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Electrochemical Generation and Reactivity of Bis(tertiary phosphine)platinum(0) Complexes: A Comparison of the Reactivity of $[Pt(PPh_3)_2]$ and $[Pt(PEt_3)_2]$ Equivalents

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Electrochemical reduction of *cis*-$[PtCl_2(PR_3)_2]$ (R = Ph, Et) in CH_3CN/C_6H_6 containing NBu_4ClO_4 at a Hg pool electrode generates $[Pt(PR_3)_2]$ equivalents in solution. Where R = Ph, the $[Pt(PR_3)_2]$ equivalent may be trapped by O_2, O_2/CO_2, HCl, MeI, C_6H_5COCl, and RC≡CR (R = Ph, COOMe) but not by the less reactive substrate PhCl. Where R = Et, the $[Pt(PR_3)_2]$ equivalent reacts with the NBu_4^+ cation to ultimately generate *trans*-$[PtH(Cl)(PEt_3)_2]$. Prolonged electrolyses cause reduction of *trans*-$[PtH(Cl)(PEt_3)_2]$ leading to hydride attack on the CH_3CN solvent and ultimately forming *trans*-$[PtH(CH_2CN)(PEt_3)_2]$. In the presence of bases such as NBu_3, *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ is isomerized in CH_3CN solution producing *trans*-$[PtCN(CH_3)(PEt_3)_2]$. The use of electroinactive trapping agents such as PhCl or PhCN as cosolvents for the reduction of *cis*-$[PtCl_2(PEt_3)_2]$ allows trapping of the $[Pt(PEt_3)_2]$ equivalents as *trans*-$[PtPh(X)(PEt_3)_2]$ (X = Cl, CN).

Introduction

Until recently the chemistry of two-coordinate, 14-electron bis(tertiary phosphine)platinum(0) complexes has been restricted to examples where sterically demanding tertiary phosphines limited reactivity.[1] Thus, $[PtL_2]$ complexes where L = $P(t\text{-}Bu)_3$,[2] $P(t\text{-}Bu)_2Me$,[3] $P(t\text{-}Bu)_2Ph$,[2] $P(c\text{-}Hx)_3$,[2,4] or $P(i\text{-}Pr)_3$[2] are well-known with reactivity toward oxidative addition addenda increasing with decreasing steric bulk of the tertiary phosphine ligand.[1,5] Synthetic strategies for $[PtL_2]$ complexes have typically included the chemical reduction of platinum(II) precursors,[2] e.g., $[PtCl_2L_2]$, or substitution of labile platinum(0) intermediates,[2,3] e.g. $[Pt(cod)_2]$. These strategies routinely fail when L is not sterically demanding, and 3- or 4-coordinate platinum(0) complexes,[2,6] or platinum(II) hydrides,[7] are typically formed.

In recent years alternative synthetic methods have been developed on the basis of photochemical or thermal reduction of suitable platinum(II) precursors. Thus, Trogler[8,9] has succeeded in generating $[Pt(PEt_3)_2]$ equivalents via photolysis of the oxalate $[Pt(C_2O_4)(PEt_3)_2]$. The reactivity of this uncrowded complex far exceeds that of its more hindered analogues. Clark has shown[4] that thermolysis of *trans*-$[PtH_2(P\{c\text{-}Hx\}_3)_2]$ produces $[Pt(P\{c\text{-}Hx\}_3)_2]$ via the reductive elimination of dihydrogen, and, more recently, Whitesides[10] has generated the novel intermediate $[Pt\{c\text{-}Hx\}_2PCH_2CH_2P\{c\text{-}Hx\}_2]$ via thermolysis of $[PtH(CH_2CMe_3)(\{c\text{-}Hx\}_2PCH_2CH_2P\{c\text{-}Hx\}_2)]$. The generation of $[PtL_2]$ complexes containing triarylphosphine ligands by thermal or photochemical reductive methods is more problematic. Thus, it is reported[11] that platinum(0) complexes can be generated from $[Pt(C_2O_4)(PPh_3)_2]$, but the characterization of several of the reaction products has been questioned. Similarly, generation of $[Pt(PPh_3)_2]$ by reductive elimination of methane from the corresponding hydridomethyl complex[13] is inconvenient since the reaction proceeds at −25 °C and disproportionation occurs.

Despite the challenges in synthesis, interest in the reaction chemistry of $[PtL_2]$ complexes remains high.[14] Otsuka and co-workers[1] have investigated the activation of water by $[PtL_n]$ (n = 2,3) systems, and, more recently, Trogler[15] has reported a remarkable catalytic cycle for the anti-Markovnikov addition of water to terminal alkenes producing 1-alkanols, which implicates $[Pt(PMe_3)_2]$ as an intermediate. Both Otsuka[1] and Hoffmann[16] have described theoretical treatments which predict high reactivity for nonlinear $[PtL_2]$ fragments and Whitesides has demonstrated[10] that the presumably bent intermediate $[Pt(\{c\text{-}Hx\}_2PCH_2CH_2P\{c\text{-}Hx\}_2)]$ reacts in carbene-like fashion with a variety of sp, sp^2, and sp^3 carbon–hydrogen bonds. The studies of Trogler[8,9,15] and Whitesides[10] suggest that interesting and potentially useful chemistry may evolve from studies of unhindered and/or structurally distorted $[PtL_2]$ complexes.

The use of electrochemical methods to generate low-valent intermediates, of the type $[PtL_2]$, has received scant attention in the past although such methods may show advantages over chemical, photochemical, or thermal reductive strategies. For example, the generation of $[Pt(PPh_3)_2]$ via photolysis of $[Pt(C_2O_4)(PPh_3)_2]$[11] or thermo-

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lysis of *trans*-$[PtH(CH_3)(PPh_3)_2]$[13] is problematic (vide supra) and other chemical approaches have not been successful, in large part due to the tendency for ligand P–C bond cleavage to occur in coordinatively unsaturated complexes containing arylphosphine ligands.[17] Thus, thermolysis of $[Pt(PPh_3)_4]$ produces $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ and $[Pt_3(\mu\text{-}PPh_2)_3(PPh_3)_2Ph]$.[18] Similarly, passing N_2 through a solution of $[Pt(C_2H_4)(PPh_3)_2]$ results not only in displacement of ethylene but also in formation of $[Pt_2(\mu\text{-}PPh_2)_2(PPh_2C_6H_4)_2]$ and benzene.[19] Unlike the PEt_3 analogue,[8,9] photolysis of $[Pt(C_2O_4)(PPh_3)_2]$ under hydrogen[20] does not produce a simple dihydride but rather, after precipitation with $NaBF_4$, the cationic cluster $[Pt_3(\mu\text{-}PPh_2)_2(\mu\text{-}H)(PPh_3)_3]^+$. In contrast, prior reports[21,22] of the controlled potential bulk reductive electrolysis of $[PtCl_2(PPh_3)_2]$ suggest that an electrochemical approach to the generation of $[Pt(PPh_3)_2]$ might be successful. Thus, electrochemical reduction of $[PtCl_2(PPh_3)_2]$ followed by addition of HCl gas yields a hydride complex, although no details of characterization were given.[21] Interestingly, electrochemical reduction followed by the addition of water[22] also yields a hydride, characterized by an IR absorption at 2232 cm^{-1}, whereas electrochemical reduction of $[PtCl_2(PPh_3)_2]$ in the presence of excess PPh_3 (where initial formation of $[PtCl(PPh_3)_3]Cl$ might be anticipated) is reported[22] to produce $[Pt(PPh_3)_3]$, characterized by elemental analysis only.

Here we report the electrochemical reduction of *cis*-$[PtCl_2(PPh_3)_2]$ and *cis*-$[PtCl_2(PEt_3)_2]$ as routes for the in situ generation of $[Pt(PPh_3)_2]$ and $[Pt(PEt_3)_2]$ equivalents. A comparison of the reactivity of these platinum(0) fragments with oxidative addition addenda and coordinating substrates and in acid/base reactions shows dramatic differences between the two systems. Preliminary results of our studies on $[Pt(PPh_3)_2]$[23] and $[Pt(PEt_3)_2]$[24] have been reported previously.

