C-X AND C-H CLEAVAGE BY ELECTROCHEMICALLY GENERATED NON-LINEAR [PtL₂] COMPLEXES

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Abstract—The electrochemical reduction of $[PtX_2L_2]$ (X = halide, L₂ = bidentate diphosphine: Ph₂PCH₂CH₂PPh₂, dppe; Cy₂PCH₂CH₂PCy₂, dcpe; Cy₂P{CH₂}₃PCy₂, dcpp) has been used as a method of generating non-linear $[PtL_2]$ compounds whose reactivity with substrates Ar—X (X = Cl, Br, CN, H, C=CPh) has been examined. Generation of $[PtL_2]$ (L₂ = dppe or dcpe) in the presence of excess Ph—X (X = Cl, Br) produces $[PtXPhL_2]$ efficiently. Similarly, generation of $[PtL_2]$ (L₂ = dppe or dcpe) in the presence of PhC=CPh)]. Generation of $[PtL_2]$ (L₂ = dppe or dcpe) in the presence of PhC=CPh)]. Generation of $[PtL_2]$ (L₂ = dppe or dcpe) in the presence of PhC = CPh results in trapping to form $[PtL_2(PhC=CPh)]$. Generation of $[PtL_2]$ (L₂ = dppe or dcpe) in the presence of PhCN or PhH results in indiscriminate reactions that do not produce tractable products. In contrast, reduction of $[PtCl_2(dcpp)]$ in CH₃CN/C₆H₆/Bu₄NClO₄ produces [PtHPh(dcpp)] with considerable selectivity via aromatic C—H activation by [Pt(dcpp)]. At room temperature the complex [PtHPh(dcpp)] undergoes exchange with C₆D₆ to generate $[PtD(C_6D_5)(dcpp)]$.

In a recent series of papers Whitesides and coworkers¹⁻³ have shown that C_{2n} [PtL₂] complexes can react with hydrocarbon substrates, including alkanes, by C-H oxidative addition. Thus, thermolysis of the alkylhydride [PtH(CH₂CMe₃) $(Cy_2PCH_2CH_2PCy_2)$ (Me = methyl, Cy = cyclohexyl) was shown to result in reductive elimination of neopentane and reaction of the resulting nonlinear [PtL₂] fragment with an organic substrate present in excess. We have demonstrated⁴⁻⁷ that electrochemical reduction of cis-[PtCl₂L₂] complexes generates $[PtL_2]$ equivalents and that in the case where L_2 is a bidentate tertiary phosphine ligand⁷ the non-linear intermediate may be trapped by other bidentate ligands to produce $[PtL_2L_2^*]$. Here we report on the reactions of non-linear $[PtL_2]$ equivalents, generated by electrochemical reduction, with organic substrates including examples where C-X (X = halogen) and C-H oxidative additions are observed.

Initially we believed that the electrochemical generation of non-linear $[PtL_2]$ equivalents by reduction of $[PtX_2L_2]$ might prove to be prob-

lematic since the electrochemical method requires the use of a relatively polar solvent and a background electrolyte, both of which might participate in indiscriminate reactions with the C_{2v} intermediate. However, work with bidentate ligands as trapping agents⁷ showed that unselective reactions with the solvent/electrolyte could largely be avoided provided a suitable trap was already present in solution as the [PtL₂] intermediate was generated. Thus, in order to probe the reactions of non-linear $[PtL_2]$ complexes with organic substrates we sought suitable compounds to act as trapping agents. The requirements are quite stringent since the trapping agent must survive the very negative potentials required to reduce the $[PtX_2L_2]$ precursors (typically⁴⁻⁷ ca - 1.50 to -2.40 V vs Ag/AgCl). Additionally, we sought trapping agents that would not react with the $[PtX_2L_2]$ precursors, a problem that we had previously encountered in using bidentate ligands as trapping agents.⁷ Based upon these requirements we examined compounds of the type Ph—X (where X = Cl, Br, CN, H, C=CPh) which could either be used as solvents for electrochemical reduction or added to a solvent/electrolyte system of acetonitrile/TBAP [TBAP = tetra(n-butyl)ammonium perchlorate]. In order to probe ligand effects on the reactivity of non-linear [PtL2] com-

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pounds we have examined complexes of dppe $(PhPCH_2CH_2PPh_2)$ and dcpe $(Ph_2PCH_2CH_2PPh_2)$ with each trapping agent. Some experiments have also been performed with complexes of dcpp $(Cy_2P \{CH_2\}_3PCy_2)$.

RESULTS AND DISCUSSION

Our initial experiments utilized PhX (X = Cl, Br, CN) as both solvent and trapping agent for the electrochemical reduction of $[PtX_2(dppe)]$ and $[PtX_2$ (dcpe)]. None of these solvents is truly suitable for electroanalytical work since each has a low dielectric constant⁸ (PhCl: 5.62; PhBr: 5.40; PhCN: 25.20; cf. CH₃CN: 37.50) and this is manifested in the cyclic voltammograms of $[PtI_2(dppe)]$ shown in Fig. 1. Based on these and similar measurements for other complexes we selected appropriate potentials for controlled potential bulk reductive electrolysis experiments. Each electrolysis experiment was performed utilizing the three-compartment cell, equipped with a mercury pool working electrode, a Ag/AgCl reference electrode and a platinum auxiliary electrode that we have described previously.⁶ In many of the experiments described here we found that the low dielectric constant solvents led to low current flow resulting in long electrolysis times which made coulometry unreliable as a guide to determining the extent of reaction. Accordingly, many experiments were terminated at an arbitrary



Fig. 1. Cyclic voltammograms of [PtI₂(dppe)] as a 10⁻⁴ M solution in a solvent that is 0.08 M in TBAP, measured using a Hg/Au amalgam working electrode (1.77 mm²) at a scan rate of 200 mV s⁻¹ with a Ag/AgCl reference electrode. Solvents used were : (a) chlorobenzene, (b) bromobenzene, (c) benzonitrile and (d) acetonitrile.

point where the starting material had not been fully consumed.

