ELECTROCHEMICAL REDUCTION OF PLATINUM(II) COMPLEXES CONTAINING BIDENTATE TERTIARY PHOSPHINE LIGANDS: EVIDENCE FOR THE GENERATION OF NON-LINEAR TWO-COORDINATE COMPLEXES

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Abstract—The electrochemical reduction of $[PtCl_2L_2]+L_2^*$ (L_2 and $L_2^* = Ph_2PCH_2CH_2$ PPh₂, dppe; $Cy_2PCH_2CH_2PCy_2$, dcpe; "Bu₂PCH₂CH₂P"Bu₂, dbpe) systems may proceed via two different routes. Path 1 involves reduction of $[PtCl_2L_2]$ to produce $[PtL_2]$ which is trapped by L_2^* to form $[PtL_2L_2^*]$. Path 2 involves prior reaction of $[PtCl_2L_2]$ with L_2^* to form $[PtL_2L_2^*]^{2+}$ which is reduced to form $[PtL_2L_2^*]$. The extent of prior reaction of $[PtCl_2L_2]$ with L_2^* has been monitored by both cyclic voltammetry, which detects only the electroactive components in solution, and by ³¹P{¹H} NMR spectroscopy, which allows structural assignments to be made. Bulk electrolyses have been performed at potentials sufficient to reduce both $[PtCl_2L_2]$ and $[PtL_2L_2^*]^{2+}$ and also at potentials sufficient to reduce $[PtL_2L_2^*]^{2+}$ but not to reduce $[PtCl_2L_2]$. Product analyses by ³¹P{¹H} NMR spectroscopy show that path 1 is operative in sterically congested systems, path 2 is operative in uncongested systems, and both pathways may be operative in systems with intermediate steric congestion. Reactions via path 2 produce $[PtL_2L_2^*]$ efficiently, whereas reactions via path 1 are complicated by alternative trapping reactions of $[PtL_2]$ with the solvent/electrolyte system which compete with trapping by L_2^* .

Recently we have shown that two-coordinate platinum(0) complexes containing either triphenylphosphine or triethylphosphine as ligands may be generated by electrochemical reduction of the corresponding *cis*-[PtCl₂L₂] complexes, ¹⁻³ eq. (1):

$$cis-[PtCl_2L_2] + 2e^- \longrightarrow [PtL_2] + 2Cl^-. \quad (1)$$

These relatively unhindered $[PtL_2]$ compounds exhibit enhanced reactivity in comparison with their better-known, more sterically crowded analogues, such as $[Pt(PCy_3)_2]$ (Cy = cyclohexyl).⁴ The electrochemical method of generation appears complementary to the previously reported photochemical⁵ [e.g. eq. (2)] or thermal⁴ [e.g. eq. (3)] techniques and the better-known chemical approaches⁶ to the

generation of [PtL₂] complexes :

$$[Pt(C_2O_4)(PEt_3)_2] \xrightarrow{h\nu} [Pt(PEt_3)_2] + 2CO_2 \quad (2)$$

trans-[PtH₂(PCy₃)₂]
$$\xrightarrow{\Delta}$$
[Pt(PCy₃)₂]+H₂. (3)

Interest in the chemistry of $[PtL_2]$ complexes was recently spurred by Whitesides and co-workers' reports⁷⁻⁹ that the C_{2v} intermediate $[Pt(Cy_2P CH_2CH_2PCy_2)]$, generated by thermolysis of an alkylhydride, reacts with alkanes and a variety of other organic substrates by C—H oxidative addition.¹⁰ Here we describe an initial investigation into the utility of electrochemical reductive strategies for the generation of such non-linear $[PtL_2]$ compounds from simple $[PtCl_2L_2]$ precursors.

RESULTS AND DISCUSSION

In a preparative scale electrochemical experiment both a relatively polar solvent and a background

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electrolyte are required and we felt that generation of a non-linear [PtL₂] compound in such a system might lead to indiscriminate reaction with these components. An experiment involving the bulk reductive electrolysis of $[PtCl_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in CH_3CN/C_6H_6 (1/1, v/v) containing tetra(n-butyl)ammonium perchlorate (TBAP, 0.08 M) at a mercury pool electrode employing a potential of -1.75 V (vs Ag/AgCl; -35 mV vs SCE) confirms this expectation. The ${}^{31}P{}^{1}H$ NMR spectrum of the product mixture showed that multiple products were formed, none of which could be identified by comparison of spectroscopic data with literature values. Data from this experiment are included in the Experimental for completeness. Given this situation, we felt that a trapping agent was necessary which would effectively compete for any non-linear [PtL₂] intermediate that might be generated. Such a trapping agent has to survive the very negative potentials required to reduce [PtCl₂L₂] complexes and bind strongly to any [PtL₂] fragment generated. Accordingly we sought to use bidentate ligands as traps for potential [PtL₂] fragments since the resulting $[PtL_2L_2^*]$ complexes are quite robust species.¹¹ The choice of such a set of trapping agents is not without inherent problems since it allows two possible reaction pathways, as illustrated in Scheme 1. The first path involves reduction of [PtCl₂L₂] to generate $[PtL_2]$ which is subsequently trapped by L_2^* to produce $[PtL_2L_2^*]$. The second path involves prior reaction of $[PtCl_2L_2]$ with L_2^* to generate $[PtL_2L_2^*]^{2+}$ which is subsequently reduced to produce $[PtL_2L_2^*]$. Thus, the pathway of the reaction