Results and Discussion

Generation and Reactivity of $[Pt(PPh_3)_2]$ Equivalents. A cyclic voltammogram of *cis*-$[PtCl_2(PPh_3)_2]$ dissolved in acetonitrile/benzene (7/3, v/v) containing tetra-*n*-butylammonium perchlorate (TBAP, 10^{-1} M) exhibits a single cathodic peak at −1.60 V vs Ag/AgCl (−35 mV vs SCE) on a mercury amalgam elecrode at a scan rate of 200 mV s^{-1}. The dependence of the peak current and peak potential on scan rate and the absence of a coupled oxidation at any scan rate investigated (100 mV s^{-1} to 50 V s^{-1}) are indicative of a diffusion-controlled, irreversible reduction. Details of cyclic voltammetric studies of the cis and trans isomers of $[PtCl_2(PPh_3)_2]$ have been reported previously by ourselves[25] and others.[26] Controlled potential bulk reductive electrolysis experiments have been performed in a three-compartment cell, equipped with a mercury pool working electrode, a platinum spiral wire counterelectrode, and a Ag/AgCl reference electrode. *cis*-$[PtCl_2(PPh_3)_2]$ is dissolved in a preelectrolyzed acetonitrile/benzene (5/2, v/v) solvent system containing TBAP (10^{-1} M) and suspended activated alumina. Electrolysis at −1.60 V vs Ag/AgCl, under an argon atmosphere, leads to the formation of a clear, bright orange solution. Coulometry indicates a two-electron reduction (eq 1) with

$$cis\text{-}[PtCl_2(PPh_3)_2] \xrightarrow{2e} [Pt(PPh_3)_2] + 2Cl^- \qquad (1)$$

integrations typically in the range of 1.9–2.1 electrons when the electrolysis is terminated at a point where the current vs time curve has a slope indistinguishable from zero, corresponding to negligible current flow.

The electrochemically reduced solution is exceedingly air-sensitive, and $^{31}P\{^1H\}$ NMR studies of the reactivity of the reduced solution with O_2 and with air show that the chemistry initially follows the expected pathways for a platinum(0) complex.[27] Thus, reaction with O_2 for 30 min produces significant amounts of $[PtO_2(PPh_3)_2]$[28] and $OPPh_3$[29] while reaction with air for 30 min produces $[Pt(CO_3)(PPh_3)_2]$[30] and $OPPh_3$.[29] Interestingly we found that exposure of the reduced solution to air for 7 days, followed by concentration and examination by $^{31}P\{^1H\}$ NMR spectroscopy, showed the presence of not only $[Pt(CO_3)(PPh_3)_2]$ and $OPPh_3$ observed previously after 30 min exposure to air but also a new species (δ 24.4 [$^1J(Pt,P)$ = 3156 Hz]) formed in ca. 7% spectroscopic yield with NMR data corresponding to the known compound *trans*-$[PtPh(Cl)(PPh_3)_2]$ (δ 24.2 [$^1J(Pt,P)$ = 3152 Hz] in $CDCl_3$ solution).[31] Formation of this minor product was found to be reproducible,[32] but separation and isolation attempts proved fruitless. Preliminary experiments suggest that this minor product arises from reactivity attributable to $[PtO_2(PPh_3)_2]$ and not to the electrochemically generated platinum(0) complex.[33] Further studies in this area are in progress.

The addition of unsaturated substrates to the bright orange solution formed by the electrochemical reduction of *cis*-$[PtCl_2(PPh_3)_2]$ allows efficient trapping of the $[Pt(PPh_3)_2]$ equivalent. Thus, addition of PhC≡CPh or MeOOCC≡CCOOMe produces the corresponding acetylene complex in high spectroscopic yield (Scheme I) with

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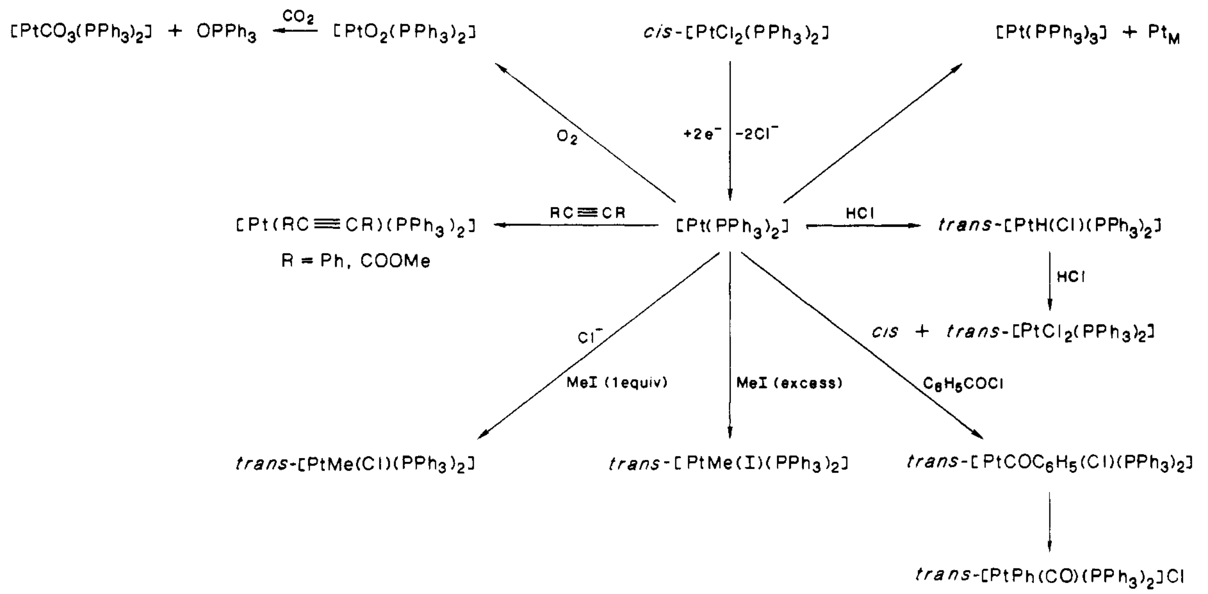
(32) Two experiments performed with different batches of *cis*-$[PtCl_2(PPh_3)_2]$, solvents, and background electrolyte both produced this minor component.

(33) $^{31}P\{^1H\}$ NMR studies suggest an intermediate *cis*-bis(phosphine) complex with two different anionic ligands, one of which has a very low trans influence.

Scheme I



deviations from 100% caused by trace quantities of starting material and/or triphenylphosphine oxide. As is common in electrosynthetic procedures of this general type, separation of the reaction products from the background electrolyte can be tedious. In these cases, chromatography on alumina proved to be satisfactory (see Experimental Section), allowing isolation of the $[Pt(RC{\equiv}CR)(PPh_3)_2]$ complexes in 77% (R = Ph) and 78% (R = COOMe) yields. These yields are comparable with most traditional syntheses of platinum acetylene complexes[34] and are an improvement on many methods. The high spectroscopic and isolated yields in these reactions are indications that electron transfer (eq 2), and other destructive processes (e.g. ligand P–C bond cleavage, vide supra) are not significant in these systems.

$$Pt(II) + Pt(0) \rightarrow 2Pt(I) \qquad (2)$$

The $[Pt(PPh_3)_2]$ equivalent may also be trapped with the oxidative addition addenda HCl, MeI, and C_6H_5COCl (Scheme I) but not by the less reactive substrate PhCl. In these cases spectroscopic yields were lower and chromatography on alumina did not effect complete separation of the products from the background electrolyte. The reaction with MeI is of particular interest since addition of an excess of MeI to the reduced solution produces the expected *trans*-$[PtMe(I)(PPh_3)_2]$ whereas the addition of ca. 1 equiv of MeI produces *trans*-$[PtMe(Cl)(PPh_3)_2]$. Since the generation of $[Pt(PPh_3)_2]$ equivalents from *cis*-$[PtCl_2(PPh_3)_2]$ produces Cl^- in solution, addition of 1 equiv of MeI might result in the in situ formation of MeCl, which undergoes oxidative addition or free Cl^- might cause metathesis of the initially formed MeI oxidative addition product.