Electrolysis of [PtCl₂(dppe)] in chlorobenzene at -2.0 V was followed by a standard work-up (see Experimental) and examination by ${}^{31}P{}^{1}H{}$ NMR spectroscopy which showed the exclusive formation of [PtClPh(dppe)] and the presence of some residual starting material. Formation of the chlorophenyl complexes suggests electrochemical generation of the non-linear intermediate, [Pt(dppe)], followed by C-Cl oxidative addition. A similar reduction of $[PtI_2(dppe)]$ in chlorobenzene at -1.80 V was complicated by the fact that in this case generation of [Pt(dppe)] liberates iodide ions, which can engage in metathesis reactions with the starting material or product. Thus, ³¹P{¹H} NMR spectroscopy indicates the formation of [PtIPh(dppe)], together with the presence of starting material and its metathesis products {i.e. [PtI₂(dppe)], [PtICl(dppe)] and [PtCl₂(dppe)]}. Additionally, a trace amount of an unidentified compound ($\delta_{\rm P} = 36.7$ ppm, $J_{\rm Pt-P} =$ 4165 Hz) was detected. The electrochemical reduction of [PtI₂(dcpe)], containing the bulky σ -donor $Cy_2PCH_2CH_2PCy_2$ ligand, in chlorobenzene at -2.0 V produced [PtClPh(dcpe)] and its metathesis product, [PtIPh(dcpe)]. Some unreacted [PtI₂(dcpe)] was also detected in solution. With the dcpe ligand, no unidentified species were generated (cf. the analogous dppe reaction).

Reactions in bromobenzene were found to proceed similarly. Thus, reduction of $[PtCl_2(dppe)]$ in C₆H₃Br/CH₃CN (5:1) at -2.0 V produced [PtBrPh(dppe)] and its metathesis product, [PtClPh (dppe)]. Some residual starting material was found to be metathesized to [PtClBr(dppe)] and [PtBr₂ (dppe)]. The electrochemical reduction of [PtI₂ (dcpe)] in bromobenzene at -1.80 V produced both [PtBrPh(dcpe)] and [PtIPh(dcpe)] with some [PtI₂(dcpe)] remaining.

In each of the above experiments the compounds $[PtXPhL_2]$ (X = Cl, Br, I; L₂ = dppe, dcpe), formed by Ph—X oxidative addition, and the mixed halide complexes, $[PtXYL_2]$ (X = Cl; Y = Br, I; L₂ = dppe), formed by halide metathesis, were identified by comparison of their spectroscopic data with data obtained for independently synthesized materials. Details of these syntheses are given in the Experimental and spectroscopic data, along with pertinent literature references, are collected in Tables 1 and 2.

Electrochemical reductions of both $[PtI_2(dppe)]$ and $[PtCl_2(dcpe)]$ in benzonitrile proved to be very complex. Although our earlier work^{5,6} on the electrochemical reduction of *cis*- $[PtCl_2(PEt_3)_2]$ in PhCN had shown that *trans*- $[PtCN(Ph)(PEt_3)_2]$ could be effectively generated, neither of the present Electrochemically generated [PtL₂] complexes

	Solvent	δP _A (ppm)	δP _B (ppm)	J _{Pt—PA} (Hz)	J _{Pt-PB} (Hz)
[PtClPh(dppe)] [*]	C ₆ D ₆	37.7	37.6	1608	4092
	CDCl ₃	38.7	37.9	1640	4098
[PtBrPh(dppe)]	C_6D_6	38.7	39.0	1615	4083
[PtIPh(dppe)]	C_6D_6	39.2	39.0	1654	3999
[PtClPh(dcpe)]	C ₆ D ₆	60.7	50.7	1692	3956
	CDCl ₃	62.0	51.8	1718	4062
[PtBrPh(dcpe)]	C ₆ D ₆	59.4	51.7	1689	3969
	CDCl ₃	60.7	53.1	1710	4059
[PtIPh(dcpe)]	C ₆ D ₆	57.8	50.7	1686	3850
	CDCl ₃	59.0	52.7	1702	3922

Table 1. ³¹P{¹H} NMR data of phenylplatinum(II) complexes^a

" P_A is the phosphorus *trans* to the halide, P_B is the phosphorus *trans* to the phenyl group. Data for independently synthesized samples (see Experimental).

^{*b*} Literature data (ref. 9), δP_A 38.7; δP_B 36.9 ppm; J_{Pt-P_A} 1638; J_{Pt-P_B} 4192 Hz.

