If one assumed that 2-d_0 and 2-d_3 have the same reactivity toward 1 (k_A and k_B = k), the decreasing rate of 1 in Scheme III is expressed as

$$-\frac{d[1]}{dt} = k[1]([2\text{-}d_0] + [2\text{-}d_3])$$ (6)

Since in the presence of added 2 the side reaction affording 2 and 3,3'-bitolyl in reaction 1 can be ignored, the total concentration of 2-d_0 and 2-d_3 in Scheme III is maintained at the initial concentration of added 2, i.e., $[2\text{-}d_0] + [2\text{-}d_3]$ = $[2]_{ad}$. Thus, eq 6 can be expressed as follows:

$$-\frac{d[1]}{dt} = k[1][2]_{ad}$$ (7)

From eq 7, the concentration of 1 at time t is derived as

$$[1] = [1]_0 \exp(-k[2]_{ad}t)$$ (8)

where $[1]_0$ stands for the initial concentration of 1. On the other hand, in Scheme III the decreasing rate of 2-d_0 can be expressed as

$$-\frac{d[2\text{-}d_0]}{dt} = k[1][2\text{-}d_0]$$ (9)

From eq 8 and 9

$$-\frac{d[2\text{-}d_0]}{dt} = k[1]_0 \exp(-k[2]_{ad}t)[2\text{-}d_0]$$ (10)

From eq 10 the concentration of 2-d_0 at time t is given as follows:

$$[2\text{-}d_0] = [2]_{ad} \exp\left[\frac{[1]_0}{[2]_{ad}}\{\exp(-k[2]_{ad}t) - 1\}\right]$$ (11)

Since the concentration of nondeuterio-m-xylene at time t ([ArCH$_3$]) is given by

$$[ArCH_3] = [2]_{ad} - [2\text{-}d_0]$$ (12)

the following equation is derived from eq 11 and 12:

$$[ArCH_3] = [2]_{ad}\left[1 - \exp\left\{\frac{[1]_0}{[2]_{ad}}(\exp(-k[2]_{ad}t) - 1)\right\}\right]$$ (13)

Thus

$$\lim_{t\to\infty}[ArCH_3] = [2]_{ad}\left\{1 - \exp\left(-\frac{[1]_0}{[2]_{ad}}\right)\right\}$$ (14)

On the other hand

$$\lim_{t\to\infty}[ArCD_3] + \lim_{t\to\infty}[ArCH_3] = [1]_0$$ (15)

where [ArCD$_3$] stands for the concentration of trideuterio-m-xylene at time t. From eq 14 and 15

$$\lim_{t\to\infty}[ArCD_3] = [1]_0 - [2]_{ad}\left\{1 - \exp\left(-\frac{[1]_0}{[2]_{ad}}\right)\right\}$$ (16)

Theoretical values for the ratio of trideuterio- to nondeuterio-m-xylene at the end of the reaction ($\lim_{t\to\infty}$([ArCD$_3$]/[ArCH$_3$])) can be derived from eq 14 and 16.

Communications

Electrochemical Generation and Reactivity of Bis(triethylphosphine)platinum(0): Formation of a Platinum Hydride via a Hoffman Elimination Reaction with the Tetra-n-butylammonium Cation

Julian A. Davies* and Cassandra T. Eagle

Department of Chemistry, University of Toledo
Toledo, Ohio 43606

Summary: Controlled potential bulk reductive electrolysis of *cis*-[PtCl$_2$(PEt$_3$)$_2$] at a mercury pool electrode in acetonitrile/benzene (5/2) solution containing tetra-n-butylammonium perchlorate results in the generation of [Pt(PEt$_3$)$_2$]. This two-coordinate, 14-electron complex acts as a base under specific reaction conditions to abstract a β-H from the tetra-n-butylammonium cation initiating a Hoffman degradation and subsequently forming *trans*-[PtH(Cl)(PEt$_3$)$_2$] after reattack of Cl$^-$. Under different reaction conditions, other basic/nucleophilic chemistry of [Pt(PEt$_3$)$_2$] is observed which includes reactions with weakly activated C–H and/or C–C σ bonds.