In the absence of trapping reagents, disproportionation to $[Pt(PPh_3)_3]$ and platinum metal occurs (eq 3). $[Pt(PPh_3)_3]$ has been identified by $^{31}P\{^1H\}$ NMR spectroscopy[35] and discoloration indicates formation of platinum metal. The time scale of this disproportionation is such that it does not adversely affect trapping of the $[Pt(PPh_3)_2]$ equivalent (vide supra). This is particularly significant since it is known that generation of $[Pt(PPh_3)_2]$ by reductive elimination of methane from the corresponding hydridomethyl complex in toluene solution leads to disproportionation at temperatures above −25 °C.[13] It is possible that the solvent system that we employ (CH_3CN/C_6H_6) participates in stabilizing the low-valent intermediate. Indeed, stabilization of $[Pt(PEt_3)_2]$ equivalents by coordination of benzene[8,9] and of $[Pt(PPh_3)_2]$ equivalents by coordination of hard donor solvents[36] have been proposed previously. Despite these quantitative observations all attempts to use low-temperature NMR methods to observe $[Pt(PPh_3)_2]$ directly have failed since we have been unable to unambiguously assign resonances to the two-coordinate compound. For later comparison with $[Pt(PEt_3)_2]$, it is important to note that in the absence of trapping agents we observe only disproportionation with the triphenylphosphine system and observe no products derived from C–H or C–C cleavage reactions with the solvent/electrolyte system.

$$3[Pt(PPh_3)_2] \rightarrow 2[Pt(PPh_3)_3] + Pt_M \qquad (3)$$

Generation and Reactivity of $[Pt(PEt_3)_2]$ Equivalents. The generation of $[Pt(PEt_3)_2]$ equivalents by photolysis of $[Pt(C_2O_4)(PEt_3)_2]$ has been demonstrated by Trogler,[8,9] who has documented an extensive reactivity for this low-valent intermediate. Accordingly we sought to investigate the utility of the electrochemical methodology in generating this highly reactive compound.[24]

A cyclic voltammogram of *cis*-$[PtCl_2(PEt_3)_2]$ dissolved in acetonitrile/benzene (7/3, v/v) containing TBAP (10^{-1} M) exhibits a single cathodic peak at −2.05 V vs Ag/AgCl on a mercury amalgam electrode at a scan rate of 200 mV s^{-1}. No coupled oxidation is observed at scan rates over the range 200 mV s^{-1} to 50 V s^{-1}, and the dependence of the peak current and peak potential on scan rate is indicative of an irreversible, diffusion-controlled reduction.[37] Controlled pontential bulk reductive electrolysis at −2.10 V, employing the same conditions as those described for the PPh_3 analogue, leads to the formation of a yellow solution, from which the complex *trans*-$[PtH(Cl)(PEt_3)_2]$ may be isolated. The hydride was characterized by ^1H, ^{31}P, and $^{31}P\{^1H\}$ NMR and IR methods and by elemental analysis (see Experimental Section). The progress of the

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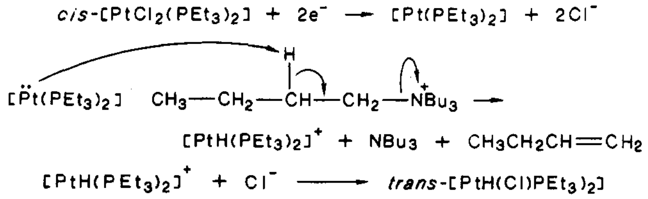
electrochemical reduction differs somewhat from the triphenylphosphine system since toward the end of the reaction (i.e. when the slope of the current vs time curve approaches zero, corresponding to consumption of two electrons) some decomposition is apparent by discoloration of the initially yellow solution and some residual current flow remains. In order to obtain a maximum yield (63.3%) of *trans*-[PtH(Cl)(PEt$_3$)$_2$], the reduction is terminated as soon as discoloration becomes apparent, corresponding to uptake of 1.70–1.85 electrons.

The isolation of *trans*-[PtH(Cl)(PEt$_3$)$_2$] from the electrochemical reduction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] in the absence of any trapping agents is in striking contrast to the chemistry of the triphenylphosphine system where simple disproportionation is observed. This result prompted us to determine (i) if [Pt(PEt$_3$)$_2$] is initially generated in this system and (ii) the source of hydridic hydrogen in the product. The involvement of electrochemically generated [Pt(PEt$_3$)$_2$] equivalents in the reaction was readily confirmed by a series of trapping reactions, detailed below. The source of hydridic hydrogen proved to be more elusive. Since [Pt(PR$_3$)$_2$] equivalents are implicated in systems for the activation of water via H–OH oxidative addition,[1,15] it was of concern to establish whether or not adventitious water in our solvent system was involved in hydride formation. Two experiments indicate that adventitious water is not responsible for product formation. Thus, when the electrochemical reduction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] is repeated *without* activated alumina suspended in the solvent, the yield of hydride is decreased and not increased.[38] Similarly, when the reduction is performed in the absence of activated alumina and with small aliquots of water deliberately added, the yield of *trans*-[PtH(Cl)(PEt$_3$)$_2$] decreases and other reaction chemistry involving activation of water is observed.[38] Thus, we postulated that C–H bond cleavage of a component of the solvent/electrolyte system must be responsible for hydride formation. However, substitution of the benzene component of the solvent system by benzene-d_6 (99%) led to formation of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with no formation of *trans*-[PtD(Cl)(PEt$_3$)$_2$] detectable spectroscopically. Aromatic C–H bond cleavage was thus excluded as the source of hydridic hydrogen. If this lack of reactivity with aromatic C–H bonds is general, then it seemed that replacement of the acetonitrile component of the solvent system by benzonitrile, which lacks the moderately acidic α-protons,[39] might shed light on the reaction pathway. We found that using an acetonitrile/benzene (5/2, v/v) solvent system, 0.1 M in TBAP, containing 5–10 equiv of benzonitrile yields *trans*-[PtH(Cl)(PEt$_3$)$_2$] exclusively. However, using a solvent mixture of acetonitrile (35 mL), benzonitrile (20 mL), and benzene (20 mL) produces *trans*-[PtCN(Ph)(PEt$_3$)$_2$][40] as the major platinum-containing product (68% spectroscopic yield) and only a trace of *trans*-[PtH(Cl)(PEt$_3$)$_2$] is detected. When the acetonitrile component of the solvent is totally replaced by benzonitrile, *trans*-[PtCN(Ph)(PEt$_3$)$_2$][40] is the major product (61% spectroscopic yield) and no detectable hydride is formed. These results are significant since they show not only that [Pt(PEt$_3$)$_2$] reacts via oxidative addition with the C–CN bond of benzonitrile under ambient conditions[40] but also that this substrate must be present in large excess to prevent hydride formation. Although these experiments point toward acetonitrile as the source of hydridic hydrogen, it seemed to us that such a conclusion might be erroneous since we have no relative rate data for the potentially competing processes of hydride formation and C–CN oxidative addition. Accordingly, we sought to examine the background electrolyte, TBAP, as the remaining possible source of hydridic hydrogen. We found that under the specific conditions employed in these experiments, electrochemically generated [Pt(PEt$_3$)$_2$] reacts selectively as a strong base with the tetra-n-butylammonium cation via a Hofmann elimination reaction[41] (Scheme II). Formation of tri-n-butylamine in the reaction was confirmed by gas chromatography, and furthermore, comparison with standard samples of NBu$_3$ allowed us to quantitate the reaction and show that 1 equiv of NBu$_3$ is formed for each equivalent of *cis*-[PtCl$_2$(PEt$_3$)$_2$] consumed. Since the reduction is performed under a continuous argon purge, we have yet to find experimental conditions which permit detection of 1-butene. In qualitative terms the reaction of [Pt(PEt$_3$)$_2$] with NBu$_4$$^+$, involving C–H and C–N bond cleavage, must be quite rapid since by the end of the electrolysis the air-stable complex *cis*-[PtH(Cl)(PEt$_3$)$_2$] has already been largely formed (vide infra).

Scheme II



In order to obtain some qualitative ideas on the rate of hydride formation, we performed experiments where trapping agents were added to the solution after the reduction was essentially complete (i.e. when the slope of the current vs time curve approaches zero) and estimated the relative yield of trapped product by $^{31}P\{^1H\}$ NMR spectroscopy. Using PhC≡CPh as a trapping agent produced [Pt(PhC≡CPh)(PEt$_3$)$_2$] in 18–22% (2 experiments) yield,[42] while using methyl iodide as a trapping agent produced *trans*-[PtCl(Me)(PEt$_3$)$_2$] in 16% yield,[43] indicating that ca. 80–85% of the [Pt(PEt$_3$)$_2$] equivalents have already been consumed by the time the reduction is terminated and the trapping agent is added. Despite the reactivity of [Pt(PEt$_3$)$_2$] with the background electrolyte, it still proved possible to design synthetically useful trapping experiments. Thus, reactions with benzonitrile as a substrate for oxidative addition (vide supra) were possible provided

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[38] Scavenging of adventitious water by activated alumina has significant effects on electroanalytical measurements on platinum(II) phosphine complexes; see ref 25 and 26. In the absence of activated alumina and the presence of added water, electrochemical reduction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] leads to water activation and formation of acetamide (identified by ^{13}C NMR) by hydrolysis of acetonitrile. Trogler has investigated closely related systems employing nonelectrochemical methods and so further investigations were not pursued. See: Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.

[39] For acetonitrile, pK_a = 25, see: Streitwieser, J. A.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; MacMillan, New York, 1985.

[40] Note that [Pt(PEt$_3$)$_3$] reacts with PhCN by C–CN oxidative addition at refluxing toluene temperatures, see: Muetterties, E. L.; Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *94*, 3543.

[41] In organic electrochemistry there is good evidence for proton abstraction from tetra-n-alkylammonium cations by electrochemically generated organic bases. For general discussion see: Baizer, M. M.; Lund, H. *Organic Electrochemistry*, 2nd. ed.; Marcel Dekker, New York, 1983, p 244.