Table 2. ³¹P{¹H} NMR data of mixed haloplatinum(II) complexes^a

	δP _A (ppm)	δP _B (ppm)	J _{Pt—PA} (Hz)	J _{Pt-PB} (Hz)	J _{P—P} (Hz)
[PtClI(dppe)]	42.6	43.7	3550	3428	0.7
[PtBrCl(dppe)]	43.5	42.6	3562	3542	0.8
[PtIBr(dppe)]	45.2	45.0	3394	3523	1.0
[PtClI(dcpe)]	66.5	65.8	3379	3523	4.9
[PtBrCl(dcpe)]	66.4	64.9	3547	3550	5.1
[PtIBr(dcpe)]	66.3	67.5	3394	3502	5.3

^{*a*} P_A refers to the phosphorus *trans* to the first named halide, P_B refers to the phosphorus *trans* to the second named halide. Data for independently synthesized samples (see Experimental).

systems produced tractable products. Indeed, current flow in these experiments continued past the anticipated 2 electrons/equivalent, perhaps indicating that any *cis*-phenylcyano complexes generated were unstable under the reaction conditions. In this regard it is noteworthy that our attempts to independently synthesize [PtCN(Ph)(dppe)] by treatment of [PtClPh(dppe)] with cyanide ion (see Experimental) invariably led to decomposition.

Diphenylacetylene proved to be an effective trapping agent for non-linear $[PtL_2]$ equivalents. Thus, electrochemical reduction of $[PtX_2(dppe)]$ in CH₃CN/C₆H₆ containing one equivalent of PhC= CPh produced [Pt(PhC=CPh)(dppe)] in high yield (X = Cl: 93.5%; X = Br: 94.5%; X = I: 87.0%; estimated from peak heights in the ³¹P{¹H} NMR spectra). A similar reduction of $[PtI_2(dcpe)]$ in the presence of PhC=CPh generated [Pt(PhC=CPh) (dcpe)] but here the yield was reduced to 56% with other, unidentified by-products also present. The complex [Pt(PhC=CPh)(dppe)] was identified by comparison of its spectroscopic data with those of a sample independently synthesized by NaBH₄ reduction of [PtI₂(dppe)] in the presence of PhC=CPh (see Experimental). The dcpe analogue was identified by comparison of its spectroscopic data with those extant in the literature.¹

The results in the preceding paragraphs show that electrochemical reduction of $[PtX_2L_2]$ precursors containing bidentate ligands produces nonlinear $[PtL_2]$ equivalents which can be trapped by Ph—X (X = Cl, Br) oxidative addition or by coordination to PhC=CPh. As mentioned in the introductory paragraphs, we thought that reduction of $[PtX_{2}L_{2}]$ in the absence of a trapping agent but in the presence of a relatively polar solvent (e.g. CH₃CN or CH₃CN/C₆H₆) containing a background electrolyte (e.g. TBAP) might lead to indiscriminate reaction of the non-linear [PtL₂] intermediate. Indeed, reduction of [PtCl₂(dppe)] (at -1.75 V) or [PtBr₂(dppe)] (at -1.60 V) in CH_3CN/C_6H_6 (1:1, v/v, 0.1 M TBAP) produced product mixtures containing many components (see Experimental), none of which could be identified by comparison of ${}^{31}P{}^{1}H{}$ NMR data with literature values. However, reduction of [PtI2(dppe)] (at -1.40 V) in CH₃CN/C₆H₆ (1:2, v/v, 0.1 M TBAP) gave an indication that some meaningful chemistry might evolve from this area since the ${}^{31}P{}^{1}H{}NMR$ spectrum of the complicated product mixture contained resonances attributable to [PtIPh(dppe)], suggesting that C-H cleavage of the benzene component of the solvent mixture might have occurred, although ligand cleavage might also serve as a source of phenyl groups.

Similar indications of aromatic C—H activation were found in experiments using $[PtCl_2(dcpe)]$. Thus, although reduction in CH₃CN (0.1 M TBAP) at -2.25 V produced only unidentifiable products, reduction in CH₃CN/C₆H₆ (1:2, v/v, 0.1 M TBAP) at -2.25 V generated a product mixture whose ¹H NMR spectrum showed the presence of a component with a Pt—H bond and a component with a Pt—Ph bond (by the characteristic pattern¹ for the *ortho* protons). The ³¹P{¹H} NMR spectrum of this product mixture showed that several platinum phosphine complexes were formed but no resonances attributable to the known compound [PtHPh(dcpe)]¹ could be identified. Thus, it seems likely that the Pt—H and Pt—Ph groups observed in the ¹H NMR spectrum are present in different compounds. In this case ligand cleavage cannot be a source of phenyl groups and so C—H activation of benzene seems likely.

After examining several precursors, we found that electrochemical reduction of $[PtCl_2(dcpp)]$ (where dcpp = $Cy_2P\{CH_2\}_3PCy_2$) in CH_3CN/C_6H_6 (1:1, v/v, 0.1 M TBAP), followed by a standard work-up (see Experimental) and examination of a C_6D_6 solution by ${}^{31}P\{{}^{1}H\}$ NMR spectroscopy, produced the spectrum shown in Fig. 2(a). The presence of two doublets and the magnitudes of the couplings to platinum¹ suggested the compound formed was [PtHPh(dcpp)]. However,



Fig. 2. ³¹P{¹H} NMR spectra (C₆D₆ solution) of the product mixture arising from the electrochemical reduction of [PtCl₂(dcpp)] in CH₃CN/C₆H₆ (1 : 1, v/v, 0.1 M TBAP) : (a) immediately after work-up and (b) after 6 h in solution.

after 6 h in solution the ${}^{31}P{}^{1}H$ NMR spectrum had changed to that shown in Fig. 2(b): From this spectrum it is clear that both a new compound is being formed (indicated by *), and that one of the two doublets assigned to [PtHPh(dcpp)] has been transformed into a more complex multiplet while the other doublet has remained unchanged. A 2D- ${}^{31}P{}^{1}H$ -COSY spectrum of the solution demonstrated unambiguously that the doublet at 17.1 ppm is coupled to the new multiplet at 4.7 ppm and that no other coupling to phosphorus is involved in generating this multiplet. Accompanying these changes in the ${}^{31}P{}^{1}H$ NMR spectrum over time are changes in the 'H NMR spectrum. The initial ¹H NMR spectrum shows characteristic resonances for Pt-H and Pt-Ph with coupling constants entirely in accord¹ with the proposed structure, [PtHPh(dcpp)]. Six hours later, the hydride and Pt—Ph resonances are no longer present and only resonances utributable to coordinated dopp are observed.