We have previously shown[1] that the controlled potential bulk reductive electrolysis of *cis*-[PtCl$_2$(PPh$_3$)$_2$] produces a two-coordinate, 14-electron complex, [Pt(PPh$_3$)$_2$].[2] This complex can be trapped by stoichiometric quantities of acetylenes (RC≡CR; R = Ph, COOMe) and oxidized to Pt(II) by the addition of small molecules such as MeI and PhCOCl. In the absence of trapping agents, disproportionation is observed (eq 1). The [Pt(PPh$_3$)$_2$] complex

$$3[Pt(PPh_3)_2] \rightarrow 2[Pt(PPh_3)_3] + Pt_M$$ (1)
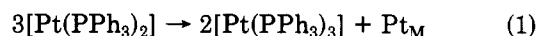
does not undergo any meaningful reaction chemistry with the C–H or C–C bonds present in the components of the solvent system (5/2 acetonitrile/benzene) or with the background electrolyte (tetra-n-butylammonium perchlorate, TBAP) used in the electrolysis.[1]

To increase the reactivity of the 14-electron species,[2] triphenylphosphine was replaced by the more powerful σ donor triethylphosphine. The basicity of triethylphosphine is anticipated to cause the electron density at the metal center to be greater than in the triphenylphosphine ana-

(1) Davies, J. A.; Eagle, C.; Otis, D. E.; Venkataraman, U. *Organometallics* **1986**, *5*, 1264.

(2) It is possible that the Pt(0) species is stabilized through weak coordination of benzene or acetonitrile solvent molecules. This type of solvation would not be excluded for [Pt(PEt$_3$)$_2$]. Trogler has postulated this type of solvation by benzene (see ref 5), and solvation by hard donor solvents has also been postulated for [Pt(PPh$_3$)$_2$]; see: Siedle, A. R.; Newmark, R. A.; Gleason, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 767.
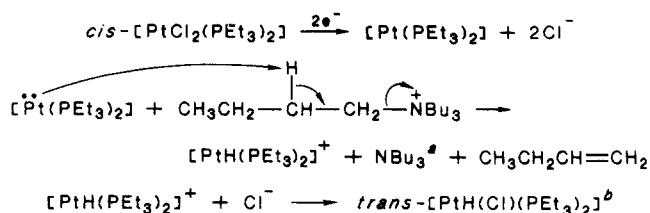
logue[3] and thus lead to enhanced basic/nucleophilic properties. The basic character of some tertiary phosphine complexes of platinum(0) has previously been documented by Otsuka.[4] In 1982, Trogler reported that photolysis of [Pt(PEt₃)₂(C₂O₄)] leads to the formation of [Pt(PEt₃)₂] equivalents which readily undergo oxidative addition reactions with small molecules such as MeCl and PhCl.[5,6] We have electrochemically generated the same reactive species by the two-electron reduction of cis-[PtCl₂(PEt₃)₂]. The two-coordinate complex can be trapped by coordinating and oxidative addenda (vide infra). In the absence of trapping agents, however, we do not observe the simple disproportionation exhibited by the triphenylphosphine analogue (eq 1) but instead find nearly quantitative formation of *trans*-[PtH(Cl)(PEt₃)₂].[7]

The controlled potential bulk reductive electrolysis experiments are typically performed in a three-compartment cell, equipped with a mercury pool working electrode, a platinum spiral wire auxillary electrode, and a Ag/AgCl reference electrode (−35 mV vs. SCE). cis-[PtCl₂(PEt₃)₂] (0.5 mmol) is dissolved in a preelectrolyzed acetonitrile/benzene (5/2) solvent system which is 0.1 M in TBAP. Activated alumina is placed in the cell to scavenge any possible adventicious water.[8] Electrolysis at a potential of −2.10 V vs. Ag/AgCl, under an argon atmosphere, leads to the formation of a yellow solution with some evidence of precipitated platinum metal. It is clear that decomposition is not extensive because a 63.3% isolated yield of the analytically pure product *trans*-[PtH(Cl)(PEt₃)₂] is obtained. Coulometry indicates a two-electron reduction (eq 2).

$$cis\text{-}[PtCl_2(PEt_3)_2] \rightarrow [Pt(PEt_3)_2] + 2Cl^- \quad (2)$$

To obtain a maximum yield of *trans*-[PtH(Cl)(PEt₃)₂], the electrolysis is stopped at the point where decomposition becomes apparent by discoloration of the solution. This gives integrations in the range of 1.70–1.85 electrons. The reaction of [Pt(PEt₃)₂] to form *trans*-[PtH(Cl)(PEt₃)₂] occurs quite rapidly; by the end of the electrolysis, the air-stable complex *trans*-[PtH(Cl)(PEt₃)₂] has been formed and was identified by ³¹P{¹H} NMR, ³¹P NMR, ¹H NMR,