[42] $^{31}P\{^1H\}$ NMR: δ = 11.8 ppm [^1J(Pt,P) = 3299 Hz]. Data for this compound appear previously unreported but are in agreement with those of the well-known PPh$_3$ analogue (see Scheme I).

[43] In situ generation of MeCl followed by oxidative addition or oxidative addition of MeI followed by metathesis produces this compound. $^{31}P\{^1H\}$ NMR: δ = 15.9 ppm, [^1J(Pt,P)] = 2816 Hz]. See ref 9 for literature data.

the benzonitrile was present in large excess during the electrochemical generation of $[Pt(PEt_3)_2]$. Accordingly it seemed likely that other substrates could be employed provided that they were electroinactive in the potential range of interest[44] and had suitable physical properties for inclusion in the solvent/electrolyte system. In addition to benzonitrile, other substituted aromatics such as chlorobenzene and fluorobenzene meet these criteria.

Thus, electrochemical reduction of *cis*-$[PtCl_2(PEt_3)_2]$ in a chlorobenzene/acetonitrile (1/1, v/v) solvent system, 0.1 M in TBAP, produced a clear, colorless solution with no evidence of deposition of platinum metal. The electrolysis was terminated at a point where the slope of the current vs time curve was indistinguishable from zero, corresponding to negligible current flow, representing consumption of 1.88 electrons. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of *trans*-$[PtPh(Cl)(PEt_3)_2]$[45] (92% by peak height) and traces of *trans*-$[PtH(Cl)(PEt_3)_2]$ (4%) and *trans*-$[PtH(CH_2CN)(PEt_3)_2]$[46] (2%, vide infra). This experiment shows efficient trapping of $[Pt(PEt_3)_2]$ by chlorobenzene and contrasts with attempted trapping reactions of $[Pt(PPh_3)_2]$ using chlorobenzene, where no C–Cl oxidative addition was observed.

Use of fluorobenzene as a cosolvent for the electrochemical reduction of *cis*-$[PtCl_2(PEt_3)_2]$ produced no fluoride-containing products. In these experiments, $^{31}P\{^1H\}$ NMR spectroscopy indicated a complex mixture of products, including *trans*-$[PtH(Cl)(PEt_3)_2]$ (18.6% spectroscopic yield), *trans*-$[PtH(CH_2CN)(PEt_3)_2]$[46] (20.6%), *trans*-$[PtCH_3(CN)(PEt_3)_2]$[46] (13.2%), and other products, none of which exhibited $^{31}P-^{19}F$ coupling in the $^{31}P\{^1H\}$ NMR spectrum.[47]

In reactions employing chlorobenzene or fluorobenzene as a cosolvent we observed formation of a pair of structural isomers, *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ and/or *trans*-$[PtCH_3(CN)(PEt_3)_2]$. The identity of both products was confirmed by independent synthesis and comparison of spectroscopic properties ($^{31}P\{^1H\}$ NMR, ^1H NMR, IR) with the authentic samples. Formation of these two products is interesting since *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ is the *formal* product of C–H oxidative addition of acetonitrile to $[Pt(PEt_3)_2]$ whereas *trans*-$[PtCH_3(CN)(PEt_3)_2]$ is the *formal* product of C–C oxidative addition of acetonitrile to $[Pt(PEt_3)_2]$. Further examination (vide infra) showed that these products in fact arise from a novel, circuitous pathway.

As a first step in investigating the formation of these compounds we sought to discover if the presence of chlorobenzene or fluorobenzene was a prerequisite for their formation. It is not. Thus, electrolysis of *cis*-$[PtCl_2(PEt_3)_2]$ in an acetonitrile/benzene (5/2, v/v) solvent system, 0.1 M in TBAP, produces *trans*-$[PtH(Cl)(PEt_3)_2]$ almost exclusively[48] when the electrolysis is terminated as soon as discoloration of the solution becomes apparent, corresponding to uptake of 1.88 electrons (vide supra). However, in cases where the electrolysis is allowed to continue past this point and the electrolyzed solution is then allowed to stand in the air for several days, we observed reproducible formation of significant amounts of *trans*-$[PtCH_3(CN)(PEt_3)_2]$. Initially[24] we allowed ourselves to be misled into postulating that oxygen might be involved in initiating a radical reaction[49] leading to *trans*-$[PtCH_3(CN)(PEt_3)_2]$. This postulate must be incorrect, since we have now found that electrolysis past the point where a maximum yield of *trans*-$[PtH(Cl)(PEt_3)_2]$ is obtained leads to formation of *trans*-$[PtH(Cl)(PEt_3)_2]$, *trans*-$[PtH(CH_2CN)(PEt_3)_2]$, and *trans*-$[PtCH_3(CN)(PEt_3)_2]$ without exposure to oxygen. On standing for several days, under an inert atmosphere, *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ vanishes (vide infra) and hence was not observed in the earlier experiments.

In a series of experiments where *cis*-$[PtCl_2(PEt_3)_2]$ was reduced at −2.1 V vs Ag/AgCl in an acetonitrile/benzene (5/2, v/v) solvent system and the electrolyses were allowed to continue past the point where the slope of the current vs time curve was indistinguishable from zero but where current flow was still significant, we repeatedly found formation of *trans*-$[PtH(Cl)(PEt_3)_2]$, *trans*-$[PtCH_3(CN)(PEt_3)_2]$, and *trans*-$[PtH(CH_2CN)(PEt_3)_2]$. The ratio of these products varied from experiment to experiment and seemed to depend on the time required for the electrolysis and the time between the electrolysis and collection of spectroscopic data. Over the course of 14 separate experiments we were unable to establish a direct relationship between these variables. From the earlier experiments with *cis*-$[PtCl_2(PEt_3)_2]$, it seemed clear that initial electrochemical reduction leads to the formation of $[Pt(PEt_3)_2]$ equivalents which react via a Hofmann elimination with the NBu_4^+ cation to produce *trans*-$[PtH(Cl)(PEt_3)_2]$. However, more exhaustive electrolyses lead to new products containing the elements of acetonitrile. Accordingly, it seemed likely to us that these new products could not be directly attributed to reactivity involving $[Pt(PEt_3)_2]$ but might instead have their origins in further electrochemistry of the Hofmann elimination product, *trans*-$[PtH(Cl)(PEt_3)_2]$. Thus, this compound was synthesized by a literature method[50] and its electrochemistry investigated.

Electrochemical Reduction of *trans*-$[PtH(Cl)(PEt_3)_2]$. Cyclic voltammograms of *trans*-$[PtH(Cl)(PEt_3)_2]$ in acetonitrile/benzene (5/2, v/v) containing TBAP (10^{-1} M) measured over the potential range −0.50 to −2.40 V vs Ag/AgCl showed no well-defined cathodic peaks on platinum or mercury amalgam electrodes. Using a platinum electrode allowed detection of a cathodic peak as a shoulder on the rising solvent cutoff at ca −2.3 V.

Thus, electrolysis at −2.1 V vs Ag/AgCl, the potential used in the reduction of *cis*-$[PtCl_2(PEt_3)_2]$, corresponds not to the peak potential for reduction of *trans*-$[PtH(Cl)(PEt_3)_2]$ but rather to the tail region of the peak where some current flow may be anticipated in the bulk electrolysis. This interpretation is consistent with the observation that the slope of the current vs time curve obtained for the reduction of *cis*-$[PtCl_2(PEt_3)_2]$ approaches zero, corresponding to uptake of two electrons, but shows a continual small but significant current flow as the generated *trans*-$[PtH(Cl)(PEt_3)_2]$ is reduced.

When *trans*-$[PtH(Cl)PEt_3)_2$ was electrochemically reduced at −2.1 V vs Ag/AgCl in CH_3CN/C_6H_6 (5/2, v/v), there was visual evidence of decomposition to platinum metal. The electrolysis was terminated at a point where the slope of the current vs time curve was indistinguishable from zero, corresponding to consumption of 1.89 electrons, with a small residual current flow. Concentration of the

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(44) Since a potential of −2.05 V vs Ag/AgCl is required to reduce *cis*-$[PtCl_2(PEt_3)_2]$, the range of trapping agents is quite limited.

(45) $^{31}P\{^1H\}$ NMR: δ = 14.3 ppm [$^1J(Pt,P)$ = 2794 Hz], See ref 9 for literature data.

(46) Identified by comparison with an authentic sample (see text for description of synthesis and Experimental Section for details).

(47) No components exhibiting $^2J(^{31}P,^{19}F)$ coupling could be identified from the spectrum of the complex product mixture.

(48) Deviations from 100% spectroscopic yield caused only by trace amounts of starting material and/or triethylphosphine oxide.

(49) For Pt(II) → Pt(IV) oxidative addition, radical-initiated mechanisms have been confirmed, see: Fergusson, G.; Monaghan, P. K.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1669.

