Cyclic Voltammetric Behaviour of some Cationic η^3-Allyl Complexes of Pd(II) and Pt(II) in Comparison with Hydride Reduction

G. CARTURAN

Facoltà di Ingegneria, Università di Trento, Mesiano, Trento, Italy

M. BIASIOLO, S. DANIELE, G. A. MAZZOCCHIN and P. UGO

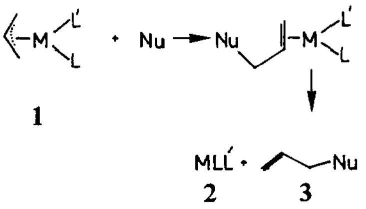
Facoltà di Chimica Industriale, Università di Venezia, S. Marta, Venice, Italy

(Received February 7, 1986; revised May 6, 1986)

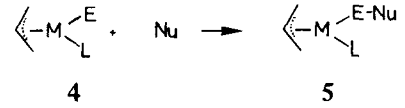
Abstract

η^3-Allyl complexes of the type $[M(\eta^3\text{-allyl})(L_2)]^+$ (M = Pd; allyl = 1-MeC_3H_4; L_2 = 1,5-C_8H_{12}, 2MeCN; allyl = C_3H_5; L_2 = 1,5-C_8H_{12}, $2PPh_3$, $2P(C_6H_{11})_3$, 2MeCN; allyl = 2-MeC_3H_4; L_2 = 1,5-C_8H_{12}, 2MeCN, $2PPh_3$; M = Pt; allyl = C_3H_5; L_2 = $2PPh_3$, $2P(C_6H_{11})_3$) are reduced by H^- and by cathodic electron transfer. In both cases the nature of the reduction products is determined by the coordination properties of L_2, elemental metal appearing when L_2 = 1,5-C_8H_{12} or 2MeCN, and ML_2 species being formed in other cases. The reduction potentials are related to the stabilities of the starting complexes, and a parallel is drawn with nucleophilic attack on η^3-allyl complexes of d^8 transition metal ions. The one-electron demand for electrochemical reduction and loss of the allyl group to form 1,5-hexadienes agree with the proposed reaction mechanism in which elimination of the allyl radical is proposed.

Introduction

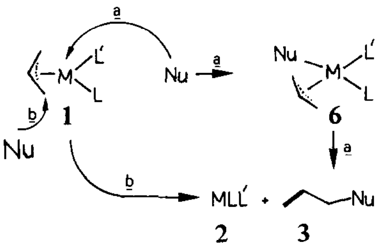


(1)



(2)

Nucleophilic attack on the η^3-allyl complexes of d^8 transition metal ions may be directed either towards the η^3-allyl group (eqn. (1)) with consequent reduction of both coordination and oxidation numbers [1–6] or towards an ancillary ligand containing a suitable electrophilic centre (eqn. (2)) [7]. Reaction (1) is by far the more frequent; it has been used successfully in preparing 14- or 16-electron species of zerovalent complexes [1, 2], but it often leads to decomposition, the coordinated ligands being unable to stabilize species 2, which behave like transient intermediates [4–6]. Considerable attention has been paid both to the effect of ancillary ligands in controlling the stereochemistry of reaction (1) [8, 9] and to the nature of the entering nucleophile [5, 10, 11]. Nucleophilic attack may or may not involve primary coordination to the metal center, so that alternative mechanisms *a* and *b* were proposed for the occurrence of type 2 species (eqn. (3)):



(3)

In order to obtain further insight into the reduction reactions (1) and (2), we compared the behaviour of some cationic η^3-allyl complexes of Pd(II) and Pt(II) in reduction by H^- nucleophilic attack with that in reduction under electrochemical conditions. Strong nucleophiles such as metal alkyls [11] or hydrides [12] are believed to attack the metal center directly, according to eqn. (3a), whereas electron transfer reduction should not promote immediate breaking of the bonds to the original ligands.