Scheme I

$$cis\text{-}[PtCl_2(PEt_3)_2] \xrightarrow{2e^-} [Pt(PEt_3)_2] + 2Cl^-$$

$$[\ddot{P}t(PEt_3)_2] + CH_3CH_2\text{—}\overset{H}{\underset{|}{C}H}\text{—}CH_2\text{—}\overset{+}{N}Bu_3 \longrightarrow$$

$$[PtH(PEt_3)_2]^+ + NBu_3{}^a + CH_3CH_2CH{=}CH_2$$

$$[PtH(PEt_3)_2]^+ + Cl^- \longrightarrow trans\text{-}[PtH(Cl)(PEt_3)_2]^b$$

a Detected by GC. *b* Identified by ¹H NMR, ³¹P NMR, ³¹P{¹H} NMR, and IR spectroscopies. Verified by elemental analysis (see ref 7).

and IR spectroscopies and by elemental analysis (see ref 7).

Our initial thoughts concerning the formation of the platinum hydride were that it may be due to the presence of adventicious water in the solvent system. Although the solvents, background electrolyte, and the cell were all stringently dried, activated alumina was added to the cell prior to electrolysis to scavenge any adventicious water. This resulted in an increase in the yield of *trans*-[PtH(Cl)(PEt₃)₂] rather than a decrease. Also, when the electrolysis was performed in the presence of small amounts of purposely added water and in the absence of activated alumina, then the amount of *trans*-[PtH(Cl)(PEt₃)₂] obtained was decreased. In fact, in the presence of water, [Pt(PEt₃)₂] exhibits other reaction chemistry (vide infra). We were thus led to postulate that the source of hydridic hydrogen was a component of the solvent system. However, replacement of the benzene component with benzene-d₆ (99%) led to formation of *trans*-[PtH(Cl)(PEt₃)₂], with no detectable amounts of *trans*-[PtD(Cl)(PEt₃)₂]. If this lack of reactivity with aromatic C–H bonds is general, then replacement of the acetonitrile component of the solvent system by benzonitrile (which lacks the moderately acidic α-protons) may shed light on the source of hydridic hydrogen. In an acetonitrile/benzene (5/2) solvent system, 0.1 M in TBAP, containing 5–10 equivalents of benzonitrile, *trans*-[PtH(Cl)(PEt₃)₂] is formed exclusively. When the electrolysis was performed by using 20 mL of benzonitrile, 35 mL of acetonitrile, and 20 mL of benzene as the solvent; however, *trans*-[PtPh(CN)(PEt₃)₂] was formed as the major platinum-containing compound in 68% yield. A trace amount of *trans*-[PtH(Cl)(PEt₃)₂] was also detected. When acetonitrile is totally replaced by benzonitrile, *trans*-[PtPh(CN)(PEt₃)₂] is the major product (61%); no *trans*-[PtH(Cl)(PEt₃)₂] was detected. These experiments are significant since they illustrate not only that [Pt(PEt₃)₂] reacts under ambient conditions with the C–C bond of benzonitrile[9] but also that a large excess of this substrate is necessary to prevent hydride formation. When acetonitrile and benzonitrile are present in a 7/4 ratio, reaction with benzonitrile is dominant, suggesting that, if hydride formation and C–C oxidative addition are at all comparable in rate, the hydride source may not be acetonitrile at all. Accordingly we then turned our attention to the background electrolyte TBAP as the remaining protic source. We found that [Pt(PEt₃)₂] reacts very selectively as a base under the specific reaction conditions employed,[7] undergoing a Hoffman elimination re-

(3) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(4) Otsuka, S.; Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T. *J. Am. Chem. Soc.* 1979, 101, 2027.

(5) Paonessa, R. S.; Trogler, W. C. *Organometallics* 1982, 1, 768.

(6) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* 1985, 4, 647.