In order to account for these observations, we postulated that the electrochemical reduction of [PtCl₂(dcpp)] produces a non-linear intermediate, [Pt(dcpp)], which reacts selectively with benzene by C-H oxidative addition, despite the presence of both CH₃CN and TBAP. The complex [PtHPh(dcpp)] when dissolved in $C_{6}D_{6}$ undergoes two competing processes: one is decomposition to generate an unknown species [indicated by * in Fig. 2(b)] and the other is a more rapid reaction with the C_6D_6 solvent to generate [PtD(C_6D_5)(dcpp)]. In order to test this postulate, we measured the 2D ${}^{31}P{}^{1}H{}$ J-resolved NMR spectrum of the solution after it had stood for several hours and then generated the ${}^{31}P{}^{1}H, {}^{31}P{}$ NMR spectrum. From these data we deduced that the multiplet shown at 4.7 ppm in Fig. 2(b) arose from coupling to the phosphorus observed at 17.1 ppm (vide supra) and coupling to a second nucleus (not ¹H or ³¹P) which generated a 1:1:1 pattern. This pattern is entirely as expected for coupling of ³¹P to deuterium and the magnitude of the observed coupling, ${}^{2}J({}^{3}{}^{P}$, 2 H) = 28 Hz, agrees well with the analogous value of ${}^{2}J({}^{3}P, {}^{1}H) = 179$ Hz for the larger of the two ³¹P-¹H couplings observed in the ¹H NMR spectrum of [PtHPh(dcpp)]. Thus, the magnitudes of the magnetogyric ratios of ¹H and ²H determine that a coupling of 28 ± 1 Hz involving deuterium will lead to a coupling of 182 ± 6 Hz for the analcgous protio compound

In order to confirm this exchange process, the solution which gave rise to the ${}^{31}P{}^{H}$ NMR spectrum shown in Fig. 2(a), i.e. largely [PtHPh(dcpp)], was rapidly evaporated *in vacuo* and an IR spectrum cf a KBr pellet of the resulting material was

obtained. The spectrum showed the presence of Pt-H with $r(Pt-H) = 1995 \text{ cm}^{-1}$. Similar treatment of a sample giving rise to the ³¹P{¹H} NMR spectrum, shown in, Fig. 2(3), i.e. largely [PtD(C₆D₆)(dcpp)], produced an IR spectrum in which the absorption at 1995 cm⁻¹ was absent and a new absorption at 1419 cm⁻¹ was present. This value agrees well with the calculated value of 1418 cm⁻¹ for replacement of hydrogen by deuterium.

The results that we describe here show interesting similarities and differences to the results of Whitesides and co-workers.¹⁻³ Thus, Whitesides demonstrated that thermal generation of [Pt(dcpe)] led to selective reactions with substrates present in excess, typically as the solvent. We found that the same intermediate could be generated electrochemically by reduction of $[PtX_2(dcpe)]$, but that unless specific trapping agents (e.g. PhCl. PhBr) were present, indiscriminate reaction with the $C_6H_6/$ CH (CN/TBAP solvent/ factor lya system vournel. Similar statements can be made for the electrochemical generation of the analogous dppe intermediate, whose thermal generation has not been described. However, use of the dcpp ligand allowed electrochemical generation of an intermediate which showed considerable selectivity in producing [PtHPh(dcpp)] via C—H oxidative addition of benzene even in the presence of reactive materials such as CH₃CN and TBAP. Whitesides and coworkers¹⁻³ observed that [PtHPh(dcpe)] could be induced to undergo exchange with $C_6 D_6$ at $\ge 79^{\circ}C$ and have reported a detailed mechanistic investigation. We found that [PtHPh(dcpp)] undergoes the same exchange process at room temperature. Presumably the difference in behaviour of the dcpe and dcpp systems relates to the degree to which the non-linear [PtL₂] intermediate can approach linearity. Thus, in our electrochemical system we find that the presumably linear $[Pt(PEt_3)_2]$ does not react with unactivated C-H bonds, the non-linear [Pt(dcpe)] with a dimethylene ligand backbone reacts indiscriminately, while the [Pt(dcpp)] intermediate with a trimethylene ligand backbone reacts quite selectively.¹⁰

EXPERIMENTAL

General procedures

The solvents, bromobenzene, chlorobenzene and benzonitrile were purified by first refluxing with anhydrous MgSO₄ (10 g dm⁻³) for 24 h, followed by distillation under argon to a dry flask containing activated alumina (25 g dm⁻³), where the first 20% of the distillate and the last 20% were discarded.

Collection temperatures were : bromobenzene 154-155°C, chlorobenzene 131-132°C and benzonitrile 190-192°C. Acetonitrile was purified as previously described.⁶ Benzene (Fisher, ACS grade) was freshly distilled from sodium wire under nitrogen prior to use. Benzene-d₆ (Aldrich) and chloroformd (Norell) were stored over molecular sieves (3 Å) and deoxygenated prior to use. Tetra(n-butyl)ammonium perchlorate (TBAP, G.F.S) was purified by recrystallization from absolute ethanol (200 g in 75 cm³) at room temperature, followed by vacuum drying for 48 h. Diphenylacetylene (Aldrich) was vacuum dried prior to use.