(50) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.

solution and examination by $^{31}P\{^1H\}$ NMR spectroscopy showed the presence of both *trans*-$[PtH(Cl)(PEt_3)_2]$ (36%) and *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ (38%), and, after standing sealed in vacuo for several weeks, *trans*-$[PtCH_3(CN)(PEt_3)_2]$ was also detected.[51]

The presence of significant amounts of *trans*-$[PtH(Cl)PEt_3)_2]$ in the product mixture, despite initial consumption of approximately two electrons, led us to postulate intermediate formation of $[Pt(PEt_3)_2]$ from the reduction of *trans*-$[PtH(Cl)(PEt_3)_2]$ since this intermediate can react with NBu_4^+ to re-form the hydride complex. The series of reactions shown in Scheme III accounts for the experimental observations. Thus, reduction of *trans*-$[PtH(Cl)(PEt_3)_2]$ occurs by a two-electron process, leading to generation of $[Pt(PEt_3)_2]$ via hydride extrusion and forming chloride ion. The hydride ion is transferred to the solvent, leading to formation of the cyanomethyl ion. The anion then attacks *trans*-$[PtH(Cl)(PEt_3)_2]$, which is re-formed via reaction of $[Pt(PEt_3)_2]$ with NBu_4^+, generating *trans*-$[PtH(CH_2CN)(PEt_3)_2]$. Formation of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ via reaction of *trans*-$[PtHCl(PEt_3)_2]$ with the cyanomethyl anion in this manner closely parallels the routine chemical synthesis of such compounds.[52] In the present case, the cyanomethyl anion is formed through attack of the electrochemically activated platinum hydride on acetonitrile rather than by reaction of an alkali-metal hydride with acetonitrile.

Scheme III

$$\textit{trans}\text{-}[PtH(Cl)(PEt_3)_2] + CH_3CN + 2e^- \rightarrow [Pt(PEt_3)_2] + Cl^- + {}^-CH_2CN + H_2$$

$$[Pt(PEt_3)_2] + NBu_4^+ + Cl^- \rightarrow \textit{trans}\text{-}[PtH(Cl)(PEt_3)_2] + NBu_3 + CH_3CH_2CH{=}CH_2$$

$$\textit{trans}\text{-}[PtH(Cl)(PEt_3)_2] + {}^-CH_2CN \rightarrow \textit{trans}\text{-}[PtH(CH_2CN)(PEt_3)_2]$$

The chemistry described in Scheme III thus accounts for our observation of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ as a product in electrochemical reductions of both *cis*-$[PtCl_2(PEt_3)_2]$ and *trans*-$[PtH(Cl)(PEt_3)_2]$ but does not address the origin of *trans*-$[PtCH_3(CN)(PEt_3)_2]$, observed in both systems.

Attempts to synthesize *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ from *trans*-$[PtH(Cl)(PEt_3)_2]$ and NaH/CH_3CN shed some light on the origin of *trans*-$[PtCH_3(CN)(PEt_3)_2]$ in the electrochemical experiments. Thus, although we were able to effectively synthesize *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ by adding 1 equiv of an oil dispersion of NaH to a CH_3CN solution of *trans*-$[PtH(Cl)(PEt_3)_2]$, we found that using 1 equiv of powdered, dry NaH led to a mixture of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$, *trans*-$[PtCH_3(CN)(PEt_3)_2]$, and unreacted *trans*-$[PtH(Cl)(PEt_3)_2]$. Accordingly it seemed probable that local excesses of the strongly basic hydride ion might lead to base-promoted reductive elimination from either *trans*-$[PtH(Cl)(PEt_3)_2]$ or *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ to produce $[Pt(PEt_3)_2]$ equivalents which oxidatively add the C–CN bond of acetonitrile.[53] To verify this postulate, we generated *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ by using the oil dispersion of NaH. Part of the solution was reduced in volume, filtered to remove NaCl, and sealed in an NMR tube. Spectrosopic examination of the solution at regular intervals over a period of several weeks showed only the expected *trans*-$[PtH(CH_2CN)(PEt_3)_2]$. The remaining solution was allowed to stir, without removing the NaCl, for 1 week. At the end of this period, spectroscopic examination showed 100% formation of *trans*-$[PtCH_3(CN)(PEt_3)_2]$. Accordingly, it seems that even a weak base, such as chloride ion, may promote a slow reductive elimination from *trans*-$[PtH(CH_2CN)(PEt_3)_2]$, producing $[Pt(PEt_3)_2]$ equivalents capable of oxidative addition of the C–CN bond of acetonitrile. Thus, in our electrochemical reduction of *cis*-$[PtCl_2(PEt_3)_2]$ we produce $[Pt(PEt_3)_2]$ equivalents which react rapidly with the 0.1 M TBAP, in preference to oxidatively adding the C–CN bond of acetonitrile, generating *trans*-$[PtH(Cl)(PEt_3)_2]$. Termination of the electrolysis at this point allows isolation of *trans*-$[PtH(Cl)(PEt_3)_2]$ while more exhaustive electrolyses lead to further reduction, generating additional $[Pt(PEt_3)_2]$ equivalents and cyanomethyl anions via attack on the solvent by the intermediate activated hydride. Regeneration of *trans*-$[PtH(Cl)(PEt_3)_2$ from $[Pt(PEt_3)_2]$ followed by attack of the cyanomethyl anion leads to formation of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$. Base-promoted reductive elimination by NBu_3, Cl^-, etc. then leads to slow formation of $[PtCH_3(CN)(PEt_3)_2]$ via C–CN oxidative addition of acetonitrile.[54] This last step is particularly important in cases where the background electrolyte has been removed since competitive hydride formation is effectively eliminated.

Conclusions

Electrochemical reduction of *cis*-$[PtCl_2L_2]$ (L = PPh_3, PEt_3) generates reactive $[PtL_2]$ equivalents in solution. Where L = PPh_3, the reactive fragment may be trapped with coordinating and oxidative addition addenda, but in the absence of trapping agents, simple disproportionation occurs. Where L = PEt_3, the reactive intermediate attacks the NBu_4^+ cation present in the electrolyte to produce *trans*-$[PtH(Cl)(PEt_3)_2]$ via a Hofmann elimination reaction. The hydride is itself reduced on prolonged electrolysis generating the cyanomethyl complex *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ via attack of the electrochemically activated hydride on the acetonitrile solvent. The hydrido cyanomethyl complex is sensitive toward reductive elimination of CH_3CN which, in the absence of competing processes, undergoes CH_3CN oxidative addition to the generated Pt(0) fragment. Trapping studies with coordinating and oxidative addition addenda implicate $[PtL_2]$

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(51) Similar results are obtained for solutions after exhaustive electrolysis of *cis*-$[PtCl_2(PEt_3)_2]$; i.e., standing for extended periods at room temperature or heating for shorter periods leads to conversion of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ into *trans*-$[PtCH_3(CN)(PEt_3)_2]$.

(52) For closely related syntheses and compounds see: Beck, W.; Schropp, K.; Oetker, C.; Schlodder, R.; Smedal, H. S. *Chem. Ber.* **1973**, *106*, 2144. Ros, R.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1976**, *118*, C53. Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1977**, *139*, 355. Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978**, *161*, 75.

(53) Hydrido alkyl complexes of platinum(II) are typically prone to reductive elimination. Inclusion of the cyanide group in the alkyl chain appears to lead to partial stabilization (see work of Ros et al. in ref 52, but even hydrido cyanoalkyl complexes reductively eliminate nitrile under the influence of nucleophiles/bases; e.g., *trans*-$[PtH(CH_2CH_2CH_2CN)(PPh_3)_2]$ reacts with $PPhMe_2$ to produce $[Pt(PPh_3)(PPhMe_2)_3]$, see: Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978**, *161*, 75. After prolonged exposure to air, we find that *trans*-$[PtH(Cl)(PEt_3)_2]$, in the presence of NBu_3, slowly forms $[Pt(CO_3)(PEt_3)_2]$, evidence for base-promoted reductive elimination of HCl: Davies, J. A.; Eagle, C. T., unreported results. Similarly, repeated recrystallization in air of *trans*-$[PtH(CH_2CN)(PEt_3)_2]$, formed from *trans*-$[PtH(Cl)(PEt_3)_2]$ in CH_3CN using an oil dispersion of NaH, ultimately led to formation of $[Pt(CO_3)(PEt_3)_2]$, see: Davies, J. A.; Eagle, C. T.; Pinkerton, A. A.; Syed, R. *Acta Crystallogr.* **1987**, *C43*, 1547.

(54) Thus, *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ has its origins in the acid/base chemistry of $[Pt(PEt_3)_2]$ whereas its structural isomer, *trans*-$[PtCH_3(CN)(PEt_3)_2]$, is formed by C–CN oxidative addition. Presumably formation of the strong Pt–CN bond is the thermodynamic driving force in this equilibration process.

fragments in the electrochemical reduction of *cis*-[$PtCl_2(PEt_3)_2$].