will in part be controlled by the extent to which the well-known halide displacement¹² of $[PtCl_2L_2]$ by L_2^* occurs prior to electrolysis. In order to investigate this question, ${}^{31}P{}^{1}H$ NMR measurements (see Experimental) were made on $[PtCl_2L_2]+L_2^*$ mixtures in CH₃CN/C₆D₆ which was 0.1 M in **TBAP.** In every case dication formation (Table 1) was detected, although it was clear that in cases where L_2 and L_2^* are both sterically demanding, the reaction does not proceed to completion in the time scale of these NMR experiments (typically 1-3 h). For example, although addition of Cy_2P $CH_2CH_2PCy_2$ (dcpe) to $[PtCl_2(dcpe)]$ did indeed produce $[Pt(dcpe)_2]^{2+}$, both free dcpe and unreacted [PtCl₂(dcpe)] were still present after several hours in solution. Thus, in every $[PtCl_2L_2] + L_2^*$ system we have investigated, both [PtCl₂L₂] and $[PtL_2L_2^*]^{2+}$ could potentially participate in an electrochemical reduction and so any differentiation between the possible pathways indicated in Scheme 1 must rely heavily on differences in the electrochemical behaviour of these components. Cyclic voltammetry $(CV)^{13-16}$ gives some insight into these differences.

Figure 1(a) shows the cyclic voltammogram of $[PtCl_2(dppe)]$ in CH₃CN (0.1 M in TBAP) at a Hg/Au amalgam electrode measured at a scan rate of 200 mV s⁻¹ over the potential range -0.50 to -2.20 V vs Ag/AgCl. On the basis of chemical evidence (*vide infra*) we assign peak A (-1.71 V) to the irreversible reduction of $[PtCl_2(dppe)]$, eq. (4):

$$[PtCl_2(dppe)] + 2e^- \longrightarrow [Pt(dppe)] + 2Cl^-. \quad (4)$$



Scheme 1.

Dication	Compound number ^b	δP ₁ (ppm)	δP ₂ (ppm)	<i>J</i> (Pt,P ₁) (Hz)	J(Pt,P ₂) (Hz)	J(P ₁ ,P _{1'}) (Hz)	$J(\mathbf{P}_2, \mathbf{P}_{2'})$ (Hz)	$\begin{array}{c} J(\mathbf{P}_1,\mathbf{P}_2) \\ (\mathrm{Hz}) \end{array}$	J(P ₁ ,P _{2'}) (Hz)
$[Pt(dppe)_2]^{2+}$	1	47.0		2375					
[Pt(dcpe)(dppe)] ²⁺	2	71.4	46.8	2256	2184	3	1.5	-15	277
$[Pt(dcpe)_2]^{2+}$	3	61.3		2187					
[Pt(dcpe)(dbpe)] ²⁺	4	67.7	49.3	2187	2155	6	-9	-20	278
[Pt(dppe)(dbpe)] ²⁺	5	49.5	46.1	2359	2290	12	12	-23	300
$[Pt(dbpe)_2]^{2+}$	6	45.0		2248					

Table 1. ³¹P{¹H} NMR data for platinum(II) dications⁴

"Recorded in C_6D_6 and referenced to external 85% H_3PO_4 with more positive values of the chemical shifts representing deshielding. Spectra of compounds 1, 3 and 6 measured at 36.2 MHz; spectra of compounds 2, 4 and 5 measured at 161.0 MHz.

^b For 2, $\widehat{P_1P_{1'}} = dcpe$, $\widehat{P_2P_{2'}} = dcppe$; for 4, $\widehat{P_1P_{1'}} = dcpe$, $\widehat{P_2P_{2'}} = dbpe$; for 5, $\widehat{P_1P_{1'}} = dppe$, $\widehat{P_2P_2} = dbpe$; for 1, 3 and 6, $P_1 = P_{1'} = P_2 = P_{2'}$.

Addition of one equivalent of dppe to the solution of $[PtCl_2(dppe)]$ followed by immediate measurement of a cyclic voltammogram produces the result shown in Fig. 1(b). Sweeping to negative potential now generates peak B, which we assign to the reduction of the dication $[Pt(dppe)_2]^{2+}$, with peak A, due to reduction of $[PtCl_2(dppe)]$, now barely visible. This interpretation is in accord with our ³¹P{¹H} NMR results (see Experimental) and with CV on independently prepared samples of both $[Pt(dppe)_2]Cl_2$ and $[Pt(dppe)_2]$.¹⁷ The reverse sweep



Fig. 1. Cyclic voltammograms measured in CH₃CN (10⁻¹ M TBAP) at a Au/Hg amalgam working electrode (1.77 mm²) using a scan rate of 200 mV s⁻¹. (a) 10⁻³ M solution of [PtCl₂(dppe)]; (b) 10⁻³ M solution of [PtCl₂(dppe)] immediately after adding one equivalent of dppe; (c) 10⁻³ M solution of [PtCl₂(dppe)] 1 h after adding one equivalent of dppe.