Cyclic voltammetry seemed particularly suitable for studying the resistence to reduction of the η^3-allyl compounds, the ability of coordinated ligands to stabilize the intermediates, and the mechanism of allyl group elimination during reduction.

0020-1693/86/$3.50

© Elsevier Sequoia/Printed in Switzerland

Experimental

Materials, Instrumentation and General Procedures

Solvents were dried by standard methods [13] and distilled under nitrogen. Reagent-grade acetonitrile was purified by repeated distillation from P_2O_5 and kept over molecular sieves under nitrogen. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte for the cyclic voltammetric and coulometric experiments; it was prepared from perchloric acid and tetrabuthylammonium hydroxide, recrystallized from methanol and dried in a vacuum oven at 50 °C.

Dimers $[PdCl(\eta^3\text{-allyl})]_2$ and the tetramer $[PtCl(allyl)]_4$ were prepared by known procedures [14, 15] $[Pd(\eta^3\text{-}2,MeC_3H_4)(1,5\text{-}C_8H_{12})]^+BF_4^-$, $[Pd(\eta^3\text{-}C_3H_5)(1,5\text{-}C_8H_{12})]^+BF_4^-$ and $[Pd(\eta^3\text{-}2,MeC_3H_4)(MeCN)_2]^+BF_4^-$ were obtained as reported previously [16, 17]. $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+BF_4^-$ and $\{Pt(\eta^3\text{-}C_3H_5)[P(C_6H_{11})_3]_2\}^+BF_4^-$ were obtained by treating $[PtCl(C_3H_5)]_4$ in CH_2Cl_2 with 2 equivalents of the appropriate phosphine and subsequent treatment with $AgBF_4$ to remove chloride. The products were recrystallized from CH_2Cl_2/ether and identified by comparison of their ^1H and $^{31}P\{^1H\}$ NMR spectra with reported data [18–20].

Infrared spectra were recorded with a Perkin-Elmer Model 597 spectrophotometer using Nujol mulls between CsI plates. ^1H NMR spectra were recorded on a Varian FT 80A spectrometer using $CDCl_3$ solutions, and $^{31}P\{^1H\}$ spectra were recorded on the same instrument at 32.204 MHz, with 85% H_3PO_4 as external standard. GLC analyses were carried out with an HP 5730A instrument equipped with an 8-foot 10% FFAP Chrom W.AW DMSC 80 - 100 column. In all cases GLC identification was based on comparison with authentic samples; quantitative measurements are based on subsequent enrichments of single components with standard amounts of the chemical species examined.

Preparation of $[Pd(\eta^3\text{-allyl})(L_2)]^+BF_4^-$ Complexes (allyl = C_3H_5: L = PPh_3, $P(C_6H_{11})_3$, MeCN; allyl = 1-MeC_3H_4: L = MeCN, L_2 = 1,5-C_8H_{12}; allyl = 2-MeC_3H_4: L = PPh_3)

A typical preparation, of $[Pd(1\text{-}MeC_3H_4)(C_8H_{12})]^+BF_4^-$, is described in detail. Other complexes were obtained by the same procedure, which is similar to well established methods [16, 17]. $[PdCl(1\text{-}MeC_3H_4)]_2$ (0.47 g, 2.4 mmol) in 30 ml of CH_2Cl_2 was treated under nitrogen with stirring at room temperature with solid $AgBF_4$ (0.47 g, 1.2 mmol); AgCl slowly separated. After 1 h a solution of 1,5-C_8H_{12} (0.27 g, 2.4 mmol) in CH_2Cl_2 was added dropwise during 1 h to the suspension, and the mixture was set aside for 2 h. The AgCl was then filtered off, the solution was concentrated to 10 ml by evaporation under reduced pressure (yield 0.75 g, 92%).

Analytical and spectroscopic data for these compounds are reported in Table I.