The ligands dppe and dcpe were purchaed from Strem Chemicals and dcpp was prepared by a literature route.¹¹ The complexes [PtCl₂(dppe)], [PtCl₂(dcpe)] and [PtCl₂(dcpp)] were prepared by displacement of 1,5-cyclooctadiene (cod) from [PtCl₂(cod)]. [PtI₂(dppe)] and [PtI₂(dcpe)] were similarly prepared from [PtI₂(cod)]. [PtBr₂(dppe)] was prepared by NaBr metathesis of [PtCl₂(dppe)] in CH₂Cl₂/acetone. The complexes [PtXPhL₂] (X = Cl, Br, I; L₂ = dppe, dcpe) were prepared (X = Cl) by displacement of 1,5-cyclooctadiene from [PtClPh(cod)] and by NaX metathesis (X = Br, I) of [PtClPhL₂].

 ${}^{31}P{}^{1}H{}$ (36.2 MHz) NMR spectra were measured on a JEOL FX 90Q spectrometer operating in the Fourier transform mode or were recorded on a Varian VXR 400 (162 MHz) spectrometer. ³P{¹H} NMR chemical shifts were measured using 85% H_3PO_4 as an external standard with positive values of the chemical shift representing deshielding. Yields were estimated from peak heights in the ${}^{31}P{}^{1}H$ NMR spectra. The 2D NMR experiments were performed using the standard software on the Varian VXR 400 spectrometer. The COSY experiments were performed using the standard COSY pulse sequence with 128×128 fid (free induction decay) collected at 162 MHz with the 2K × 2K processed using pseudo-echo shaped weighting to give the best resolution. The homonuclear 2D J-resolved spectrum was recorded using a fid grid with the 1K×1K processed using pseudo-echo shaped weighting to give the best resolution. ¹H NMR spectra were recorded on a Varian VXR 400 spectrometer and IR spectra were recorded using a Nicolet 5DX FTIR spectrometer with samples pressed as KBr pellets.

Cyclic voltammograms were obtained using a Bioanalytical Systems 100 control unit. Typically, 2.0×10^{-3} M solutions of the complexes in the appropriate solvent (10 cm³), which was 0.08 M in TBAP, were employed. A single compartment cell, controlled to a temperature of $25 \pm 1^{\circ}$ C, equipped with a Ag/AgCl reference electrode (-35 mV vs

S.C.E.), a platinum wire auxiliary electrode and a mercury/gold amalgam (Hg/Au) working electrode were used. We have discussed cyclic voltammetry of platinum(II) complexes using similar techniques previously.¹²⁻¹⁵ Controlled potential bulk reductive electrolyses (CPRE) were performed using a Bioanalytical Systems SP-2 synthetic potentiostat. A three-compartment cell was employed which was constructed in-house. The working electrode compartment contained the Ag/AgCl reference electrode and 18 cm³ of mercury 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 was equipped with a number of fitted openings to allow inert atmosphere operation and manipulation of solutions.

CPRE of [PtCl₂(dppe)] *in chlorobenzene*

Twenty-four hours prior to an experiment, the controlled potential electrolysis cell was charged with alumina (1.0 g) and a stir bar, and dried at 100°C. From this point on, all manipulations of the cell were performed under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, mercury (25 cm³) was extracted with dry chlorobenzene (10 cm³) and then mercury (18 cm³) was added to the cell which was cooled under argon. A 0.1 M solution of TBAP in chlorobenzene (60 cm³) was introduced into the cell under an argon stream. This was allowed to outgas for 1 h. The solution was then stirred and preelectrolysed for 20 min at a potential of -1.75 V.

To the pre-electrolysed solution was added [PtCl₂(dppe)] (*ca* 33.1 mg) which was purged with argon for 1 h. This was electrolysed for 2 h 45 min by which time the solution was yellow. The solution was then transferred to a Schlenk tube. Evaporation of the solvent (8 h) resulted in a white solid. This solid was extracted with benzene (2 × 10 cm³), filtered and evaporated to give a white solid which was dissolved in C₆D₆ (1 cm³) and transferred to a dry NMR tube under argon. The ³¹P{¹H} NMR spectrum showed [PtClPh(dppe)] (88.%) $\delta_{P(1)} = 37.7$ ppm, $J_{Pt-P(1)} = 1608$ Hz, $\delta_{P(2)} = 37.6$ ppm, $J_{Pt-P(2)} = 4092$ Hz; and [PtCl₂(dppe)] (11.9%) $\delta_{P} = 41.2$ ppm, $J_{Pt-P} = 3620$ Hz.

CPRE of [PtI₂(dppe)] in chlorobenzene

To the pre-electrolysed solution (-1.8 V, PhCl) was added [PtI₂(dppe)] (*ca* 30.0 mg) which was purged with argon for 1 h. This was electrolysed for 3 h with a low current flow (*ca* 0.6 electrons/

molecule) and worked-up as described above. The ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed [PtI₂(dppe)] (33.4%) $\delta_P = 45.8$ ppm, $J_{Pt-P} = 3384$ Hz; [PtIPh(dppe)] (45.3%) $\delta_{P(1)} =$ 39.2 ppm, $J_{Pt-P(1)} = 1654$ Hz, $\delta_{P(2)} = 39.0$ ppm, $J_{Pt-P(2)} = 3999$ Hz; [PtCl₂(dppe)] (2.1%) δ_P 41.2 ppm, $J_{pt-P} = 3621$ Hz; [PtCl1(dppe)] (14.9%) $\delta_{P(1)} = 42.2$ ppm, $J_{Pt-P(1)} = 3550$ Hz, $\delta_{P(2)} = 44.2$ ppm, $J_{Pt-P(2)} = 3446$ Hz; dppeO₂ (1.1%) $\delta_P = 30.4$ ppm; and a minor component (3.2%) $\delta_P = 36.7$ ppm, $J_{Pt-P} = 4165$ Hz.