(7) Experimental details are as follows. A rigorously dried three-compartment cell equipped with a mercury pool working electrode (28 cm²) and a Ag/AgCl reference electrode, separated from a platinum spiral counterelectrode by two medium porosity frits, is charged with 3.0 g of alumina (previously activated at 110 °C for 24 h), acetonitrile (50 mL, previously dried by stirring over CaH₂ followed by successive distillation from CaH₂, P₄O₁₀, and CaH₂ under nitrogen), benzene (20 mL, previously dried by distillation from sodium under nitrogen), and TBAP (2.3941 g, 7.01 × 10⁻³ mol, recrystallized five times from ethanol and dried in vacuo) and purged with argon for 1 h. The solution is then stirred and preelectrolyzed at −2.10 V to zero current. cis-[PtCl₂(PEt₃)₂] (0.0250 g, 4.98 × 10⁻⁵ mol) is added to the working electrode compartment, and the solution is purged with argon for 1 h. The solution is then electrolyzed to near zero current at −2.10 V. The solution is then filtered under argon into a Schlenk tube and evaporated. Following reduction to dryness, decolorizing charcoal is added and the solid mass is extracted with benzene (10 mL), filtered, and concentrated to a small volume. The solution is then either transferred to an NMR tube under nitrogen and sealed in vacuo for NMR studies or transferred to a short alumina column and chromatographed with benzene/hexane. Slow evaporation of the eluent allows isolation and collection of the product *trans*-[PtH(Cl)-(PEt₃)₂] in a 63.3% yield. Spectroscopic data: δ_H −16.88 (²J_{P-H} = 14.5 Hz, ¹H_{Pt-H} = 1271.2 Hz), δ_P 23.13 (¹J_{Pt-P} = 2723 Hz) (in C₆D₆); ν(Pt–H) = 2186 cm⁻¹ (Nujol). Anal. Calcd: C, 30.8; H, 6.6. Found: C, 31.7; H, 6.9.

(8) Mazzocchin, G.; Bontempelli, G. *J. Electroanal. Chem.* 1984, 179, 269.

(9) The reaction of [Pt(PEt₃)₂] with C₆H₅CN to form *trans*-[PtPh-(CN)(PEt₃)₂] is precedented by the reaction of [Pt(PEt₃)₃] with C₆H₅CN in refluxing toluene to give the same adduct: Muetterties, E. L.; Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P. *J. Am. Chem. Soc.* 1971, 94, 3543. The 14-electron complex [Pt(PEt₃)₂] would be predicted to be more reactive toward oxidative addition than the 16-electron complex [Pt(PEt₃)₃] which explains why the former reacts with C₆H₅CN at room temperature.

action with the tetra-*n*-butylammonium cation, producing nearly quantitative amounts of *trans*-[PtH(Cl)(PEt₃)₂] (Scheme I).

The presence of NBu₃, a product of the Hoffman elimination, was detected by GC analysis of the electrolyzed solution, and comparison of the peak area with that of standard samples showed formation of one equivalent of NBu₃ for each equivalent of *cis*-[PtCl₂(PEt₃)₂] precursor. Since the reduction is performed under a continuous argon purge, detection of but-1-ene was not possible. The reaction of [Pt(PEt₃)₂] with the β-C-H bonds of TBAP must occur quite rapidly since by the end of the electrolysis the air-stable complex *trans*-[PtH(Cl)(PEt₃)₂] has been formed.[7]

When the electrolysis is performed in the presence of small amounts of purposely added water (vide supra) and in the absence of activated alumina, then the amount of *trans*-[PtH(Cl)(PEt₃)₂] obtained is decreased (although this is still the major platinum-containing product) and the reaction pathway is diverted to an alternate route leading to the formation of acetamide. In this case, [Pt(PEt₃)₂] acts as a base promoting the reaction between water and acetonitrile.[10-12] Any possible heterogeneous mechanisms for acetamide formation are ruled out by the fact that the electrolysis takes place in the presence of liquid mercury, a poison for heterogeneous systems.[13]

The preference of [Pt(PEt₃)₂] to act as a base is quite marked. Substrate molecules for trapping or oxidative addition reactions must be added prior to electrolysis since by the end of the electrolysis, most of the [Pt(PEt₃)₂] has already reacted to form *trans*-[PtH(Cl)(PEt₃)₂]. We were able to trap a small amount of the unreacted [Pt(PEt₃)₂] by the addition of 1 equiv of PhC≡CPh immediately after the electrolysis.[14] Although the major product was still *trans*-[PtH(Cl)(PEt₃)₂], 22% of the platinum-containing species, estimated from peak heights in the ³¹P{¹H} NMR spectrum, was a new complex with NMR data (δₚ 11.8 (¹J_{Pt-P} = 3299 Hz)) typical for a compound of the type [Pt(PhC≡CPh)(PEt₃)₂]. Even with 5-10 equiv of oxidative addenda (i.e., PhCN, PhCl) for each equivalent of the *cis*-[PtCl₂(PEt₃)₂] precursor added prior to the electrolysis, the reduced complex still reacts as a base via the Hoffman elimination reaction rather than undergoing oxidative addition. We have found that only when the concentration of oxidative addenda greatly exceeds that of TBAP will [Pt(PEt₃)₂] oxidatively add small molecules (such as those mentioned above). Studies into the exploitation of this chemistry as a new synthetic method are currently in progress. When TBAP is replaced by a nonprotic background electrolyte (i.e., NaClO₄), a small amount of *trans*-[PtH(Cl)(PEt₃)₂] is formed, presumably from the reaction of [Pt(PEt₃)₂] with the mildly acidic C-H bonds of acetonitrile (p*K*ₐ = 25),[15] but decomposition to platinum metal is quite extensive, hindering mechanistic studies.