Reactions with $LiBEt_3H$ in Tetrahydrofuran

(a) Reaction of $[Pd(\eta^3\text{-}C_3H_5)(1,5\text{-}C_8H_{12})]^+$

A solution of the 1,5-C_8H_{12} complex (0.34 g, 1 mmol) in 20 ml of THF was treated at –80 °C under nitrogen with 1 ml of 1 M $LiBEt_3H$ in THF. The solution darkened immediately as Pd metal precipitated. GLC analysis of the solution revealed the quantitative formation of propene and 1,5-C_8H_{12}. Under identical experimental conditions the acetonitrile complex $[Pd(\eta^3\ C_3H_5)(MeCN)_2]^+$ gave Pd metal, propene, and MeCN.

(b) Reaction of $\{Pd(\eta^3\text{-}C_3H_5)[P(C_6H_{11})_3]_2\}^+$

The complex (0.79 g, 1 mmol) in 25 ml of solvent was treated at –80 °C with 1 ml of a 1 M THF solution of the hydride. The solution was put aside for 4 h, during which it turned pale yellow. GLC analysis showed that propene had been formed quantitatively. The solution was evaporated to dryness under reduced pressure and the residual solid extracted with toluene. The product was precipitated by addition of methanol, and identified as $\{Pd[P(C_6H_{11})_3]_2\}$ (0.51 g) on the basis of its ^{31}P NMR spectrum in $CD_3C_6D_5$ (δ = 38.2 ppm at –70 °C) [21].

Reaction of $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+BF_4^-$ with $LiBEt_3H$ in Acetonitrile

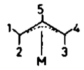
A solution of the complex (0.15 g, 0.2 mmol) in 30 ml of MeCN (0.1 M in TBAP) was treated at –80 °C with a stoichiometric amount of the hydride (0.1 M in THF). The temperature was raised to –20 °C, and the solution turned reddish-brown and propene was quantitatively evolved. The solution was siphoned off under argon into the three-electrode cell and studied immediately by cyclic voltammetry.

Electrochemical Apparatus and Procedures

Voltammetric experiments were carried out in a three-electrode cell. The working electrode was a glassy carbon surrounded by a spiral PT counter-electrode. The potential of the working electrode was calibtrated by use of a Luggin capillary-reference compartment which could be adjusted (syringe barrel).

Coulometric experiments were carried out in a H-shaped cell with cathodic and anodic compartments separated by a sintered glass disc. The working electrode was a platinum gauze; a mercury pool was used as counter electrode. In all cases an aqueous saturated calomel electrode (SCE) was used as reference. The voltammetric unit employed was a

TABLE I. Analytical and Spectroscopic Data for $[M(\eta^3\text{-allyl})(L_2)]^+BF_4^-$ Complexes

Compound	Melting point[a] (℃)	Analytical data[b]			^{1}H NMR[c] allyl resonances 					Other resonances	^{31}P NMR[d]
		%C	%H	%N	1,4	2,3			5		
$[Pd(C_3H_5)(MeCN)_2]^+$ [e,f]	107	26.9 (26.56)	3.5 (3.48)	9.0 (8.85)	4.32(2H) J_5 = 7.1 J_{1-4} = 1.5	3.15(2H) J_5 = 12.5			5 62(1H)	2.30(6H)	
$[Pd(C_3H_5)(C_8H_{12})]^+$	160	38.9 (38.57)	5.0 (4.97)		4.90(2H) J_5 = 7.3	3.75(2H) J_5 = 13.3			6.02(1H)	2.48(8H) 6.20(4H)	
$[Pd(C_3H_5)(PPh_3)_2]^+$	155	61.6 (61.72)	4.5 (4.62)		4.0(2H)[g]	3.50(2H)[g]			6.04(1H)[g]	7.7–7.0 (30 H)	22.90
$\{Pd(C_3H_5)[P(C_6H_{11})_3]_2\}^+$	140	59.1 (58.93)	8.8 (8.94)		4.47(2H)[g]	2.99(2H)[g]			5.42(1H)[g]	1.1–1.7 (66 H)	35.68
$[Pd(2\text{-}MeC_3H_4)(PPh_3)_2]^+$	197	62.0 (62.16)	4.7 (4.79)		see ref. 32						24.05
					Me	2	3	4	5		
$[Pd(1\text{-}MeC_3H_4)(MeCN)_2]^+$ [e]	h	30.1 (29.07)	3.8 (3.94)	8.6 (8.48)	1.30(3H) J_2 = 6.3	4.04 J_5 = 12.3	2.83 J_5 = 12.2	3.99 J_5 = 7.8	5.35	2.22(6H)	
$[Pd(1\text{-}MeC_3H_4)(C_8H_{12})]^+$	189	40.0 (40.43)	5.2 (5.33)	–	1.79(3H) J_2 = 6.5	4.95 J_5 = 13.5	3.63 J_5 = 13.7	4.70 J_5 = 7.9	5.95	2.60(8H) 6.21(4H)	