CPRE of [PtI₂(dcpe)] in chlorobenzene

To the pre-electrolysed solution (-2.0 V, PhCl) was added [PtI₂(dcpe)] (*ca* 34.6 mg) which was then purged with argon for 1 h. Electrolysis resulted in a low current flow and was stopped after 3 h 10 min, after which the clear solution was evaporated (10 h 15 min) and worked-up as described above. The ³¹P{¹H} NMR spectrum of a CDCl₃ solution showed [PtIPh(dcpe)] (68.9%) $\delta_{P(1)} = 59.0$ ppm, $J_{P1-P(1)} = 1702$ Hz, $\delta_{P(2)} = 52.7$ ppm, $J_{P(1)-P(2)} = 3922$ Hz; [PtI₂(dcpe)] (16.0%) $\delta_{P} = 66.9$ ppm, $J_{P1-P(1)} = 62.0$ ppm, $J_{P1-P(1)} = 1718$ Hz, $\delta_{P(2)} = 51.8$ ppm, $J_{P1-P(2)} = 4062$ Hz.

CPRE of $[PtCl_2(dppe)]$ in bromobenzene/acetonitrile

To the pre-electrolysed solution (-1.8 V,PhBr/CH₃CN, 5:1, v/v) was added [PtCl₂(dppe)] (ca 30.2 mg) which was then purged with argon for 1 h. Electrolysis resulted in a large current flow. A dark orange solution was produced in the oxidation compartment which began to travel to the reduction compartment. Accordingly, electrolysis was stopped after 1 h 20 min. Evaporation of the solvent required 8 h and resulted in a brown solid. The ${}^{31}P{}^{H}$ NMR spectrum of a C₆D₆ extract (which leaves a white precipitate) gave the following data: [PtClBr(dppe)] (26.5%), [PtBrPh(dppe)] (20.2%), [PtBr₂(dppe)] (10.8%), [PtClBr(dppe)] (11.1%) and dppeO₂ (18.4%), with one complex undefined with data: $\delta_{\rm P} = 42.3$ ppm, $J_{\rm Pt-P} = 2310$ Hz (12.5%). A CDCl₃ solution of the white precipitate left from the extraction showed only [PtClPh(dppe)].

CPRE of [PtI₂(dcpe)] in bromobenzene

To the pre-electrolysed solution (-1.8 V, PhBr)was added [PtI₂(dcpe)] (*ca* 33.4 mg) which was then purged with argon for 1 h. Electrolysis resulted in a small current flow and was continued for 2 h 50 min. Work-up produced a light yellow solid and the ³¹P{¹H} NMR spectrum of a CDCl₃ solution showed only [PtI₂(dcpe)]. This electrolysis was repeated with an electrolysis time of 6 h, with the current remaining at a low level. Evaporation of the solvent (11 h) and work-up produced a light yellow solid. The ³¹P{¹H} NMR spectrum of a CDCl₃ solution showed the presence of [PtI₂(dcpe)] (50.0%), [PtIPh(dcpe)] (30.0%) and [PtIBr(dcpe)] (20%).

CPRE of [PtI₂(dppe)] in benzonitrile

To the pre-electrolysed solution (-1.7 V, PhCN) was added [PtI₂(dppe)] (*ca* 31.8 mg) which was then purged with argon for 1 h. Electrolysis resulted in a very large current flow and after 16 min coulometry indicated consumption of 2.25 electrons/molecule. The resulting orange solution turned yellow by the time the evaporation of the solvent *in vacuo* was complete (10 h, warm water bath). After the workup, the ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed only the presence of [PtI₂(dppe)].

CPRE of [PtCl₂(dcpe)] in benzonitrile

To the pre-electrolysed solution (-1.5 V, PhCN) was added [PtCl₂(dcpe)] (*ca* 27.0 mg) which was then purged for 1 h with argon. Electrolysis resulted in a large current flow and was halted after 2.1 electrons/molecule had been consumed. The dark yellow solution was evaporated (20 h) and after work-up the ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed approximately 68 peaks including one set of resonances identifiable as a platinum complex: $\delta_P = 71.5$ ppm, $J_{Pt-P} = 3024$ Hz. ¹H NMR data: $\delta_H = -1.14$ ppm, $J_{P(1)-H} = 179.6$ Hz, $J_{P(2)-H} = 14$ Hz, J_{Pt-H} was not observed. No strong $\nu(C=N)$ was observed in the IR spectrum.

CPRE of $[PtCl_2(dppe)]$ in the presence of Ph—C \equiv C—Ph

To the pre-electrolysed solution $(-1.7 \text{ V}, \text{CH}_3\text{CN}/\text{C}_6\text{H}_6, 1:1, \text{v/v})$ which contained Ph—C=C—Ph (0.1804 g) was added [PtCl₂(dppe)] (*ca* 27.7 mg) which was purged for 1 h with argon. The electrolysis to essentially zero current was performed at -1.7 V for 1 h. Coulometry indicated 1.85 electrons/molecule were consumed. After work-up the ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed [Pt(Ph—C=C—Ph)(dppe)] (93.5%) $\delta_P = 49.1 \text{ ppm}, J_{Pt-P} = 3143 \text{ Hz}$ and peaks at $\delta_P = 38.9 \text{ ppm} (4.0\%); \delta_P = 40.2 \text{ ppm} (2.5\%)$ of unknown origin.