It may not be surprising that products resulting from acid/base chemistry are more readily observed in electrochemical experiments than in photochemical ones.[5,6] In

the photochemical experiments, a base such as NaOH must be added to observe acid/base chemistry, such as acetonitrile hydration, due to the generation of the Lewis acid CO₂ from the photolysis of [Pt(C₂O₄)(PEt₃)₂].[16]

We have also found that under a different set of reaction conditions, which allow O₂ to enter into the reaction pathway, *trans*-[PtMe(CN)(PEt₃)₂][17] is formed through a reaction with the CH₃CN component of the solvent system. Although benzonitrile readily undergoes C-C oxidative addition (vide supra), we find that O₂ is necessary before we observe C-C oxidative addition of acetonitrile. It is possible that two different mechanistic pathways are involved here which are governed by the amount of O₂ present under the reaction conditions. This type of mechanistic diversity has recently been shown in the case of Pt(II) → Pt(IV) oxidative addition reactions.[18] Since an S_{N}2-type mechanism for the reaction of CH₃CN and [Pt(PEt₃)₂] is highly unlikely,[19] it is quite possible that O₂ present in the system allows a free radical nonchain reaction to take place, leading to the observed product *trans*-[PtMe(CN)(PEt₃)₂]. An alternative mechanism involving interaction of the substrate with the metal center prior to bond cleavage may be possible for the aromatic substrate benzonitrile.

The reactions of [Pt(PEt₃)₂] with organic substrates are of considerable interest since the observed products result from formal C-H bond activation of TBAP and C-C bond activation of CH₃CN and C₆H₅CN. Detailed mechanistic studies of this dichotomy in reactivity are currently underway.

(10) Acetamide was detected by ¹³C NMR spectroscopy: δ 178.2, 22.1 (in H₂O/CD₃OD).

(11) The formation of acetamide from [Pt(PEt₃)₃], H₂O, and CH₃CN has been reported by Otsuka and co-workers; see ref 4.

(12) The formation of acetamide from the reaction of *trans*-[PtH(Cl)(PEt₃)₂] with NaOH in 50/50 H₂O/CH₃CN at 80 °C has been reported; see: Trogler, W. C.; Jensen, C. M. *J. Am. Chem. Soc.* 1986, *108*, 723.

(13) Anton, D. R.; Crabtree, R. H. *Organometallics* 1983, *2*, 855.

(14) PhC≡CPh has a reduction potential less negative than *cis*-[PtCl₂(PEt₃)₂]; therefore, it cannot be added prior to the electrolysis.

(15) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985.

(16) We thank a reviewer for sharing with us these unpublished results.

(17) Identified by ³¹P{¹H} NMR spectroscopy: δₚ 13.7 (*J*_{Pt-P} = 2620 Hz) (in C₆D₆). See: Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* 1968, 2700.

(18) Ferguson, G.; Monaghan, P. K.; Parvez, M.; Puddephatt, R. J. *Organometallics* 1985, *4*, 1669.

(19) The displacement of CN⁻ is said to be unknown during S_{N}2 processes in organic chemistry; see ref 15.

Iridium Hydride Complexes Formed by the Intramolecular N-H Addition of Hybrid Phosphine Amines to Iridium(I)

Soonheum Park, David Hedden, and D. Max Roundhill*
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Summary: The complexes [MCl(1,5-COD)]₂ react with *o*-Ph₂PC₆H₄NHR to give tetracoordinated complexes MCl(1,5-COD)(*o*-Ph₂PC₆H₄NHR) (M = Rh, Ir, R = CH₂Ph; M = Rh, R = Et) where the amine moiety is uncoordinated. Treating IrCl(1,5-COD)(*o*-Ph₂PC₆H₄NHR) with AgClO₄ gives the bis-chelate complexes [Ir(1,5-COD)(*o*-Ph₂PC₆H₄NHR)]ClO₄ (R = CH₂Ph, Et). Thermolysis of [Ir(1,5-COD)(*o*-Ph₂PC₆H₄NHCH₂Ph)]ClO₄ causes C-