[a] All compounds decompose on melting. [b] Calculated values in parentheses. [c] δ values ±0.01 ppm; J values, ±0.5 Hz; spectra recorded in $CDCl_3$ at 233 K. [d] δ values, ±0.04 ppm. [e] ν_{CN} at 2298 and 2320 cm^{-1}. [f] ^{1}H NMR spectra registered at 298 K. [g] Broad coalescence singlet. [h] Unstable above 60 ℃.

three-electrode system assembled with MP-system 1000 equipment connected to a digital logic function generator Amel Model 568. Depending on the scale rate employed, the recording device was either an Amel Model 863 X–Y recorder or a Tracor Northern NS 570 A digital storage oscilloscope/waveform digitizer with analogue output for X–Y recorders.

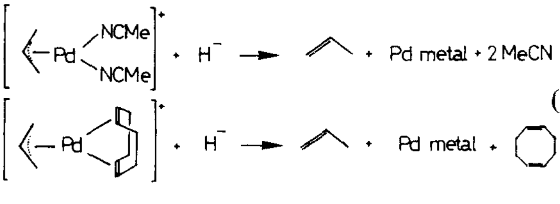
In controlled-potential electrolyses an Amel Model 552 potentiostat was used; the associated coulometer was an Amel Model 731 integrator.

All experiments were performed under rigorously dried argon at a constant temperature of 25 °C.

Results and Discussion

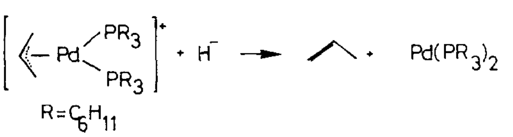
The $[M(\eta^3\text{-allyl})(L_2)]^+$ complexes used were selected in order to provide information about the influence of the nature of metal ions (M = Pd, Pt), of the type of allyl moiety (allyl = C_3H_5, 1-MeC_3H_4, 2-MeC_3H_4), and of the nature of the various ligands on the metal (L_2 = 1,5-C_8H_{12}; L = PPh_3, $P(C_6H_{11})_3$, MeCN) in electrochemical reduction. It seemed appropriate in some cases to compare electrochemical reduction with hydride reduction.

$[Pd(\eta^3\text{-}C_3H_5)(1,5\text{-}C_8H_{12})]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(MeCN)_2]^+$ react with stoichiometric amounts of $LiBEt_3H$ in THF at –80 °C according to eqn. (4):



(4)

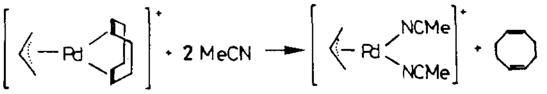
Under the same conditions, $\{Pd(\eta^3\text{-}C_3H_5)[P(C_6H_{11})_3]_2\}^+$ gives $\{Pd(P(C_6H_{11})_3]_2\}$ (eqn. (5)):