CPRE of $[PtBr_2(dppe)]$ in the presence of Ph—C \equiv C—Ph

To the pre-electrolysed solution $(-1.6 \text{ V}, \text{CH}_3\text{CN/C}_6\text{H}_6, 1:1, \text{v/v})$ which contained Ph— C=C—Ph (0.1513 g) was added [PtBr₂(dppe)] (28.5 mg in one experiment and 26.7 mg in a second experiment) which was purged for 1 h with argon. This was electrolysed to essentially zero current for 1 h 20 min. Coulometry indicated 1.8 electrons/molecule consumed. After work-up, the ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed [Pt(Ph—C=C—Ph)(dppe)] (94.5%) $\delta_P = 49.1$ ppm, $J_{Pt-P} = 3146$ Hz and a peak at $\delta_P = 38.9$ ppm (5.5%) of unknown origin.

CPRE of $[PtI_2(dppe)]$ in the presence of Ph—C \equiv C—Ph

To the pre-electrolysed solution $(-1.4 \text{ V}, \text{CH}_3\text{CN/C}_6\text{H}_6, 1:1, \text{v/v})$ which contained Ph— C=C—Ph (0.1371 g) was added [PtI₂(dppe)] (29.8 mg in one experiment and 28.4 mg in a second experiment) which was then degassed for 1 h with argon. Electrolysis to essentially zero current at -1.4 V took 1 h 20 min. Coulometry indicated 2.1 electrons/molecule consumed. After work-up the ³¹P{¹H} NMR spectrum of a C₆D₆ solution showed [Pt(Ph—C=C-Ph)(dppe)] (87%) $\delta_P = 49.1 \text{ ppm},$ $J_{Pt-P} = 3146 \text{ Hz}$ and the following peaks of unknown origin: $\delta_P = 38.9 \text{ ppm} (7.7\%), \delta_P = 48.5 \text{ ppm} (1.5\%), \delta_P = 37.8 \text{ ppm} (3.8\%).$

CPRE of $[PtI_2(dcpe)]$ in the presence of Ph—C \equiv C—Ph

To the pre-electrolysed solution (-1.95 V, CH_3CN/C_6H_6 , 1:1, v/v) which contained Ph-C=C-Ph (0.1616 g) was added $[PtI_2(dcpe)]$ (28.1 mg in one experiment and 26.7 mg in a second experiment) which was purged for 1 h with argon. Electrolysis was performed at -1.7 V for 33 min, at which time coulometry indicated that 2.1 electrons/molecule were consumed. After work-up the ${}^{31}P{}^{1}H$ NMR spectrum of a C₆D₆ solution showed [Pt(Ph-C=C-Ph)(dcpe)] (55.9%) $\delta_{\rm P} = 66.9$ ppm, $J_{Pt-P} = 3010$ Hz; with two unknown complexes $\delta_{\rm P} = 74.2$ ppm, $J_{\rm Pt-P} = 1753$ (27.8%) and $\delta_{P(1)} = 60.7 \text{ ppm}, J_{Pt-P(1)} = 1803 \text{ Hz}, \delta_{P(2)} = 60.6$ ppm, $J_{Pt-P(2)} = 1750$ Hz (16.3%). ¹H NMR spectroscopy revealed a hydride signal $\delta_{\rm H} = -0.34$ ppm, $J_{P-H} = 17.6$ Hz, $J_{P-H} = 189$ Hz, $J_{Pt-H} =$ 1230 Hz.

CPRE of [PtI₂(dppe)] *in* CH₃CN/C₆H₆/TBAP

To the pre-electrolysed solution (-1.5 V, CH_3CN/C_6H_6 , 2:4 v/v) was added [PtI₂(dppe)] (ca 32.5 mg) which was purged with argon for 1 h and electrolysed to essentially zero current at -1.4 V. This required 2 h and coulometry indicated 1.8 electrons/molecule consumed. After work-up the dark orange solution generated a brown solid. The ${}^{31}P{}^{1}H$ NMR spectrum of a C₆D₆ solution was obtained which gave the following data: $\delta_{P(1)} = 51.1$ ppm, $J_{Pt-P(1)} = 3700 \text{ Hz}$; $\delta_{P(2)} = 50.1 \text{ ppm}$, $J_{Pt-P(2)}$ = 2875 Hz, $J_{P(1)-P(2)} = 60$ Hz; [PtIPh(dppe)]: $\delta_{P(1)} = 39.2 \text{ ppm}, J_{Pt-P(1)} = 3959 \text{ Hz}; \delta_{P(2)} = 39.3$ ppm, $J_{Pt-P(2)} = 1656$ Hz. In a similar manner to this experiment, electrolyses of $[PtCl_2(dppe)](-1.75 V)$, $[PtBr_2(dppe)]$ (-1.60 V) and $[PtCl_2(dcpe)]$ (-2.25 V) were performed. In none of these experiments were any identifiable components present in the complex product mixtures.