of the cyclic voltammogram shown in Fig. 1(b) produces peak B* which we assign to re-oxidation of $[Pt(dppe)_2]$. The question of reversibility of the processes generating peaks B and B* is redundant since the platinum(II)/platinum(0) interconversion is accompanied by a structural change between square-planar and tetrahedral geometries, and hence this reaction is perhaps best described as an EC process. In the absence of a structural change we would ideally anticipate a peak separation of 29.5 mV for the two-electron process. The actual separation of peaks B and B* in Fig. 1(b) is 150 mV. After standing for 1 h, the solution of [PtCl₂ (dppe)]+dppe produced the cyclic voltammogram shown in Fig. 1(c), i.e. no [PtCl₂(dppe)] was detected and the only electroactive component found in solution was $[Pt(dppe)_2]^{2+}$.

Based on the ${}^{31}P{}^{1}H$ NMR and CV results, it is not surprising that controlled potential bulk reductive electrolysis of [PtCl₂(dppe)] in the presence of one equivalent of dppe at a potential of -1.75 V (i.e. just negative of peak A) produces [Pt(dppe)₂] efficiently. As is common in bulk electrolyses of the type described here,¹⁻³ separation of the products from the background electrolyte, which is present in large excess, can be exceedingly difficult. Since we are primarily interested in the solution chemistry we have not typically performed such separations. In the present case, ${}^{31}P{}^{1}H{}$ NMR spectroscopy showed [Pt(dppe)₂] (83% estimated by peak heights in the spectrum) and traces of dppe, dppe oxide (dppeO) and dppe dioxide $(dppeO_2)$ to be present after electrolysis. The traces of phosphine oxides were present in approximately the same amount as impurities in the original dppe added to the reaction mixture (see Experimental).

Figure 2 shows a series of cyclic voltammograms



Fig. 2. Cyclic voltammograms measured in CH₃CN (10^{-1} M TBAP) at a Au/Hg amalgam working electrode (1.77 mm^2) using a scan rate of 200 mV s⁻¹. (a) 10^{-3} M solution of [PtCl₂(dppe)]; (b) 10^{-3} M solution of [PtCl₂(dppe)] immediately after adding one equivalent of dcpe; (c) 10^{-3} M solution of [PtCl₂(dppe)] 1 h after adding one equivalent of dcpe.

illustrating the effect of adding one equivalent of dcpe to $[PtCl_2(dppe)]$. Immediately after addition the sterically demanding dcpe ligand has generated only a small amount of dication and significant $[PtCl_2(dppe)]$ remains. After 1 h [Fig. 2(c)], no $[PtCl_2(dppe)]$ is detected and only the dication is observed. In the voltammogram shown in Fig. 2(c) the peak current for the reduction of $[Pt(dppe)(dcpe)]^{2+}$ is less than the peak current for the associated re-oxidation (i.e. $B < B^*$). This effect arises since reduction of $[Pt(dppe)(dcpe)]^{2+}$ occurs at all potentials more negative than B and the reduced species, which apparently adsorbs on the

electrode, is then stripped off by re-oxidation at one potential (B*) on the reverse sweep. The CV results for the [PtCl₂(dppe)]+dcpe system are in agreement with the ${}^{31}P{}^{1}H$ NMR results, where [Pt (dppe)(dcpe)]²⁺ was identified as the major species in solution (Table 1). Also detected was some [PtCl₂(dcpe)] formed by displacement of dppe by the stronger σ -donor dcpe, but this minor component is not detected in the cyclic voltammograms shown in Fig. 2. Given these results, the controlled potential bulk reductive electrolysis of $[PtCl_2(dppe)] + dcpe$ at -1.75 V might be anticipated to produce [Pt(dppe)(dcpe)] as a major product and this is indeed the case (Table 2). In addition to this product (54% by peak heights), some [Pt(dppe)₂] was also detected (8.5%), along with unreduced $[PtCl_2(dcpe)]$ (8.5%) and trace ligand impurities.

The reaction of dppe with [PtCl2(dcpe)] proceeds in a different manner to the reaction of dcpe with [PtCl₂(dppe)] (vide supra). Thus, addition of dppe to [PtCl₂(dcpe)] followed by immediate measurement of a cyclic voltammogram [Fig. 3(b)] shows some formation of a dication (peak B), but considerable [PtCl₂(dcpe)] remains. Interestingly, after scanning through peak A, the reverse scan gives rise to peak B* with a larger current than peak B. We interpret this as being due to the fact that traversing peak A generates [Pt(dcpe)], some of which is trapped by dppe to produce [Pt(dcpe)(dppe)]. On the reverse scan, the oxidation of [Pt(dcpe)(dppe)] thus produces an enhanced current for peak B*. After 1 h in solution the $[PtCl_2(dcpe)] + dppe$ system produces the voltammogram shown in Fig. 3(c). On the forward scan, peak B, corresponding to dication reduction, shows that significant amounts of this species are present. Peak A shows that some [PtCl₂(dcpe)] remains also. On the reverse scan, no