(5)

These results indicate that the coordination properties of the ancillary ligands determine whether it is possible to isolate metal reduction compounds. The formation of $\{Pd[P(C_6H_{11})_3]_2\}$ in reaction (5) may account for the much greater stabilizing effect of two $P(C_6H_{11})_3$ ligands than of 1,5-C_8H_{12} in eqn (4); the Pd(O)–C_8H_{12} system is unstable even though two dienes are coordinated to the metal [22]. The quantitative evolution of propene in reaction (4) is consistent with previous reports on $NaBH_4$ reduction of η^3-allyl Pd(II) complexes [12] and excludes the involvement of an olefinic centre of the coordinated 1,5-C_8H_{12} in the H^- nucleophilic attack. If the Pd centre is assumed to be the primary site of H^- coordination, propene elimination from the intermediate of type **6** in eqn. (3) is strongly favoured owing to the adjacent position of H- and C_3H_5- groups and the energy gain arising from C–H bond formation [23]

The electrochemical behaviour of the $[M(\eta^3\text{-allyl})(L_2)]^+$ complexes was studied in MeCN solution. Compounds with L_2 = 1,5-C_8H_{12} were involved in the reaction:



(6)

GLC analysis of the MeCN solutions of these complexes after distillation at low temperature under reduced pressure revealed the presence of a quantitative amount of 1.5 C_8H_{12}, indicating that the complexes are converted into the corresponding bis-MeCN species

Table II lists the peak potentials obtained; in all cases the reduction step is irreversible as confirmed by cyclic voltammograms recorded at high scan rate up to 100 V s^{-1}. No oxidation peak could be observed even at the higher scan rates.

TABLE II. Peak Potential Values from Voltammograms for $[M(\eta^3\text{-allyl})(L_2)]^+$ Complexes, Quoted *vs.* Aqueous SCE[a]

M	Allyl	L_2	Cathodic Peak (V)	Anodic peak (V)
Pd	C_3H_5	2MeCN	–1.020	–
Pd	1,MeC_3H_4	2MeCN	–1.150	–
Pd	2 MeC_3H_4	2MeCN	–1.150	–
Pd	C_3H_5	$2PPh_3$	–1.450	–0.050
Pd	2-MeC_3H_4	$2PPh_3$	–1.550	–0.050
Pd	C_3H_5	$2P(C_6H_{11})_3$	–1.750	–0.100
Pt	C_3H_5	$2PPh_3$	–1.450	–0.080
Pt	C_3H_5	$2P(C_6H_{11})_3$	–1.730	–0.120

[a] Solvent = acetonitrile; scan rate = 0.1 V s^{-1}; T = 25 °C; [Complex] = 2.5×10^{-3} M; [TBAP] = 0.1 M; potential values ±0.005 V.

Allyl–phosphino complexes were reduced at the cathode to give well-defined chemical species available for anodic oxidation, whereas the allyl–MeCN compounds gave Pd metal. Figure 1 shows the cyclic voltammetric curves obtained from $[Pd(\eta^3\text{-}C_3H_5)(MeCN)_2]^+$ (solid line) and $\{Pd(\eta^3\text{-}C_3H_5)[P(C_6H_5)_3]_2\}$ (dotted line). In the former case formation of Pd metal is shown by precipitation of a black powder during the coulometric experiments; these results are consistent with eqns. (4) and (5).