Experimental Section

General Procedures. Acetonitrile (Fischer, HPLC grade) was stirred with CaH_2 for 48 h, decanted, and distilled from P_4O_{10}. The fraction boiling in the range 79–82 °C was refluxed with CaH_2 for 8 h and then fractionally distilled. The fraction boiling in the range 80–82 °C was stored under nitrogen over Al_2O_3, activated at 110 °C for 24 h.[55] Benzene (Baker) was freshly distilled from sodium wire under nitrogen prior to use. Benzene-d_6 was stored over molecular sieves and deoxygenated prior to use. Benzonitrile (Aldrich) was passed through a 230–400 mesh Kieselgel column under a positive pressure of nitrogen, stirred over CaH_2 for 4 h, filtered, and fractionally distilled, first alone and then from P_4O_{10}. The fraction boiling in the range 190–192 °C was stored over activated Al_2O_3 under nitrogen.[56] Chlorobenzene (Matheson) and fluorobenzene (Aldrich) were each fractionally distilled from magnesium sulfate and stored under nitrogen over activated Al_2O_3. Benzoyl chloride (Eastman) was stored over magnesium sulfate and deoxygenated prior to use. Methyl iodide (Alfa) was freshly distilled from magnesium sulfate under nitrogen prior to use. Hydrogen chloride (Matheson) was used as supplied. Tetra-*n*-butylammonium perchlorate (TBAP, G.F.S.) was recrystallized five times from absolute ethanol and dried in vacuo at room temperature prior to use. Dimethyl acetylenedicarboxylate (Aldrich) was stored over magnesium sulfate and deoxygenated prior to use. Diphenylacetylene (Aldrich) was used as supplied. Tetraethylammonium chloride (Aldrich) was used as supplied. [$PtO_2(PPh_3)_2$] was purchased from Strem. *cis*-[$PtCl_2(PPh_3)_2$],[57] *cis*-[$PtCl_2(PEt_3)_2$],[57] and *trans*-[$PtH(Cl)(PEt_3)_2$][58] were prepared by literature methods.

IR spectra were obtained as Nujol mulls between KBr plates over the range 4000–400 cm^{-1} by using a Nicolet 60-SX FTIR spectrometer. ^1H (89.56 MHz), $^{13}C\{^1H\}$ (22.5 MHz), and ^{31}P and $^{31}P\{^1H\}$ (36.2 MHz) NMR spectra were measured on a JEOL FX90Q spectrometer or at the appropriate frequencies on a Varian VXR-400 spectrometer operating in the Fourier transform mode. For ^1H and $^{13}C\{^1H\}$ NMR spectra, chemical shifts are cited relative to tetramethylsilane, using the residual protons of the deuterated solvent as a secondary reference. ^{31}P and $^{31}P\{^1H\}$ NMR chemical shifts were measured by using an 85% H_3PO_4 external standard. More positive values of the chemical shift represent deshielding. Elemental analyses were performed by MicAnal, Arizona (now Desert Analytics).

Cyclic voltammograms were obtained by using either a Model CV-1A Bioanalytical Systems control unit or a Bioanalytical Systems 100 control unit. Typically, 10^{-3} M solutions of the complexes in CH_3CN/C_6H_6 (7/3, v/v) which was 10^{-1} M in TBAP were employed. A single compartment cell, thermostated to 25 ± 1 °C, equipped with a Ag/AgCl reference electrode (−35 mV vs SCE), a platinum spiral wire auxiliary electrode, and a platinum or mercury/gold analgam working electrode was used. Full details of cyclic voltammetry measurements are given elsewhere.[25] Controlled potential bulk reductive electrolyses were performed by using a Bioanalytical Systems SP-2 synthetic potentiostat. A three-compartment cell was employed that was constructed in-house. The working electrode compartment contained the Ag/AgCl reference electrode and 28 mL of Hg, connected to the potentiostat by a platinum wire. The auxiliary electrode compartment contained a platinum spiral wire electrode. The two compartments were separated by two medium-porosity frits. The cell is equipped with a number of fitted openings to allow inert-atmosphere operation and manipulation of solutions.

Controlled Potential Bulk Reductive Electrolysis of *cis*-[$PtCl_2(PPh_3)_2$]. Twenty-four hours prior to an experiment, the controlled potential electrolysis cell was charged with alumina (3.0 g) and dried at 110 °C. From this point on, all manipulations of the cell were done under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, 28 mL of mercury and a small magnetic stirrer bar were added to the cell which had been cooled under argon. A 0.1 M solution of TBAP (70 mL) in acetonitrile/benzene (5/2, v/v) was introduced to the cell under a nitrogen stream. This was allowed to outgas for 1 h. The solution was then stirred and preelectrolyzed to zero current at −1.60 V.

The preelectrolyzed solution was then transferred under argon into a Schlenk tube containing ca. 70 mg of *cis*-[$PtCl_2(PPh_3)_2$]. After the complex had dissolved, the solution was transferred back into the cell, purged for 1 h, and electrolyzed to essentially zero current at −1.60 V. This typically took 2–3 h. Coulometry indicated a two-electron reduction with integrations typically in the range of 1.9–2.1 electrons.

Experiments with Electrochemically Generated [$Pt(PPh_3)_2$] Equivalents. Disproportionation Reaction. One hour after the electrolysis the electrolyzed solution was transferred under argon into a degassed Schlenk tube. The solvent was then evaporated in vacuo. The solid mass was extracted with 3 × 10 mL portions of benzene and filtered into a second degassed Schlenk tube. The solution was concentrated to ca. 5 mL and transferred under nitrogen to an NMR tube and sealed for spectroscopic studies. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of [$Pt(PPh_3)_3$] (δ = 49.1 ppm [$^1J(Pt,P)$ = 4460 Hz]) and small amounts of $O{=}PPh_3$ (δ = 24.1 ppm), presumably formed by oxidation with adventitious air or with perchlorate ion present in the electrolyte.

Reaction with HCl Gas. HCl was bubbled through the cell after the electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ and ^1H NMR spectroscopies showed formation of *trans*-[$PtH(Cl)(PPh_3)_2$]: $\delta(P)$ = 28.9 ppm [$^1J(Pt,P)$ = 3008 Hz], $\delta(H)$ = −16.8 ppm [$^2J(P,H)$ = 14.6 Hz, $^1J(Pt,H)$ = 1195 Hz] (50% as determined by peak heights). *cis*- and *trans*-[$PtCl_2(PPh_3)_2$] were also detected. Separation attempts were not successful.

Reactions with MeI. (a) MeI (1.08 equiv) was injected into the cell after electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of *trans*-[$PtMe(Cl)(PPh_3)_2$] (δ = 28.5 ppm [$^1J(Pt,P)$ = 3148 Hz] (54% as determined by peak heights)) and trace amounts of $O{=}PPh_3$.

(b) MeI (10.0 equiv) was injected into the cell after electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of *trans*-[$PtMe(I)(PPh_3)_2$] (δ = 26.78 ppm [$^1J(Pt,P)$ = 3064 Hz] (50–52% as determined by peak heights)) and trace amounts of $O{=}PPh_3$.

Reaction with PhCOCl. PhCOCl (1.14 equiv) was injected into the cell after electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of *trans*-[$PtCOPh(Cl)(PPh_3)_2$] (δ = 19.2 ppm [$^1J(Pt,P)$ = 3412 Hz] (67% as determined by peak heights)) and trace amounts of $O{=}PPh_3$. An analogous reaction with PhCl showed no formation of *trans*-[$PtPh(Cl)(PPh_3)_2$].

Reaction with MeOOCC≡CCOOMe. MeOOCC≡CCOOMe (1.07 equiv) was injected into the cell after electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of [$Pt(MeOOCC{\equiv}CCOOMe)(PPh_3)_2$] ($\delta$ = 18.3 ppm [$^1J(Pt,P)$ = 3721 Hz] (88% as determined by peak heights)) and trace amounts of $O{=}PPh_3$. The complex was isolated by passing the benzene solution through a small activated alumina plug, followed by reduction to dryness: yield 78%; ^1H NMR δ(aromatic) = 6.90–7.90 (mult), $\delta(CH_3)$ = 3.23 (s); ^{13}C NMR δ(aromatic) = 129.5, 131.5, 132.4, 134.2, 134.3, 134.4, 134.45, 135.6, 136.1, δ(CO) = 165.2, $\delta(CH_3)$ = 58.5, δ(acetylene) not observed; IR 2964 (s), 2938 (m), 2876 (m), 1727 (w), 1699 (m), 1685 (m), 1476 (m), 1435 (m), 1310 (w), 1232 (m), 1207 (m), 1179 (m), 1157 (m), 998 (w), 883 (w), 742 (m), 694 (m), 622 (s), 542 (m), 521 (m), 512 (m). Anal. Calcd: C, 58.54; H, 4.21. Found: C, 58.06; H, 5.81. Despite good agreement in carbon analyses, hydrogen analyses were repeatedly variable.

