal Pentadienyl Prepared by Reacting a Metal Carbyne with an Enyne

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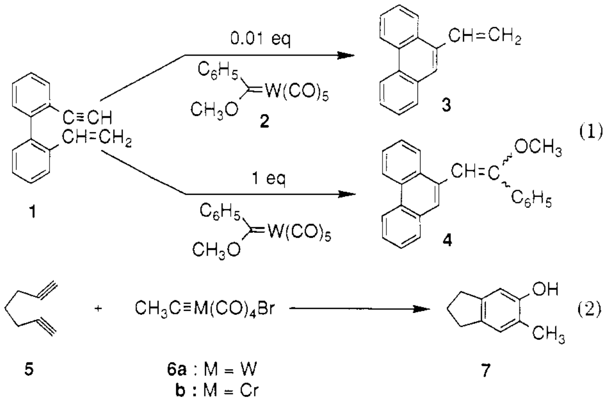
Unlike essentially all isolable metal pentadienyls, the tungsten pentadienyl 8 has a sickle shape. This material is produced in a novel reaction when bromotetracarbonyl(ethylidyne)tungsten is combined with 2-ethenyl-2′-ethynyl-1,1′-biphenyl. The structure, analyzed by X-ray diffraction, appears to consist of vinyl and distorted allyl moieties bonded to the metal. The chromium analogue of the metal carbyne forms not the chromium analogue of 8 but two hydrocarbons, one a protonation product of a metal pentadienyl and the other an indene. Mechanisms are suggested for the transformations.

Among a variety of transformations that occur when metal carbenes or metal carbynes combine with alkenes,[1] alkynes,[2] enynes,[3] and diynes[4] are those illustrated in eq 1 and 2. The enyne **1** is transformed by small amounts of metal carbene **2** into structure **3** and by stoichiometric amounts into structure **4** (eq 1).[3a] Diyne **5** is transformed by stoichiometric amounts of metal carbynes **6a** and **6b** into phenol **7** (eq 2).[4b] However, the combination of **1** with **6** represents a permutation of which no example has previously been reported.



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