The parallel between chemical and electrochemical reductions was confirmed for compound $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$. Figure 2 shows the cyclic voltam-

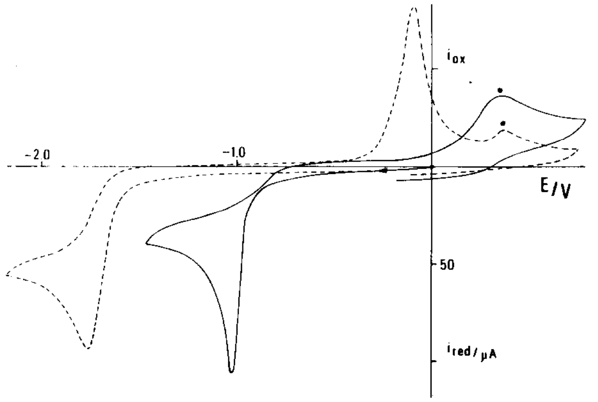


Fig. 1. Cyclic voltammetric curves for $[Pd(\eta^3\text{-}C_3H_5)(MeCN)_2]^+$ (solid line) and for $\{Pd(\eta^3\text{-}C_3H_5)[P(C_6H_{11})_3]_2\}^+$ (dotted line). 25 °C, [TBAP] = 0.1 M, [Complex] = 2.5 × 10^{-3} M; working electrode = glassy carbon; scan rate 100 mV s^{-1}.

metric behaviour of this compound (solid line), the cathodic peak at −1.45 V being attributed to allyl compound reduction and the anodic peak at −0.050 V to the oxidation of this reduced species. Under the same conditions $[Pd(\eta^3\text{-}(C_3H_5)(PPh_3)_2]^+$ was treated with a stoichiometric amount of $LiBEt_3H$ in the three-electrode cell; the solution, which contained the chemically reduced species formed in reaction (5), displayed (dotted line) an anodic peak at −0.05 V identical to that observed in oxidation of the species obtained by cathodic reduction of $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$. However, the cathodic process occurred at a more negative potential and gave a complex reduction pattern, with concomitant disappearance of the original cathodic peak at −1.45 V. These results confirmed the identity of the H^- and electron reduction products and the irreversibility of the reduction of the allyl complex.

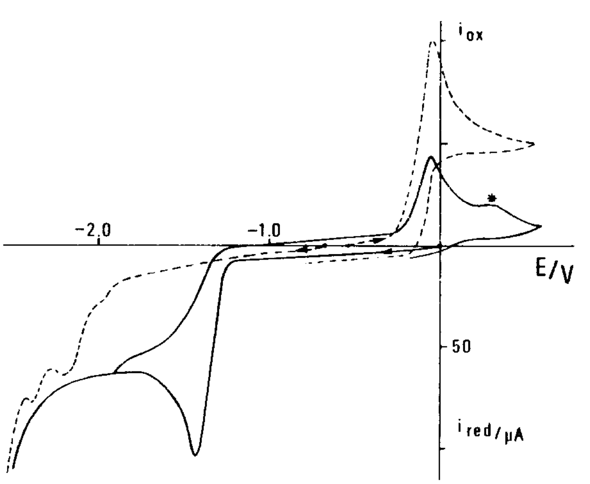
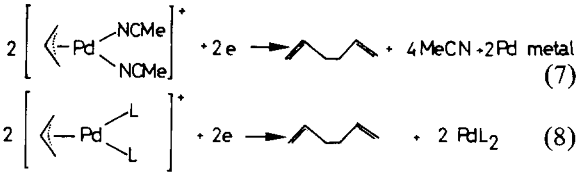


Fig. 2. Cyclic voltammetric curves for $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$ (solid line) and for '$Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$ + $LiBEt_3H$ (dotted line). For experimental conditions, see Fig. 1.

In all cases the cathodic reactions involved a one-electron process, as revealed by coulometric measurements; GLC analysis of the reduction products revealed the presence as the major organic product of the diene corresponding to the combination of two allyl fragments. The cathodic reduction of $[Pd(\eta^3\text{-allyl})(L_2)]^+$ compounds may involve labile species still retaining the allyl fragment in the metal coordination sphere, and decomposition of these complexes may involve the solvent, with the formation of different organic products. These labile species are probably responsible for a broad anodic peak observed at positive potentials (see asterisks in Figs. 1 and 2).