Reaction with PhC≡CPh. PhC≡CPh (1.14 equiv) in 10 mL of acetonitrile was added to the cell under a nitrogen stream after

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electrolysis was complete. After 20 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of [Pt(PhC≡CPh)$(PPh_3)_2$] (δ = 27.4 ppm [^1J(Pt,P) = 3454 Hz (91% as determined by peak heights)) and trace amounts of O=PPh_3. The complex was isolated by passing the benzene solution through a small activated alumina plug, followed by reduction to dryness: yield 77%; ^{1}H NMR δ(aromatic) = 6.90–8.50 (mult); ^{13}C NMR δ(aromatic) = 125.5, 127.4, 134.45, 134.5, 134.6, 134.65; IR 2942 (s), 2937 (s), 2877 (s), 2013 (w), 1475 (s), 1384 (m), 883 (m), 756 (m), 755 (m), 691 (s), 622 (s), 510 (m). Anal. Calcd: C, 66.9; H, 4.5. Found: C, 67.7; H, 5.0.

Reaction with Oxygen. Oxygen was bubbled through the electrolyzed solution for 30 min. The sample was then worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of *cis*-[$PtO_2(PPh_3)_2$] (δ = 16.4 ppm [^1J(Pt,P) = 4059 Hz]), [$Pt(PPh_3)_3$] (δ = 49.1 ppm [^1J(Pt,P) = 4460 Hz]), and $OPPh_3$ (δ = 24.1 ppm).

Reactions with Air. (a) The electrolyzed solution was exposed to air and then worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of [$PtCO_3(PPh_3)_2$] (δ = 6.34 ppm [^1J(Pt,P) = 3697 Hz] and O=PPh_3.

(b) The electrolyzed solution was exposed to air immediately after electrolysis and allowed to stand for 1 week. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of [$PtCO_3(PPh_3)_2$] and O=PPh_3. There was a detectable amount of a compound tentatively identified as *trans*-[PtPh(Cl)$(PPh_3)_2$] δ = 24.4 ppm [^1J(Pt,P) = 3156 Hz].

Controlled Potential Bulk Reductive Electrolysis of *cis*-[$PtCl_2(PEt_3)_2$]. Twenty-four hours prior to an experiment, the controlled potential electrolysis cell was charged with alumina (3.0 g) and dried at 110 °C. From this point on, all manipulations of the cell were done under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, mercury (28 mL) and a small magnetic stirrer bar were added to the cell which had been cooled under argon. A 0.1 M solution of either TBAP or $NaClO_4$ in CH_3CN/C_6H_6 (70 mL, 5/2, v/v) was introduced to the cell under a nitrogen stream. This was allowed to outgas for 1 h. The solution was then stirred and preelectrolyzed to approximately zero current at a potential of −2.1 V.

The preelectrolyzed solution was then transferred under argon into a Schlenk tube containing *cis*-[$PtCl_2(PEt_3)_2$] (ca. 25 mg). After the complex was dissolved, it was transferred back into the cell, purged for 1 h, and electrolyzed to essentially zero current at a voltage of −2.1 V. This took from 45 min to 15 h. Reductions were typically terminated when precipitated platinum metal became evident. At the point of termination of the electrolysis, coulometry indicated approximately a 2-electron reduction, with integrations in the range of 1.6–2.26 electrons.

The following is a description of a typical experiment leading to essentially quantitative formation of *trans*-[PtH(Cl)$(PEt_3)_2$]. After a preelectrolysis at −2.10 V, *cis*-[$PtCl_2(PEt_3)_2$] (0.0250 g, 4.98×10^{-5} mol) was added to the working electrode compartment and the solution was purged with argon for 1 h. The solution was then electrolyzed to near zero current at −2.10 V. The solution took on a clear beige appearance as small particles of platinum metal precipitated. The reduction was discontinued after 3 h. Coulometry indicated a 1.80-electron reduction. The solution was then filtered under argon into a Schlenk tube and evaporated. Following reduction to dryness, decolorizing charcoal was added and the solid mass was extracted with benzene (10 mL), filtered, and concentrated to a small volume. The solution was then transferred to a short alumina column and chromatographed with benzene/hexane. Slow evaporation of the eluent allowed isolation and collection of the product *trans*-[PtH(Cl)$(PEt_3)_2$] in a 63.3% yield. Spectroscopic data: δ(H) = −16.88 ppm [^2J(P,H) = 14.5 Hz, ^1J(Pt,H) = 1271 Hz]; δ(P) = 23.13 ppm [^1J(Pt,P) = 2723 Hz (in C_6D_6)]; ν(Pt–H) = 2186 cm^{-1} (Nujol). Anal. Calcd: C, 30.8; H, 6.6. Found: C, 31.7; H, 6.9.

Experiments with Electrochemically Generated [Pt$(PEt_3)_2$] Equivalents. Reaction with MeI. *cis*-[$PtCl_2(PEt_3)_2$] was electrochemically reduced as described above. Coulometry indicated a 1.8-electron reduction after 1 h and 45 min when the reduction was stopped and MeI (1.1 equiv) was injected into the cell. After 5 min, the solution was worked up under an inert environment as described above with the exception that the products were not purified by column chromatography. Analysis of the products by $^{31}P\{^1H\}$ NMR specroscopy showed the formation of *trans*-[PtMe(Cl)$(PEt_3)_2$] (16%): δ(P) = 15.86 ppm [^1J(Pt,P) = 2816 Hz].

Reaction with PhC≡CPh. PhC≡CPh (5 equiv) in benzene (10 mL) was added to the cell under a nitrogen stream after coulometry indicated consumption of 1.88 electrons (2 h and 40 min). After 15 min the solution was worked up as described above. $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of [Pt(PhC≡CPh)$(PEt_3)_2$]: δ(P) = 11.79 ppm [^1J(Pt,P) = 3298.97 Hz] (17.7% as determined by peak heights).

Reactions with PhCl. The benzene component of the solvent system described above was substituted with 35 mL of PhCl. The electrolyzed solutions were worked up as described above. The following $^{31}P\{^1H\}$ NMR data were obtained: δ(P) = 14.33 ppm [^1J(Pt,P) = 2794 Hz] (92%, sample analyzed in C_6D_6).

Attempted Reactions with PhF. The benzene and acetonitrile components of the solvent system described above were substituted with various amounts of PhF. The electrolyzed solutions were worked up as described above, with the exception of purification by column chromatography. Analysis of the product mixtures by $^{31}P\{^1H\}$ NMR spectroscopy did not reveal the presence of any phosphine complex containing a Pt–F bond.

Reactions with PhCN. The benzene and acetonitrile components of the solvent system described above were substituted with various amounts of PhCN (see Discussion). Electrolyses were carried out at either −1.6 or −2.1 V. The electrolyzed solutions were worked up as described above. Analysis of the product mixtures by $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of *trans*-[PtPh(CN)$(PEt_3)_2$] in various percentages (see Discussion): δ(P) = 19.71 ppm [^1J(Pt,P) = 2565 Hz]. Isolation attempts led to the formation of impure oils.

Reactions with Water. Electrolyses were performed in the presence of various amounts of water and in the absence of activated alumina. Products of the reduction were typically isolated by solvent evaporation followed by extraction of the resulting solid with water (1.0 mL). The products were analyzed by $^{13}C\{^1H\}$ NMR spectroscopy (3 drops of CD_3OD were added as a reference). Resonances for acetamide were found at δ = 176 and 22 ppm.

Controlled Potential Bulk Reductive Electrolysis of *trans*-[PtH(Cl)$(PEt_3)_2$]. With use of the same experimental conditions as those described for *cis*-[$PtCl_2(PEt_3)_2$], samples of *trans*-[PtH(Cl)$(PEt_3)_2$] were electrolyzed to near zero current at −2.1 V. There was visual evidence of decomposition toward the end of the electrolyses which typically took ca. 4 h, with coulometry indicating consumption of ca. 1.9 electrons. The solution was worked up as described above, and the products were characterized spectroscopically. Product ratios depended upon the time taken for the electrolysis and the time in solution before spectroscopic examination (see Discussion).