Platinum(0) complex	Compound number ^b	P ₁ (ppm)	P ₂ (ppm)	$J_{Pt-P(1)}$ (Hz)	J _{Рt—Р(2)} (Нz)	$J_{P(1)-P(2)}$ (Hz)	References
[Pt(dppe) ₂]	7	29.8		3729			11
[Pt(dcpe)(dppe)]	8	43.3	21.0	3610	3665	60	11
[Pt(dcpe) ₂]	9	30.7		3589			8
[Pt(dcpe)(dbpe)]	10	44.9	5.7	3613	3610	59	
[Pt(dbpe)(dppe)]	11	29.1	18.2	3710	3629	61	
[Pt(dbpe) ₂]	12	18.2		3629			

Table 2. ³¹P{¹H} NMR data for platinum(0) phosphine complexes^a

"Recorded in C_6D_6 and referenced to external 85% H₃PO₄ with more positive values of the chemical shifts representing deshielding. Spectra of compounds 7, 8, 9, 10 and 12 measured at 36.2 MHz; spectrum of 11 measured at 161.0 MHz.

^b For 8, $\widehat{P_1P_1} = dcpe$, $\widehat{P_2P_2} = dppe$; for 10, $\widehat{P_1P_1} = dcpe$, $\widehat{P_2P_2} = dbpe$; for 11, $\widehat{P_1P_1} = dppe$, $\widehat{P_2P_2} = dbpe$; for 7, 9 and 12, $P_1 = P_2$.



Fig. 3. Cyclic voltammograms measured in CH₃CN (10^{-1} M TBAP) at a Au/Hg amalgam working electrode (1.77 mm^2) using a scan rate of 200 mV s⁻¹. (a) 10^{-3} M solution of [PtCl₂(dcpe)]; (b) 10^{-3} M solution of [PtCl₂(dcpe)] immediately after adding one equivalent of dppe; (c) 10^{-3} M solution of [PtCl₂(dcpe)] 1 h after adding one equivalent of dppe.

peak for the oxidation of [Pt(dcpe)(dppe)] is seen, an occurrence for which we have no explanation. The ³¹P{¹H} NMR results on this system show only $[Pt(dcpe)(dppe)]^{2+}$ and trace ligand impurities in solution after *ca* 1 h. Controlled potential bulk reductive electrolysis at -2.2 V (i.e. just negative of peak A) produced [Pt(dcpe)(dppe)] in 50.4% spectroscopic yield, with some $[Pt(dppe)_2]$ and trace ligand impurities also detected. The unusual CV results thus remain unexplained.

The addition of one equivalent of dcpe to [PtCl₂(dcpe)] followed by immediate measurement of a cyclic voltammogram produced the result shown in Fig. 4(b). Clearly, no dication is detected. After 1 h in solution, the cyclic voltammogram shown in Fig. 4(c) is obtained. On the sweep to negative potential, peak B is barely visible with a very small current, consistent with ${}^{31}P{}^{1}H{}$ NMR measurements which show only low levels of $[Pt(dcpe)_2]^{2+}$ in solution. Square wave voltammetry unambiguously shows the presence of peak B despite its low current. Sweeping through peak A then produces peak B* in the cyclic voltammogram with a large current on the reverse sweep. Peak B* does not appear unless peak A is first traversed. This is clear evidence that traversing peak A produces [Pt(dcpe)], some of which is trapped by dcpe to generate $[Pt(dcpe)_2]$, and it is this species that is reoxidized at peak B*. This interpretation is sup-



Fig. 4. Cyclic voltammograms measured in CH₃CN (10⁻¹ M TBAP) at a Au/Hg amalgam working electrode (1.77 mm²) using a scan rate of 200 mV s⁻¹. (a) 10⁻³ M solution of [PtCl₂(dcpe)]; (b) 10⁻³ M solution of [PtCl₂(dcpe)] immediately after adding one equivalent of dcpe; (c) 10⁻³ M solution of [PtCl₂(dcpe)] 1 h after adding one equivalent of dcpe.

ported by the results of controlled potential bulk reductive electrolysis experiments. Thus, attempted electrolysis at -1.20 V (i.e. just negative of the small peak B) resulted in essentially no current flow since hardly any [Pt(dcpe)₂]²⁺ was present. Electrolysis at -2.25 V (i.e. just negative of peak A), however, results in significant generation of [Pt(dcpe)₂] (39% by peak heights) via initial formation of [Pt(dcpe)] and subsequent trapping by dcpe. Consistent with this interpretation is the observation of a second, unidentified product $[\delta = 51.6 \text{ ppm}, J(\text{Pt},\text{P}) = 3133 \text{ Hz}]$ which we feel must originate from reaction of [Pt(dcpe)] with components of the solvent/electrolyte system. These results suggest that electrochemical reduction of the $[PtCl_2(dcpe)] + dcpe$ system follows path 1 (Scheme 1) rather than path 2, which appears to dominate for the other systems described so far. It is also noteworthy that peak B* in the cyclic voltammogram shown in Fig. 4(c) may contain more than one component (vide infra). This may be due to the oxidation of transient platinum(0) species other than $[Pt(dcpe)_2]$. Species such as [Pt(dcpe)] $(solvent)_{r}$ or $[Pt(dcpe)(\eta^{1}-dcpe)]$ may be likely candidates, although, whatever the nature of this species, it is too short-lived for detection by ${}^{31}P{}^{1}H$ NMR methods.