Apart from this minor byproduct formation, cathodic reduction of $[M(\eta^3\text{-allyl})(L_2)]^+$ complexes mainly follows the routes shown in eqns. (7) and (8) for L = MeCN and L = phosphine, respectively:



(7)

(8)

The resistence to reduction (Table II) follows the order $1\text{-}MeC_3H_4 \simeq 2\text{-}MeC_3H_4 > C_3H_5$ for both reactions (7) and (8). This sequence is consistent with data for the reactivity of η^3-allyl Pd(II) complexes [24, 25], and is associated with the electron donor character of the methyl group, which makes the metal centers less prone to electron transfer. Similarly, the greater resistence to reduction of $P(C_6H_{11})_3$ complexes compared with PPh_3 analogues can be attributed to back donation by π-bonding from metal to PPh_3 via electron delocalization on phenyl rings. PPh_3 is less basic than $P(C_6H_{11})_3$ [26, 27], so that a minor electrophilic character may be better envisaged for the metal center in the case of $\{M(\eta^3\text{-allyl})[P(C_6H_{11})_3]_2\}^+$. The reduction potentials for Pd(II) and Pt(II) complexes when composed of the same ligands are remarkably close, in agreement with a general pattern in the reactivity of species $[M(\eta^3\text{-allyl})(L_2)]^+$ (M = Pd, Pt) which undergo reaction (1) under almost identical experimental conditions whenever M = Pd or Pt [1, 2].

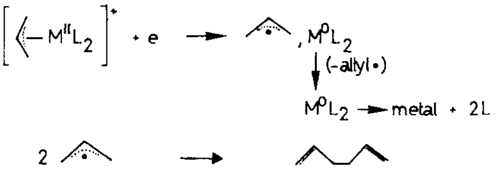
In cases where L = phosphine, the anodic process may be attributed to oxidation reaction (9). Coulometric experiments indicate that this is a two-electron process occurring on reaction (8) products, probably

$$[ML_2(MeCN)_n] \longrightarrow [ML_2(MeCN)_n]^{2+} + 2e \qquad (9)$$

holding a different number of coordinated solvent molecules, *i.e.* MeCN, for $L = PPh_3$ or $P(C_6H_{11})_3$.

Cathodic reduction of these oxidized species displays a complex pattern involving at least two steps and cannot be interpreted simply. On the other hand, the identical value of –0.05 V for the oxidation of $[Pd(PPh_3)_2(MeCN)]_n$ species obtained by reduction of $[Pd(\eta^3\text{-allyl})(PPh_3)_2]^+$ (allyl = C_3H_5, 1-MeC_3H_4) is significant, and agrees with and tests the occurrence of reaction (8) irrespective of allyl group nature or its irreversibility.

In conclusion, electrochemical and hydride reductions of $[M(\eta^3\text{-allyl})(L_2)]^+$ complexes obey the same parameters. The observed one-electron reduction agrees with previous findings concerning other η^3-allyl complexes of d^8 metal ions [28–30]. In our case, the occurrence of the diene molecules formed by two allyl groups suggests the following reaction mechanism:



where decomposition to metal occurs for L = MeCN. The diene formation agrees with experimental and theoretical results on allyl radical interactions [31] and should not involve the metal or the metal complex.

Acknowledgement

We wish to acknowledge financial support for this study from the M.P.I (Rome).

References

1 W. Kuran and A. Musco, *J. Organomet. Chem., 40,* C47 (1972); *Inorg. Chim. Acta, 12,* 187 (1975).

2 A. Immirzi A. Musco, P. Zambelli and G. Carturan, *Inorg. Chim. Acta, 13,* L13 (1975).

3 (a) R. Baker *Chem. Rev., 73,* 487 (1973); (b) B. M. Trost *Acc. Chem. Res. 13,* 385 (1980); (c) J. Tsuji, *Acc. Chem. Res., 2,* 144 (1969); (d) B. M. Trost *Tetrahedron, 33,* 2615 (1977).

