tendency to bend inward toward the opposite metal atom, an effect shown also by all the equatorial ligands in 5 (Ru′–Ru–C in the range 85.0 (2)–88.7 (2)°), but only by the carbonyl ligands in 2 (Ru′–Ru–C(1) = 85.1 (3)°), and by an equatorial isocyanide ligand cis to each carbonyl group (Ru′–Ru–C(2) = 86.0 (3)°). The other equatorial isocyanide ligands in 2 bend away from the opposite ruthenium atom (Ru′–Ru–C(3) = 90.5 (3) and Ru′–Ru–C(4) = 92.4 (3)°). Another interesting effect is observed for 5 where a pair of trans radial isocyanides have the phenyl groups bending *inward* toward the center of the dinuclear unit, while the phenyl groups of the other ligand pair are bent away from the center of the molecule. In this regard, it is noteworthy that the smallest dihedral angles 38.2 (5) and 39.2 (5)° each involve ligands on opposite ruthenium atoms for which the phenyl groups bend away from the center of the dimer. It is thus apparent that in both 2 and 5, the ligand arrangement reflects reduced steric interactions not only within each half of the molecules but also between each half of the dimers. An examination of the nonbonded contacts for 2 and also of space-filling models further suggests that the ligand arrangement observed crystallographically for 2 represents sterically the best possible arrangement and that the dinuclear unit should be considered to be sterically saturated. It is thus conceivable that the low-temperature ^{1}H NMR effects can be attributed to nonequivalent methyl groups in individual *tert*-butyl isocyanide ligands, while the introduction of further *tert*-butyl isocyanide ligands is to be considered unlikely due to prohibitive steric interactions, thus possibly explaining the lack of further substitution of 2.

In conclusion, it is clear that the complex *catena*-[Ru(CO)$_2$(O$_2$CCH$_3$)] under suitable experimental conditions provides a most unusual synthetic precursor in ruthenium(I) chemistry. We are actively pursuing this further.

Registry No. 1, 26317-70-4; 2, 101377-32-6; 3, 101377-27-9; 4, 101377-29-1; 5, 101377-30-4; 6, 101402-18-0; Me$_3$CNC, 7188-38-7; PhCH$_2$NC, 10340-91-7; 2,6-Me$_2$C$_6$H$_3$NC, 2769-71-3; Ru, 7440-18-8.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 2 and 5 and tables of analytical and spectroscopic data for 2–6 (43 pages). Ordering information is given on any current masthead page.

Electrochemical Generation and Reactivity of Bis(triphenylphosphine)platinum(0): An Electrosynthesis of Platinum–Acetylene Complexes

Julian A. Davies,* Cassandra T. Eagle, Deborah E. Otis,[†] and Uma Venkataraman

Department of Chemistry, University of Toledo
Toledo, Ohio 43606

Received August 15, 1985

Summary: **Controlled potential bulk reductive electrolysis of *cis*-[PtCl$_2$(PPh$_3$)$_2$] results in the generation of [Pt(PPh$_3$)$_2$] in solution. This 2-coordinate, 14-electron compound is efficiently trapped by acetylenes, RC$\equiv$CR (R = Ph, COOMe), to produce [Pt(PPh$_3$)$_2$(RC$\equiv$CR)] quantitatively and by oxidative addition addenda (e.g., C$_6$H$_5$COCl, MeI) to produce the corresponding oxidative addition products in high yield. No products arising through ligand disproportionation, Pt(0)/Pt(II) electron transfer, or ligand P–C bond cleavage are produced.**