Addition of dppe to $[PtCl_2(dbpe)]$ (where dbpe = ${}^{n}Bu_2PCH_2CH_2P^{n}Bu_2$) gave rise to the cyclic



Fig. 5. Cyclic voltammograms measured in CH_3CN (10^{-1} M TBAP) at a Au/Hg amalgam working electrode (1.77 mm^2) using a scan rate of 200 mV s⁻¹. (a) 10^{-3} M solution of [PtCl₂(dbpe)]; (b) 10^{-3} M solution of [PtCl₂(dbpe)] immediately after adding one equivalent of dppe; (c) 10^{-3} M solution of [PtCl₂(dbpe)] 1 h after adding one equivalent of dbpe.

voltammograms shown in Fig. 5. Immediately after the addition, substantial $[Pt(dbpe)(dppe)]^{2+}$ is formed while some $[PtCl_2(dbpe)]$ persists. This situation is essentially unchanged after 1 h [Fig. 5(c)]. The ³¹P{¹H} NMR spectrum agrees with this assignment exactly (see Experimental). Controlled potential bulk reductive electrolysis at -2.40 V (i.e. just negative of peak A) produces largely [Pt (dbpe)(dppe)], as expected (63% by peak heights), but small amounts of $[Pt(dppe)_2]$ and an unidentified product [$\delta = 44.2$ ppm, J(Pt,P) = 2245Hz] are also formed. The latter component presumably has its origins in a reaction of [Pt(dbpe)], produced by reduction of $[PtCl_2(dbpe)]$, with components of the solvent/electrolyte system.

We find that addition of the more sterically demanding dcpe to $[PtCl_2(dbpe)]$ proceeds in a different manner to the reaction of dppe with $[PtCl_2(dbpe)]$. Thus, Fig. 6 shows the CV results for the addition of one equivalent of dcpe to $[PtCl_2(dbpe)]$. Immediately after addition, a sweep to negative potential reveals the reduction of $[Pt(dbpe)(dcpe)]^{2+}$ (peak B) followed by reduction of $[PtCl_2(dbpe)]$ (peak A). The latter process generates [Pt(dbpe)] which we might anticipate leads to the formation of additional [Pt(dbpe)(dcpe)] via possible intermediates such as $[Pt(dbpe)(solvent)_x]$ and/or $[Pt(dbpe)(\eta^1-dcpe)]$. Thus, the reverse sweep reveals peak B* with a larger current than peak B



Fig. 6. Cyclic voltammograms measured in CH₃CN (10⁻¹ M TBAP) at a Au/Hg amalgam working electrode (1.77 mm²) using a scan rate of 200 mV s⁻¹. (a) 10⁻³ M solution of [PtCl₂(dbpe)]; (b) 10⁻³ M solution of [PtCl₂(dbpe)] immediately after adding one equivalent of dcpe; (c) 10⁻³ M solution of [PtCl₂(dbpe)] 1 h after adding one equivalent of dcpe.

and containing several components for oxidation of the different platinum(0) species present. Consistent with this interpretation, we find that after 1 h in solution [Fig. 6(c)], the reaction of [PtCl₂(dbpe)] with dcpe has proceeded to completion and only $[Pt(dbpe)(dcpe)]^{2+}$ is detected on the scan to negative potential. Since reduction of the cation occurs at all potentials more negative than peak B, the reverse sweep causes stripping of adsorbed platinum(0) at the potential of peak B*, which now corresponds to the re-oxidation of just one species, [Pt(dbpe)(dcpe)]. Controlled potential bulk reductive electrolysis results support these conclusions. Thus electrolysis at -1.25 V (i.e. just negative of peak B) produces [Pt(dbpe)(dcpe)] essentially quantitatively. However, electrolysis at -2.40 V (i.e. just negative of peak A) produces not only [Pt(dbpe)(dcpe)] (49% by peak heights) but also the disproportionation products $[Pt(dbpe)_2]$ and [Pt(dcpe)₂] as well as several unidentified species, formed in low yield, presumably by reaction of [Pt(dbpe)] with components of the solvent/ electrolyte system. ³¹P{H} NMR data for these unidentified minor components are listed in the Experimental for completeness.

Interestingly, we found that controlled potential electrolysis of an independently synthesized sample of $[Pt(dbpe)_2]Cl_2$, performed at a potential of -1.50 V, generated not only $[Pt(dbpe)_2]$ but also

an unidentified complex (see Experimental), suggesting that the reduction of four-coordinate dbpe complexes may involve ligand dissociation, producing reactive fragments.