4 (a) B. Åkemark, G. Åkemark, L. S. Hegedus and K. Zettemberg, *J. Am. Chem. Soc., 103,* 3037 (1981); (b) B. Åkemark, J. E. Backvall A. Lowemborg and K. Zettemberg, *J. Organomet. Chem., 166,* C33 (1979).

5 (a) B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc., 102,* 4730 (1980); (b) B. M. Trost and L. Weber, *J. Am. Chem. Soc., 97,* 1611 (1975); (c) B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc., 100,* 3435 (1978).

6 S. Numata and H. Kurosawa, *J. Organomet. Chem., 131,* 301 (1977).

7 A. Scrivanti, G. Carturan and B. Crociani, *Organometallics, 2,* 1612 (1983).

8 J. S. Temple, M. Riediken and J. Schwartz, *J. Am. Chem. Soc., 104,* 1310 (1982).

9 (a) B. Åkemark, K. Zetteberg, S. Honsson, B. Krakenberg and A. Vitagliano, *Organometallics, 3,* 679 (1984); (b) B. Åkemark and A. Vitagliano, *Organometallics, 4,* 1275 (1985).

10 (a) Y. Takahashi, K. Tsukiyama, S. Sakai and Y. Ishii, *Tetrahedron Lett.,* 1913 (1970); (b) R. F. Heck, *J. Am. Chem. Soc., 90,* 5542 (1968).

11 T. Hayashi, M. Konosci and M. Kumada, *J. Chem. Soc., Chem. Commun.,* 107 (1984).

12 (a) M. L. Bullpitt and W. Kitching, *J. Organomet. Chem., 46,* 21 (1972); (b) E. Keinan and N. Greenspoon, *Tetrahedron Lett., 23,* 241 (1982).

13 D. D. Perrin, W. L. F. Amarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, 1966.

14 F. R. Hartley and S. R. Jones, *J. Organomet. Chem., 66,* 465 (1974).

15 J. H. Lukas and J. E. Blom, *J. Organomet. Chem., 26,* C25 (1971).

16 D. J. Mabott, B. E. Mann and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.,* 294 (1977).

17 D. A. White, *Inorg. Synth., 13,* 61 (1972).

18 N. M. Boag, M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc. Dalton,* 1208 and 1200 (1980).

19 T. G. Attig and H. C. Clark, *J. Organomet. Chem., 94,* C49 (1975).

20 (a) B. E. Mann and A. Musco, *J. Organomet. Chem., 181,* 439 (1979); (b) K. Vrieze and H. C. Volger, *J. Organomet. Chem., 9,* 537 (1967); (c) G. Carturan, A. Scrivanti, U. Belluco and F. Morandini, *Inorg. Chim. Acta, 27,* 37 (1978).

21 B. E. Mann and A. Musco, *J. Chem. Soc., Dalton Trans.,* 1673 (1975).

22 M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 271 (1977).

23 J. Halpern, *Acc. Chem. Res., 15,* 238 (1982).

24 G. Carturan and G. Strukul, *J. Organomet. Chem., 157,* 475 (1978).

25 J. Powell and A. W. L. Chau, *J. Organomet. Chem., 35,* 203 (1972).

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

27 R. Mason and D. W. Meek, *Angew. Chem., Int. Eng. Ed., 96,* 193 (1978).

28 N. G. Connelly and E. W. Geiger, 'Advances in Organomet. Chem.', Vol. 23, Academic Press, New York, 1984, pp. 37–38.

29 L. S. Hegedus and E. L. Waterman, *J. Am. Chem. Soc., 96,* 6789 (1974).

30 G. Bontempelli, S. Daniele and M. Fiorani, *J. Electroanal. Chem., 160,* 249 (1984).

31 N. Trong Anh, 'Les Règles de Woodward–Hoffmann', Ediscience, Paris, Chap. 4.

32 J. Powell and B. L. Show, *J. Chem. Soc. A,* 774 (1968).