Stable, 2-coordinate, 14-electron bis(tertiary phosphine)platinum(0) complexes [PtL$_2$] are well-known where L is sterically demanding, e.g., P(t-Bu)$_3$,[1] P(t-Bu)$_2$Me,[2] P(t-Bu)$_2$Ph,[1] P(c-Hx)$_3$,[1,3] or P(i-Pr)$_3$,[1] with chemical reactivity appearing to increase with decreasing steric demand. The unhindered complex [Pt(PEt$_3$)$_2$] has been generated photochemically in situ from the oxalate [Pt(C$_2$O$_4$)(PEt$_3$)$_2$] and shown to be extremely reactive toward coordinating and oxidative addition addenda.[4,5] It is reported[6] that platinum(0) complexes can be similarly generated from [Pt(C$_2$O$_4$)(PPh$_3$)$_2$], but the characterization of several of the reaction products has been questioned.[7] The generation of [Pt(PPh$_3$)$_2$] is problematic because of the tendency for ligand P–C bond cleavage to occur in coordinatively unsaturated complexes containing arylphosphine ligands.[8] Thus, passing nitrogen through solutions of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] results in not only loss of ethylene but also formation of benzene and generation of the ortho-metalated phosphido-bridged cluster [Pt$_2$(μ-PPh$_2$)$_2$(PPh$_2$C$_6$H$_4$)$_2$].[9] Similarly, thermolysis[10] of [Pt(PPh$_3$)$_4$] produces [Pt$_2$(μ-PPh$_2$)$_2$(PPh$_3$)$_2$] and [Pt$_3$(μ-PPh$_2$)$_3$(PPh$_3$)$_2$Ph] whereas photolysis[11] of [Pt(C$_2$O$_4$)(PPh$_3$)$_2$] under hydrogen does not produce [PtH$_2$(PPh$_3$)$_2$] (cf. the PEt$_3$ analogue)[4,5] but rather, after precipitation with NaBF$_4$, the cluster [Pt$_3$(μ-PPh$_2$)$_2$(μ-H)(PPh$_3$)$_3$]$^+$.

Use of electrochemical methods to generate low-valent intermediates, such as [Pt(PPh$_3$)$_2$], has recieved scant attention in the past, although such methods may show distinct advantages over thermal and photochemical techniques. In the past it has been reported that controlled potential bulk reductive electrolysis of [PtCl$_2$(PPh$_3$)$_2$], followed by addition of HCl gas,[12] yields a hydrido complex, although no details of characterization were given. Interestingly, electrochemical reduction of [PtCl$_2$(PPh$_3$)$_2$], followed by the addition of water, also yields a hydride,[13] characterized by an IR absorption at 2232 cm^{-1}, whereas electrochemical reduction in the presence of excess triphenylphosphine is reported[13] to produce [Pt(PPh$_3$)$_3$], characterized by elemental analysis only.

Here we report on the controlled potential bulk reductive electrolysis of *cis*-[PtCl$_2$(PPh$_3$)$_2$][14] to generate [Pt(PPh$_3$)$_2$] and trapping reactions with coordinating and oxidative addition addenda. This method provides a versatile synthesis of a diverse range of platinum(0) and platinum(II) complexes from a common precursor. The electrosynthesis is described in detail for the preparation of [Pt(PPh$_3$)$_2$(RC$\equiv$CR)] complexes on a ca. 50-mg scale.[15]

[†] Permanent address: Department of Chemistry, Adrian College, Adrian, Michigan 49221.

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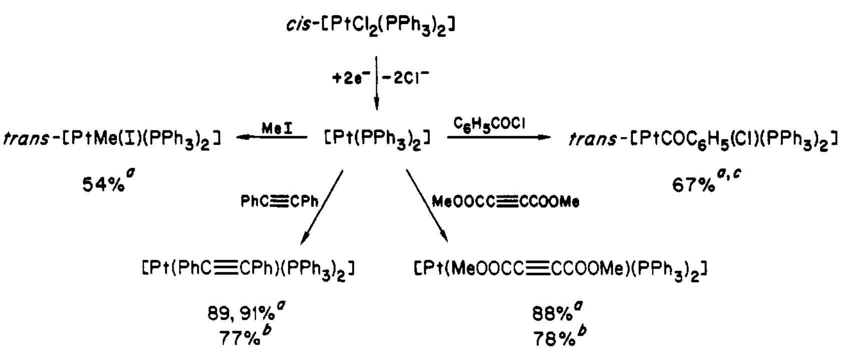
Scheme I



[a] Estimated yield by peak heights from $^{31}P\{^1H\}$ NMR spectrum of reaction product in situ (two values indicate results from two separate preparations). [b] Yield of isolated, recrystallized product. [c] Undergoes slow decarbonylation in solution to produce *trans*-$[Pt(CO)(C_6H_5)(PPh_3)_2][Cl]$.

The controlled potential bulk electrolysis experiments are typically performed in a three-compartment cell, equipped with a mercury pool working electrode, a platinum spiral wire counterelectrode, and a Ag/AgCl reference electrode (−35 mV vs. SCE). *cis*-$[PtCl_2(PPh_3)_2]$ is dissolved in a preelectrolyzed acetonitrile/benzene (5/2) solvent system containing tetra-*n*-butylammonium perchlorate (TBAP) and suspended activated alumina. Electrolysis at a potential of −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). The reduced solution is extremely

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

air-sensitive, and trace amounts of air lead to formation of substantial quantities of $[PtO_2(PPh_3)_2]$, $[Pt(CO_3)(PPh_3)_2]$, and $OPPh_3$, which have been identified in solutions after exposure to air by $^{31}P\{^1H\}$ NMR spectroscopy.