CONCLUSIONS

The work described here shows that non-linear [PtL₂] intermediates can be generated by electrochemical reduction of readily available $[PtCl_2L_2]$ precursors. In the absence of a specific trapping agent, [Pt(dppe)] was found to react indiscriminately with the components of the solvent/ electrolyte system, but in the presence of another bidentate ligand as a trapping agent some selectivity for formation of $[PtL_2L_2^*]$ was achieved. The existence of two competing pathways (Scheme 1) caused us to investigate a series of [PtCl₂L₂] precursors and L₂* trapping agents, and this work shows how the steric and electronic effects of L₂ and L₂* modify reactivity. Based upon these results, we are currently examining the electrochemical generation and reactivity of non-linear [PtL₂] complexes containing ligands other than dppe in order to achieve more selective reactions with organic substrates.18

EXPERIMENTAL

General procedures

Acetonitrile (Fisher, ACS grade) was stirred with CaH_2 for 48 h, decanted and distilled from P_4O_{10} . The first 15% of the distillate was discarded as was the last 15%. The middle 70% (b.p. 83.0° C) was refluxed with CaH₂ and then fractionally distilled. Again the first and last 15% of the distillate was discarded and the middle 70% was stored under argon over Al₂O₃, activated at 110°C for 24 h. Benzene (Fisher, ACS grade) was freshly distilled from sodium wire under nitrogen prior to use. Benzene-d₆ was purchased from Aldrich and deoxygenated prior to use. Tetra(n-butyl)ammonium perchlorate (TBAP, G.F.S.) was recrystallized five times from absolute ethanol and dried in vacuo for 48 h at room temperature. The phosphines, bis(dicyclohexylphosphino)ethane and bis(di{nbutyl}phosphino)ethane were purchased from Strem and bis(diphenylphosphino)ethane was prepared by literature methods.¹⁹ Commercial bis(dicyclohexylphosphino)ethane was purified by recrystallization from tetrahydrofuran prior to use. which removed several impurities although small

amounts of dcpeO and dcpeO₂ remained. The complexes [PtCl₂(dppe)] and [PtCl₂(dcpe)] were prepared by displacement of 1,5-cyclooctadiene from [PtCl₂(cod)]²⁰ in methylene chloride. The complex [PtCl₂(dbpe)] was synthesized by the displacement of acetonitrile from [PtCl₂(CH₃CN)₂]²¹ in acetonitrile and was recrystallized from THF. The preparation of the dication [Pt(dbpe)₂]Cl₂ was accomplished by reaction of the bis-acetonitrile complex with two equivalents of phosphine.¹²

³¹P{¹H} (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 (161 MHz) spectrometer when second-order effects were seen at the lower field of the FX 90Q spectrometer. ³¹P{¹H} NMR chemical shifts were measured using 85% H₃PO₄ as an external standard, with positive values of the chemical shift representing deshielding. Yields were estimated from peak heights in the ³¹P{¹H} NMR spectra unless cited as isolated yields.

The mixed ligand platinum(II) dications gave rise to ³¹P{¹H} NMR spectra which could be interpreted in terms of AA'BB' or AA'XX' spin systems (ignoring the effects of ¹⁹⁵Pt). Each spectrum was simulated using Varian's 6.2 software package to within an error of ± 5 Hz of the expected line positions, with the majority of the lines simulated to less than ± 1 Hz of the positions in the original spectra.

Cyclic voltammograms were obtained using a Bioanalytical Systems 100 control unit. Typically, 2.0×10^{-3} M solutions of the complexes in acetonitrile (10 cm³), which was 0.08 M in TBAP, were employed. In this solvent system the ferrocene/ ferrocenium couple appears at +0.760 V with a peak separation of 90 mV. The cobaltocene/ cobaltocenium couple appears at -0.570 V with a peak separation of 82 mV.

A single compartment cell, thermostatted to $25 \pm 1^{\circ}$ C, equipped with a Ag/AgCl reference electrode (-35 mV vs SCE), a platinum wire auxiliary electrode and a mercury/gold amalgam working electrode was used. We have discussed CV of platinum(II) complexes using similar techniques previously.¹³⁻¹⁶ Controlled potential bulk reductive electrolyses¹⁻³ 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 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.

³¹P{¹H} NMR measurements

The reactions of $[PtCl_2L_2]$ with L_2^* were monitored by ³¹P{¹H} NMR spectroscopy. Solutions were prepared in acetonitrile/benzene-d₆ and in acetonitrile/benzene-d₆ which was 0.1 M in TBAP. Essentially identical results were obtained for the two solvent systems.

(i) $[PtCl_2(dppe)] + dppe$. $[Pt(dppe)_2]^{2+}$ and dppe were identified in solution. Also present were small amounts of dppeO and dppeO₂ which were initially present as trace impurities in the dppe employed in the reaction. No insoluble material was formed.

(ii) $[PtCl_2(dppe)] + dcpe$. $[Pt(dppe)(dcpe)]^{2+}$ and $[PtCl_2(dcpe)]$ were identified in solution along with dcpeO₂, originally present as an impurity in the dcpe employed in the reaction. Some insoluble material {perhaps $[PtCl_2(dppe)]$ } was also formed.

(iii) $[PtCl_2(dcpe)] + dppe$. $[Pt(dcpe)(dppe)]^{2+}$ and dppe were identified in solution along with the ligand impurities dppeO and dppeO₂.

(iv) $[PtCl_2(dcpe)] + dcpe$. $[Pt(dcpe)_2]^{2+}$, $[PtCl_2(dcpe)]$ and dcpe were identified in solution along with the ligand impurity dcpeO₂.

(v) $[PtCl_2(dbpe)] + dppe$. $[Pt(dbpe)(dppe)]^{2+}$ and $[PtCl_2(dbpe)]$ were identified in solution. Trace amounts of unidentified compounds which did not appear to contain platinum were identified at very high signal-to-noise ratios. No insoluble material was formed.