CPRE of [PtCl₂(dcpp)] *in acetonitrile/benzene* (1:1, v/v)

Twenty-four hours prior to an experiment, the controlled potential electrolysis cell was charged with alumina (1.0 g) and dried at 110°C. From this point on, all manipulations of the cell were carried out under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, mercury (25 cm³) was extracted with dry benzene (10 cm³) and then 18 cm³ of mercury and a small magnetic stir bar was added to the cell which was cooled under argon. A 0.1 M solution of TBAP in acetonitrile/benzene (60 cm³, 1:1, v/v) was introduced into the cell under an argon stream. This was allowed to outgas for 1 h. The solution was then stirred and pre-electrolysed to approximately zero current at a potential of -2.10 V.

To the pre-electrolysed solution was added [PtCl₂(dcpp)] (ca 30 mg) which was purged with argon for 1 h and then electrolysed to essentially zero current at a potential of -2.1 V. This usually required 75 min to 2 h and coulometry indicated approximately a 2 electrons/molecule reduction, with integrations in the range of 1.9-2.0 electrons/ molecule. When the electrolysis was complete, the solution was transferred (using inert atmosphere techniques) to a Schlenk tube and evaporated. The brownish solid was extraced with benzene (2×10) cm³) and evaporated to give a brown solid which was dissolved in $C_6 D_6$ and transferred to an NMR tube. The ${}^{31}P{}^{1}H$ NMR spectrum measured immediately [Fig. 2(a)] showed [PtHPh (dcpp)] (87.4%). ³¹P{¹H} NMR : $\delta_{P(1)} = 17.1$ ppm, $J_{\text{Pt}-\text{P(1)}} = 1793 \text{ Hz}; \delta_{\text{P(2)}} = 4.7 \text{ ppm}, J_{\text{Pt}-\text{P(2)}} = 1809$

Hz; $J_{P(1)-P(2)} = 21$ Hz. ¹H NMR: δ (hydride) = -1.58 ppm, $J_{P-H} = 21$ Hz, $J_{P-H} = 179$ Hz, $J_{Pt-H} = 1152$ Hz; δ (*o*-phenyl protons) = 7.86 ppm, $J_{H-H} = 13$ Hz, $J_{Pt-H} = 59$ Hz. IR (KBr pellet): v(Pt-H) = 1995 cm⁻¹. After several hours, the spectrum began to change and when 6 h had elapsed, the ³¹P{¹H} NMR spectrum showed [PtD(Ph-d₅)dcpp] (56.7%) and other components [Fig. 2(b)]: $\delta_{P} = 6.3$ ppm, $\delta_{P} = 0.18$ ppm, $J_{P-P} =$ 21 Hz (19.5%); $\delta_{P} = 8.9$ ppm, $\delta_{P} = -0.47$ ppm, $J_{P-P} = 24$ Hz (12.6%); $\delta_{P} = 47.6$ ppm (2.2%); $\delta_{P} = 23.7$ ppm (1.7%); $\delta_{P} = 4.37$ ppm (3.1%); $\delta_{P} = 1.18$ ppm (4.2%).

Preparation of [Pt(Ph-C=C-Ph)(dppe)]

To a Schlenk flask containing 20 cm³ of degassed ethanol was added [PtI₂(dppe)] (51.4 mg, 6.07×10^{-5} mol) and Ph--C=C-Ph (10.6 mg, 5.95×10^{-5} mol). This was heated to reflux for 30 min, then allowed to cool, and NaBH₄ (5.1 mg, 1.42×10^{-4} mol) dissolved in H₂O (3 cm³) was added and stirred. A precipitate appeared and the mixture was stirred for 3 h. This was then filtered quickly and vacuum dried to yield 25.1 mg (49.6%) of light yellow solid. The ³¹P{¹H} NMR spectrum of this solid in 1 cm³ of C₆D₆ showed [Pt(PhC=CPh)(dppe)] exclusively : $\delta_P = 49.1$ ppm, $J_{Pt-P} = 3146$ Hz.

Generation of mixed haloplatinum(II) complexes

In order to obtain spectroscopic data for comparison purposes, mixed halo complexes were generated *in situ* using the following general method cited here for the specific case of [PtClL(dppe)] as an example. [PtCl₂(dppe)] (15.1 mg, 2.27×10^{-5} mol) and NaI (4.0 mg, 2.73×10^{-5} mol) were suspended in acetonitrile (1 cm³) and then dichloromethane was added until all the solid was dissolved. After 10 min, the solution was evaporated *in vacuo* to a white solid and the soluble material was dissolved in 1 cm³ of CDCl₃. The ${}^{31}P{}^{1}H{}$ NMR spectrum shows [PtI₂(dppe)] ($\delta_{\rm P} = 46.0$ ppm, $J_{\rm Pt-P} = 3337$ Hz), [PtCl₂(dppe)] ($\delta_{\rm P} = 41.2$ ppm, $J_{\rm Pt-P} = 3621$ Hz) and [PtClI(dppe)] $(\delta_{P(1)} = 42.6 \text{ ppm}, J_{Pt-P(1)} = 3550, \delta_{P(2)} = 43.7 \text{ ppm}, J_{Pt-P(2)} = 3428 \text{ Hz}, J_{P-P} = 0.7 \text{ Hz}).$

Reaction of [PtClPh(dppe)] with NaCN

To [PtClPh(dppe)] (15.2 mg) dissolved in CH₂Cl₂ (15 cm³, dry, under argon) was added excess NaCN. This was stirred for 1 h then evaporated on a vacuum line to a white solid. A C₆D₆ (1 cm³) extract produced a ³¹P{¹H} NMR spectrum that showed only dppe ($\delta_P = -13.5$ ppm) present. Extraction with CDCl₃ also showed only dppe in the ³¹P{¹H} NMR spectrum.

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