In the absence of air, or any added substrates, a slow disproportionation to $[Pt(PPh_3)_3]$ and platinum metal occurs[16] (eq 2). $[Pt(PPh_3)_3]$ has been identified by $^{31}P\{^1H\}$

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

NMR spectroscopy, and discoloration indicates the formation of platinum metal. The time scale of this disproportionation is sufficiently slow that it does not interfere with trapping reactions of the 2-coordinate intermediate. This is particularly significant since it is known[16] that generation of $[Pt(PPh_3)_2]$ by reductive elimination of methane from the corresponding hydrido methyl complex in toluene solution leads to disproportionation at temperatures above −25 °C. In the present case it seems likely that the solvent system stabilizes the low-valent intermediate. Such stabilization by coordination of benzene[5] and by coordination of hard donor solvents[17] has been proposed previously.

Trapping reactions have generally been performed by the addition of ca. 1.1 equiv of the substrate to the solution after the reduction is complete, as indicated by coulometry. Yields estimated for products in situ and measured after isolation and purification (Scheme I) are sufficiently high that it is clear that disproportionation (eq 2), electron transfer (eq 3), or other destructive processes (e.g., ligand

$$Pt(II) + Pt(0) \rightarrow 2Pt(I) \quad (3)$$

P–C bond cleavage,[8] vide supra) are not significant. Trapping reactions with coordinating and oxidative addition addenda are summarized in Scheme I. In all cases, reaction workup[15] is performed by routine inert-atmosphere techniques, involving separation of the product from the alumina dessicant and the TBAP background electrolyte, followed by in situ examination by $^{31}P\{^1H\}$ NMR spectroscopy. Yields are estimated from peak heights with deviations from 100% caused by trace quantities of starting material and/or triphenylphosphine oxide. In the case of the acetylene complexes, products were isolated and recrystallized with yields of 77% (R = Ph) and 78% (R = COOMe). These yields are comparable with most traditional syntheses of platinum acetylene complexes[18] and are an improvement on many methods.

The reactivity of electrochemically generated $[PtL_2]$ complexes leads to a number of diverse syntheses which are possible from a common precursor. Since substrates may be added after the electrolysis is complete, the preparative method may be employed with substrates which are themselves electroactive in the potential range of interest. Unlike photochemical[4,5] or thermal methods,[10] the stability of the trapped product is not a controlling factor with this methodology.

The use of controlled potential electrolysis to generate $[PtL_2]$ intermediates is not restricted to the case where L = PPh_3. We have also examined cases where L = PEt_3 and where L_2 = dppe.[19] In both cases we see enhanced reactivity in comparison with the triphenylphosphine system.

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(15) Experimental details for the preparation of the $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$ complex are as follows. A rigorously dried three-compartment cell equipped with a mercury pool working electrode (28 cm^2) 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 CaH_2 followed by successive distillation from CaH_2, P_2O_5, and CaH_2 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 −1.60 V to zero current. *cis*-$[PtCl_2(PPh_3)_2]$ (0.0608 g, 7.7×10^{-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 zero current at −1.60 V. Coulometry indicates a two-electron reduction with integrations typically in the range of 1.9–2.1 electrons. In this specific case the integration indicated an uptake of 2.09 electrons. The solution is then filtered under argon into a Schlenk tube and the acetylene (1.14 equiv) added. Following reduction to dryness, the solid mass is extracted with benzene (10 mL), filtered, and concentrated to small volume. The solution is then either transferred to an NMR tube under argon and sealed in vacuo for NMR studies or transferred to a short alumina column and chromatographed with benzene/ethanol. Slow evaporation of the eluent allows isolation and collection of the products in 77% yield. Anal. Calcd: C, 66.9; H, 4.5. Found: C, 67.7; H: 5.0. The corresponding complex of MeOOCC≡CCOOMe was prepared in 78% yield in an entirely analogous manner.