(vi) $[PtCl_2(dbpe)] + dcpe$. $[Pt(dbpe)(dcpe)]^{2+}$, $[Pt Cl_2(dcpe)]$ and $[Pt(dbpe)_2]^{2+}$ were identified in solution along with the trace ligand impurity dcpeO₂.

Controlled potential electrolyses (CPE)

Each CPE described below was repeated at least twice with consistent results.

(i) CPE of [PtCl₂(dppe)] in the presence of dppe. 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 done 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 the mercury (18 cm³) and a small magnetic stirrer bar were 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 -1.75 V.

To the pre-electrolysed solution was added $[PtCl_2(dppe)]$ (ca 30 mg) and one equivalent of dppe (ca 18 mg) which was purged with argon for 1 h. This was then electrolysed to essentially zero current at a potential of -1.75 V. This usually required 30 min to 1 h and coulometry indicated approximately a 2-electrons/equivalent reduction, with integrations in the range of 1.9-2.1 electrons/ equivalent. When the electrolysis was complete, the solution was transferred (using inert atmosphere techniques) to a Schlenk tube and evaporated. The yellowish solid was extracted with benzene $(2 \times 10 \text{ cm}^3)$ and evaporated to give a yellow solid which was dissolved in C_6D_6 and transferred to an NMR tube. ${}^{31}P{}^{1}H$ NMR spectroscopy showed [Pt(dppe)₂], $\delta_{\rm P} = 29.8$ ppm, $J_{\rm Pt-P} = 3729$ Hz (82.9%); dppe, $\delta = -13.4$ ppm (4.6%); dppeO, $\delta_{P(1)} = 26.8$ ppm, $\delta_{P(2)} = -12.5$ ppm, $J_{P-P} = 34$ Hz (5.6%); dppeO₂, $\delta = 28.1$ ppm (5.9%).

(ii) *CPE* of [PtCl₂(dppe)] in the presence of dcpe. To the pre-electrolysed (-1.75 V, CH₃CN) solution was added [PtCl₂(dppe)] (*ca* 30 mg) and one equivalent of dcpe (*ca* 20 mg) which was then purged with argon for 1 h and electrolysed to essentially zero current at -1.75 V. This usually required 30 min to 1 h and coulometry indicated approximately a 2-electrons/equivalent reduction, with integrations in the range of 2.0-2.1 electrons/ equivalent. After work-up as previously described, ³¹P{¹H} NMR spectroscopy showed [Pt(dppe) (dcpe)] (54.0%), [Pt(dppe)₂] (8.5%); [PtCl₂(dcpe)] (7.5%); dcpe, $\delta = 0.36$; dcpeO, $\delta_{P(1)} = 45.8$, $\delta_{P(2)} =$ 1.2 ppm, $J_{P-P} = 37$ Hz; dcpeO₂, $\delta = 47.7$ ppm.

(iii) CPE of $[PtCl_2(dcpe)]$ in the presence of dppe. To the pre-electrolysed solution (-2.20 V,CH₃CN) was added [PtCl₂(dcpe)] (ca 30 mg) with one equivalent of dppe (ca 18 mg) which was purged with argon for 1 h and electrolysed to zero current flow (1-1.5 h) with coulometry indicating a 2-electrons/equivalent reduction (range 1.9-2.1 electrons/equivalent). Collection of a yellow solid which precipitated the acetonitrile vielded from [Pt(dcppe)(dppe)] (50.4% isolated yield). A trace of dppeO₂ was seen by ${}^{31}P{}^{1}H$ NMR. In the solution, which was worked-up as previously described, remained [Pt(dppe)₂] (17.0%); dppeO₂ (25.1%), dppeO (28.0%); dppe (11.4%); and dcpeO₂ (18.5%).

(iv) CPE of $[PtCl_2(dcpe)]$ in the presence of dcpe. (a) To the pre-electrolysed solution (-2.20 V, CH₃CN) was added $[PtCl_2(dcpe)]$ (ca 30 mg) and one equivalent of dcpe (ca 19 mg) which was purged with argon for 1 h and electrolysed to zero current flow (1.5–2.5 h) with coulometry indicating a 2-

electrons/equivalent reduction (range 1.9–2.3 electrons/equivalent). After work-up, ³¹P{¹H} NMR (C₆D₆) showed [Pt(dcpe)₂] (39.2%); dcpeO₂ (18.2%); dcpeO (10.2%); dcpe (25.5%); and a platinum complex with the data: $\delta = 51.6$ ppm, $J_{Pt-P} = 3133$ Hz (6.9%).

(b) To a pre-electrolysed solution $(-1.20 \text{ V}, \text{CH}_3\text{CN})$ was added [PtCl₂(dcpe)] (*ca* 30 mg) and one equivalent of dcpe (*ca* 19 mg) which was purged with argon for 1 h and electrolysed to near zero current flow (1–2 h). The current flow was very low and coulometry indicated that only 0.15 electrons/ equivalent were consumed. After the usual workup, ³¹P{¹H} NMR (C₆D₆) showed [PtCl₂(dcpe)] (20.0%); dcpe (52.8%); dcpeO (9.1%); and dcpeO₂ (18.1%).