Reactions of *trans*-[PtH(Cl)$(PEt_3)_2$] in CH_3CN with NaH. (a) Under an inert environment, a solution of *trans*-[PtH(Cl)$(PEt_3)_2$] (66.2 mg) in CH_3CN (30 mL) was treated with NaH (8 mg, Alfa, 50% oil dispersion). This solution was stirred for 3 h, then filtered, and concentrated. By slow solvent replacement of the CH_3CN by C_6D_6 under nitrogen, $^{31}P\{^1H\}$ NMR and ^{1}H NMR data of a C_6D_6 solution of this complex were obtained: δ(P) = 18.77 ppm [^1J(Pt,P) = 2737 Hz]; δ(H) = −8.74 ppm [^1J(Pt,H) = 808 Hz, ^2J(P,H) = 18 Hz, ^3J(H,H) = 3.22 Hz]. Attempts to isolate the solid product by slow evaporation of a heptane/acetonitrile (1/2, v/v) solution under a gentle stream of nitrogen led to the formation of colorless square plate crystals, shown to be [Pt$(CO_3)(Et_3)_2$] by X-ray crystallography.

(b) Employing powdered, dry NaH under the same experimental conditions led to solutions containing *trans*-[PtH(Cl)$(PEt_3)_2$], *trans*-[PtH$(CH_2CN)(PEt_3)_2$], and *trans*-[$PtCH_3$(CN)$(PEt_3)_2$] (δ(P) = 13.9 ppm [^1J(Pt,P) = 2595 Hz]).

***trans*-[PtPh(CN)$(PEt_3)_2$].** KCN (60 mg) in Me_2CO (10 mL) was added to *trans*-[PtPh(Cl)$(PEt_3)_2$] (10 mg) in $CHCl_3$ (10 mL). There was no apparent color change. After 3 h the solution was evaporated and the resulting solid extracted with benzene. The solution was filtered, concentrated to a small volume, and analyzed by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR data of a C_6H_6 solution of this complex are as follows: δ(P) = 19.7 ppm [^1J(Pt,P) = 2565 Hz].

***trans*-[PtMe(I)(PPh$_3$)$_2$].** Under an inert environment, [Pt(PPh$_3$)$_4$] (20 mg) was dissolved in MeI (1.0 mL) at 25 °C. After 3 h of stirring, the solution was evaporated into a solid, which was extracted with C_6H_6 (0.5 mL) and analyzed by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR data of a C_6H_6 solution of this complex are as follows: $\delta(P) = 26.8$ ppm [$^1J(Pt,P) = 3066$ Hz].

***trans*-[PtMe(Cl)(PPh$_3$)$_2$].** Under an inert environment, *trans*-[PtMe(I)(PPh$_3$)$_2$] (10 mg, dissolved in 1.0 mL of CH_2Cl_2) was treated with a solution of NaCl (14 mg) dissolved in Me_2CO (10 mL). After 4 h of stirring, the solution was evaporated to a solid, which was extracted with C_6H_6 (0.5 mL) and analyzed by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR data of a C_6H_6 solution of this complex are as follows: $\delta(P) = 28.33$ ppm [$^1J(Pt,P) = 3146$ Hz (65%)]. Also present in the spectrum were peaks for residual *trans*-[PtMe(I)(PPh$_3$)$_2$] (31.3%).

Gas Chromatographic Identification of NBu$_3$. The 20-μL samples of 6×10^{-3} M solutions of NBu$_3$ in a 5/2 CH_3CN/C_6H_6 solvent system showed a retention time of 5 min. The solution (6.7 mL) resulting from the electrolysis of a 1.61×10^{-3} M solution of *cis*-[PtCl$_2$(PEt$_3$)$_2$] was concentrated to 1.8 mL (thus, if there was a stoichiometric relationship between the production of NBu$_3$ and *cis*-[PtCl$_2$(PEt$_3$)$_2$], the concentration of NBu$_3$ would be 6×10^{-3} M). This sample (20 μL) showed the same peak at a retention time of 5 min with essentially the same area as the peak for the known sample of known concentration. Experiments were performed by using a Varian 90-P3 chromatograph equipped with a 20% Apiezon L column, with a carrier gas flow rate of 40 mL/min. The column temperature was held at 180 °C.

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Registry No. *cis*[PtCl$_2$(PPh$_3$)$_2$], 15604-36-1; [Pt(PPh$_3$)$_3$], 13517-35-6; HCl, 7647-01-0; *trans*-[PtH(Cl)(PPh$_3$)$_2$], 16841-99-9; *trans*-[PtCl$_2$(PPh$_3$)$_2$], 14056-88-3; MeI, 74-88-4; *trans*-[PtMe(I)(PPh$_3$)$_2$], 28850-19-3; *trans*-[PtMe(Cl)(PPh$_3$)$_2$], 28850-21-7; C_6H_5COCl, 98-88-4; *trans*-[PtCOC$_6$H$_5$(Cl)(PPh$_3$)$_2$], 18421-48-2; [Pt(Ph(≡CPh)(PPh$_3$)$_2$], 15308-61-9; [Pt(MeOCOC≡CCOOMe)(PPh$_3$)$_2$], 22853-55-0; [PtO$_2$(PPh$_3$)$_2$], 15614-67-2; [PtCO$_3$(PPh$_3$)$_2$], 17030-86-3; OPPh$_3$, 791-28-6; *trans*-[PtPh(Cl)(PPh$_3$)$_2$], 18421-49-3; CO$_2$, 124-38-9; *cis*-[PtCl$_2$(PEt$_3$)$_2$], 15692-07-6; $H_3C(CH_2)_3N^+Bu_3$, 10549-76-5; *trans*-[PtH(Cl)(PEt$_3$)$_2$], 16842-17-4; *trans*-[PtMe(Cl)(PEt$_3$)$_2$], 13964-96-0; [Pt(PhC≡CPh)(PEt$_3$)$_2$], 75983-00-5; PhCl, 108-90-7; PhF, 462-06-6; PhCn, 100-47-0; *trans*-[PtPh(CN)(PEt$_3$)$_2$], 33914-65-7; [Pt(CO)$_3$(PEt$_3$)$_2$], 56953-87-8; *trans*-[PtH(CH$_2$CN)(PEt$_3$)$_2$], 118831-46-2; *trans*-[PtCH$_3$(CN)(PEt$_3$)$_2$], 22289-45-8; *trans*-[PtPh(Cl)(PEt$_3$)$_2$], 13938-93-7; [Pt(PPh$_3$)$_4$], 14221-02-4; MeCN, 75-05-8; *trans*-[PtPh(CO)(PPh$_3$)$_2$]Cl, 101519-44-2; PPh$_3$, 603-35-0.

A Theoretical Study of Ketene Forming Reactions Involving Halogen Abstraction by Metal Carbonyl Anions

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Hartree–Fock–Slater calculations have been carried out on the abstraction of bromine from 2-bromoacetyl chloride by $Mn(CO)_5^-$ in the reaction $Mn(CO)_5^- + ClC(O)CH_2Br \rightarrow BrMn(CO)_5 + H_2CC(O)Cl^-$. It was found that this unusual reaction step is favorable with a neglectable activation barrier and a reaction enthalpy of -79 kJ mol^{-1}. The abstraction reaction is primarily driven by the stabilization of a negative charge by the enolate. It is argued that the abstraction process is a key step in ketene forming reactions [Masters, A. P.; Sorensen, T. S.; Ziegler, T. *J. Org. Chem.* **1986**, *51*, 3558] involving metal carbonyl anions and 2-bromo-substituted acyl halides.

I. Introduction

The reaction between either alkyl halides (eq 1a) or acyl halides (eq 1b) and anionic metal carbonyls has been used[1] extensively to synthesize metal–alkyl and metal–acyl complexes.

$$M(CO)_n^- + RX \rightarrow RM(CO)_n + X^- \tag{1a}$$

$$M(CO)_n^- + R{-}C({=}O){-}X \rightarrow R{-}C({=}O){-}M(CO)_n + X^- \tag{1b}$$

The metal center in $M(CO)_n^-$ is electron rich[2] and strongly nucleophilic with basicities comparable to NH$_3$. It is thus not surprising that mechanistic studies carried out on eq 1a have revealed a S_N2 mechanism.[3]

We have recently[4] studied the reaction between $Mn(CO)_5^-$ and ω-bromoacyl halides, and for most cases where the bromine is remote from the acyl group, a simple acylation process occurs.

$$Mn(CO)_5^- + X{-}C({=}O){-}(CH_2)_nCH_2Br \rightarrow Mn(CO)_5{-}C({=}O){-}(CH_2)_nCH_2Br + X^- \tag{1c}$$

Given the numerous precedents, this reaction is entirely predictable. However, when $Mn(CO)_5^-$ reacted with a 2-bromo-substituted acyl halide, e.g. 2-bromoacetyl chloride, the product was not the expected acyl complex (eq 2a) but rather $Mn(CO)_5Br$ and ketene (eq 2b).

Some additional studies of the reaction in eq 2b have led us to suggest that $Mn(CO)_5^-$, and probably also other

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