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Where L = PEt_3, we observe reproducible reaction chemistry with the C–H and/or C–C bonds of acetonitrile and the tetra-*n*-butylammonium cation, depending upon the experimental conditions. A separate report will describe this chemistry in detail.[19]

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Registry No. *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; $[PtO_2(PPh_3)_2]$, 29894-57-3; $[Pt(CO_3)(PPh_3)_2]$, 17030-86-3; $OPPh_3$, 791-28-6; $[Pt(PPh_3)_3]$, 13517-35-6; $[Pt(PEt_3)_2]$, 66916-63-0; [Pt(dppe)], 101519-43-1; $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$, 15308-61-9; $PhC{\equiv}CPh$, 501-65-5; $[Pt(PPh_3)_2(MeOOCC{\equiv}CCOoMe)]$, 22853-55-0; $MeOOCC{\equiv}CCOOMe$, 762-42-5; *trans*-$[PtI(Me)(PPh_3)_2]$, 28850-19-3; *trans*-$[PtCOC_6H_5(Cl)(PPh_3)_2]$, 18421-48-2; *trans*-$[Pt(CO)(C_6H_5)(PPh_3)_2][Cl]$, 101519-44-2.

Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bis(arsino)gallane, Bis{bis[bis[(trimethylsilyl)methyl]arsino]chlorogallane}

Colin G. Pitt,* Andrew P. Purdy, Kelvin T. Higa, and Richard L. Wells*

Department of Chemistry
Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

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Summary: Silylarsines, $R_2AsSiMe_3$ (R = Me_3SiCH_2 and mesityl), have been used to synthesize (arsino)gallanes. Dynamic NMR spectroscopy studies of one of these, $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, show it has fluxional properties.

Despite the importance of gallium arsenide in emerging semiconductor technology,[1] the chemistry of this elemental combination had, until recently,[2] been restricted to the studies of Coates et al.[3] in the 1960s. They prepared two mono(arsino)gallanes by cleavage of one Ga–C bond in Me_3Ga with secondary arsines, resulting in the elimination of methane (eq 1). In our hands, this method became

$$\begin{gathered} \mathrm{R_2AsH + Me_3Ga \rightarrow 1/}n\mathrm{(R_2AsGaMe_2)}_n + \mathrm{CH_4} \\ \mathrm{R = Me;}\ n = 3 \\ \mathrm{R = Ph;}\ n = 2 \end{gathered} \tag{1}$$

impractical, and eventually failed, as the steric bulk of the substituents was increased;[4] it was also found to be limited to the cleavage of a single Ga–C bond, and bis- and tris(arsino)gallanes, $[(R_2As)_{3-x}GaR_x]_n$ (x = 0, 1), were inaccessible by this route.[5] A number of reports of the synthesis of main-group compounds by metathetical elimination of trimethylchlorosilane[6] prompted us to evaluate this route to (arsino)gallanes. Here we report its successful application (eq 2–4), as well as the fluxional properties of a dimeric bis(arsino)gallane.

$$\begin{gathered} \mathrm{R_2AsSiMe_3 + GaCl_3 \rightarrow 1/}n\mathrm{(R_2AsGaCl_2)}_n + \mathrm{Me_3SiCl} \\ \mathrm{R = Me_3SiCH_2;}\ n = 3 \\ \mathrm{R = Mes = mesityl;}\ n = \mathrm{?} \end{gathered} \tag{2}$$

$$\begin{gathered} \mathrm{2R_2AsSiMe_3 + GaCl_3 \rightarrow 1/}n\mathrm{[(R_2As)_2GaCl]}_n + \mathrm{2Me_3SiCl} \\ \mathrm{R = Me_3SiCH_2;}\ n = 2 \\ \mathrm{R = Mes;}\ n = \mathrm{?} \end{gathered} \tag{3}$$

$$\begin{gathered} \mathrm{R_2AsSiMe_3 + 1/}n\mathrm{[(R_2As)_2GaCl]}_n \rightarrow \mathrm{(R_2As)_3Ga + Me_3SiCl} \\ \mathrm{R = Mes} \end{gathered} \tag{4}$$

Silylarsines[7] are readily available from lithium arsenides and trimethylchlorosilane, and their reaction with trichlorogallane proceeds stepwise in hydrocarbon solvents.[8]

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(4) For example, $[(Me_3SiCH_2)_2AsGaPh_2]_2$ was prepared by this method;[2c] however, heating Ph_2AsH and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) at 60 °C for 2 days afforded impure $[(Ph_2AsGa(CH_2SiMe_3)_2]_n$, $Ph_2AsAsPh_2$, Me_4Si, H_2, and unreacted $(Me_3SiCH_2)_3Ga$; no evidence for the desired product was obtained when $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) were heated at 100–120 °C for 1 month.

(5) For example, when Ph_2AsH and Me_3Ga (2:1 molar ratio) were heated at 80–100 °C for 2 days, no evidence for any product other than CH_4, $(Ph_2AsGaMe_2)_n$, and unchanged Ph_2AsH was obtained.

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