(v) *CPE of* [PtCl₂(dbpe)] *in the presence of* dppe. To the pre-electrolysed solution $(2.40 \text{ V}, \text{CH}_3\text{CN})$ was added [PtCl₂(dbpe)] (ca 30 mg) with one equivalent of dppe (ca 20 mg) and purged with argon for 1 h. This solution was electrolysed until approximately 2 electrons/equivalent were consumed and then the electrolysis was terminated (30 min to 1 h). The formation of a precipitate occurred as the acetonitrile was concentrated and this precipitate was isolated: [Pt(dbpe)(dppe)] (52.6% isolated yield). [Pt(dbpe)(dppe)] was identified by its 161 MHz ${}^{31}P{}^{1}H$ NMR spectrum due to the secondorder nature of the spectrum obtained at 36.2 MHz. The remaining solution contained several compounds including [Pt(dbpe)(dppe)] (66.6%); [Pt $(dppe)_2$] (10.3%) along with traces of $dbpeO_2$, dppeO₂ and dppeO. The only component unidentified had the data: $\delta = 44.2 \text{ ppm}, J_{\text{Pt}-\text{P}} = 2243 \text{ Hz}.$

(vi) CPE of $[PtCl_2(dbpe)]$ in the presence of dcpe. (a) To the pre-electrolysed solution (-2.40 V,CH₃CN) was added [PtCl₂(dbpe)] (ca 30 mg) with one equivalent of dcpe (ca 22 mg). This was electrolysed until 2-electrons/equivalent were consumed (30 min to 1 h). A precipitate formed which was collected. ³¹P{¹H} NMR data of this dark yellow solid (in C₆D₆ solution) revealed [Pt(dbpe) (dcpe)] (48.8%); [Pt(dcpe)₂] (11.2%); and dcpe (33.6%). In the remaining solution was seen five platinum phosphine complexes. The data for these unidentified complexes are as follows: $\delta =$ 46.6 ppm, $J_{Pt-P} = 2270$ Hz (29.2%); $\delta_P = 49.8$ ppm, $J_{Pt-P} = 2020$ Hz (12.9%); $\delta_P = 39.6$ ppm, $J_{\text{Pt}-\text{P}} = 2619 \text{ Hz} (13.7\%); \delta_{\text{P}} = 65.0 \text{ ppm}, J_{\text{Pt}-\text{P}} =$ 2430 Hz (11.8%); $\delta_{\rm P} = 68.0$ ppm, $J_{\rm Pt-P} = 2064$ Hz (6.4%). The remaining peaks were attributed to dcpe, dbpe and the corresponding oxides.

(b) To the pre-electrolysed solution (1.50 V, CH_3CN) was added [PtCl₂(dbpe)] (*ca* 30 mg) with one equivalent of dcpe (*ca* 22 mg). This was electrolysed to near zero current at which point 2.2

electrons/equivalent were consumed and a white precipitate was collected. ${}^{31}P{}^{1}H$ NMR data of this white solid revealed [Pt(dbpe)(dcpe)] as the only phosphorus-containing product. The remaining solution contained no significant phosphorus-containing material and only traces of dcpe and dbpeO₂ were observed spectroscopically.

(vii) *CPE of* [Pt(dbpe)₂]Cl₂. To a pre-electrolysed solution (-1.50 V, CH₃CN/C₆H₆, 1:1 v/v) the complex [Pt(dbpe)₂]Cl₂ (*ca* 30 mg) was added and then purged with argon for 1 h. The solution was electrolysed to near zero current with coulometry indicating approximately 2-electrons/equivalent consumed (range 2.0–2.2 electrons/equivalent). After work-up as previously described the ³¹P{H} NMR spectrum revealed three platinum complexes in addition to peaks for the free phosphine (dbpe) and its oxides. Of the three platinum complexes two were identified as [Pt(dbpe)₂] (48.9%) and [Pt(dbpe)₂]²⁺ (19.2%). The remaining complex, $\delta_P = 36.7$ ppm, $J_{2Pt-P} = 3090$ Hz (11.5%) remains unidentified.

(vii) CPE of [PtCl₂(dppe)] in the absence of a trapping agent. To the pre-electrolysed solution $(-1.75 \text{ V}, \text{CH}_3\text{CN/C}_6\text{H}_6, 1:1 \text{ v/v})$ the complex [PtCl₂(dppe)] (ca 30 mg) was added and the solution was purged with argon for 1 h. The solution was electrolysed to near zero current with coulometry indicating consumption of 1.4 electrons/equivalent. After work-up as previously described, the ³¹P{¹H} NMR spectrum revealed the presence of the following compounds: $\delta_P = 38.3 \text{ ppm}$, $J_{Pt-P} =$ 1626 Hz; $\delta_P = 40.4 \text{ ppm}$, $J_{Pt-P} = 3587 \text{ Hz}$; $\delta_P =$ 33.4 ppm, $J_{Pt-P} = 4592 \text{ Hz}$; $\delta_P = 35.2 \text{ ppm}$, $J_{Pt-P} = 3592 \text{ Hz}$, $J_{P-P} = 8 \text{ Hz}$. The ¹H NMR spectrum of this mixture did not reveal any resonances attributable to hydrides.

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