Electroanalytical and Spectrophotometric Investigations on the Metal(II)–1,2-Bis(diphenylphosphino)ethane–Acetylacetonate System (M = Ni, Pd, or Cu) in Acetonitrile

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The soft–hard mixed-ligand complexes $[M(acac)(dppe)]^+$ [M = Ni or Pd, acac = acetylacetonate, dppe = 1,2-bis(diphenylphosphino)ethane] have been characterized by a combination of electroanalytical and spectrophotometric measurements. These species can easily be synthesized in acetonitrile both by a ligand conproportionation reaction upon starting from the corresponding acetylacetonate and diphosphine homoleptic species and from stoicheiometric amounts of $[M(dppe)_2]^{2+}$ and $acac^-$. Upon reaction of equimolar amounts of $[M(acac)_2]$ and dppe, the same synthesis can be achieved in the case of M = Pd, while for M = Ni the ligand-exchange reaction is followed by the reduction of nickel(II) to nickel(I) and nickel(O) occurring at the expense of the displaced $acac^-$. The mixed-ligand complex cannot be obtained for Cu in that copper(II) is reduced to copper(I) when dppe is present. In this low oxidation state copper is unable to co-ordinate $acac^-$ and appears to be stable as $[Cu(MeCN)_4]^+$ or $[Cu(dppe)_2]^+$.

We have recently reported on the preparation and optical properties of novel heteroleptic β-carbonylenolate diphosphine nickel(II) complexes[1] and found that they appear stable in dichloromethane solution towards ligand disproportionation. This finding suggests that such a mixed ligand set is well suited for stabilizing nickel(II) in aprotic solvents. A similar stability seems to be displayed by $[Pd(acac)(dppe)]^+$ (acac = acetylacetonate, dppe = $Ph_2PCH_2CH_2PPh_2$), while such a co-ordination sphere appears to be unable to stabilize copper(II).[2]

With the aim of obtaining further information on these metal(II) mixed-ligand complexes and, in particular, of ascertaining whether their stability is mainly due to thermodynamic reasons or to favourable kinetic factors, we have carried out an electroanalytical and spectrophotometric investigation to characterize fully the M^{II}–dppe–$acac^-$ system (M = Ni, Pd, or Cu) in acetonitrile.

Experimental

Chemicals.—All the chemicals used were of analytical reagent grade quality. Anhydrous $[Ni(acac)_2]$ and 1,2-bis(diphenylphosphino)ethane (dppe) were used as received, while $[Cu(acac)_2]$ and $[Pd(acac)_2]$ were recrystallized from dichloromethane–n-hexane. The salts $[Ni(acac)(dppe)]BPh_4$ and $[Pd(acac)(dppe)]BPh_4$ were prepared as described previously[1,2] and $[Ni(dppe)_2][NO_3]_2$ was synthesized according to the literature.[3] The salt $[Pd(dppe)_2][NO_3]_2$ was prepared by slow addition of $[Pd(dppe)_2]Cl_2$[4] (1 mmol) dissolved in ethanol (*ca.* 25 cm^3), with stirring, to an equimolar ethanol solution of $AgNO_3$ (10 cm^3). After stirring for about 1 h at 60 °C, the hot off-white suspension was filtered and the precipitate obtained was washed with ethanol, with diluted aqueous ammonia, and again with ethanol. The yellow-brown microcrystalline residue was dried under vacuum, yield 85% (Found: C, 60.2; H, 4.65; N, 2.70. Calc. for $C_{52}H_{48}N_2O_6P_4Pd$: C, 60.80; H, 4.70; N, 2.70%).

Stock solutions of tetrabutylammonium acetylacetonate in acetonitrile were prepared before use by exhaustive electrochemical reduction at −1.9 V of solutions of the acid Hacac containing tetrabutylammonium perchlorate. Similarly, stock solutions of anhydrous copper(II) perchlorate in acetonitrile were prepared by electrochemical oxidation of metallic copper in NBu_4ClO_4–acetonitrile solutions at 1.2 V. Reagent-grade acetonitrile was further purified as reported[5] and was stored over 0.4-nm molecular sieves under a nitrogen atmosphere. The supporting electrolytes NBu_4ClO_4 and tetrabutylammonium tetrafluoroborate were recrystallized from methanol and dried under vacuum at 50 °C. In all electroanalytical tests, fully deoxygenated nitrogen was used to remove dissolved oxygen from the working solution. This gas was first passed through sulphuric acid to remove traces of water and then equilibrated to the vapour pressure of acetonitrile.

Apparatus and Procedure.—Voltammetric experiments were conducted in a three-electrode cell in which the working electrode was either a platinum or a glassy-carbon disc mirror-polished with graded alumina powder prior to each set of tests. In the cell, it was surrounded by a platinum spiral counter electrode and its potential was probed by a Luggin capillary-reference electrode compartment, the position of which could be adjusted by mounting it on a syringe barrel. An aqueous saturated calomel electrode (s.c.e.) was used as the reference electrode. Copper(I) was electrogenerated in acetonitrile under controlled-potential conditions (0.1 V) in an H-shaped cell with anodic and cathodic compartments separated by a sintered glass disc. The working electrode was a copper wire and a platinum spiral served as the counter electrode; again, the reference electrode was an aqueous s.c.e. The solutions thus obtained were then transferred to the voltammetric cell under nitrogen with a degassed syringe.

The voltammetric unit was a three-electrode system assembled with a MPI-System 1000 in conjunction with a PAR

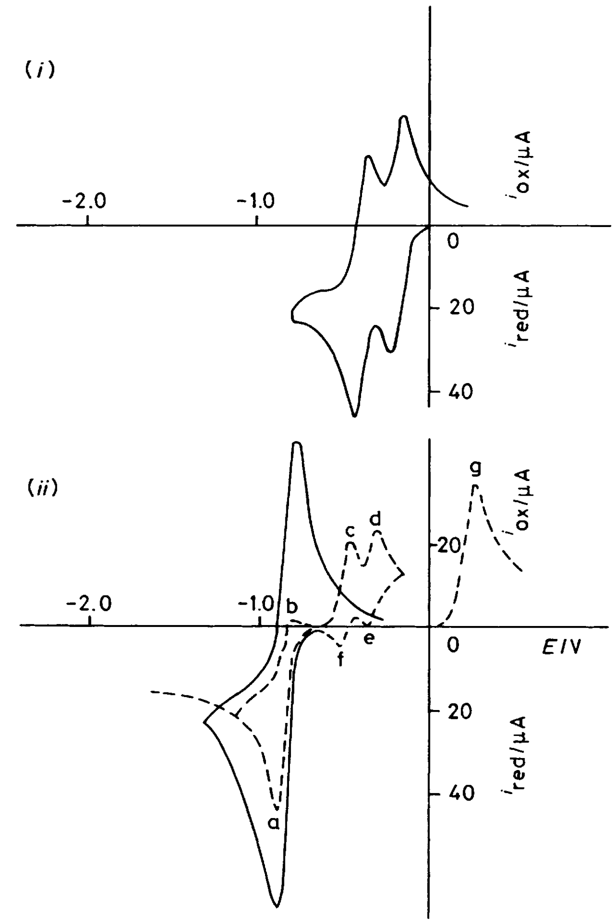


Figure 1. Cyclic voltammograms recorded at 0.1 V s^{-1} with a glassy-carbon electrode for 0.1 mol dm^{-3} NBu_4BF_4–acetonitrile solutions containing (*i*) $[Ni(dppe)_2]^{2+}$ (8.0×10^{-4} mol dm^{-3}) and (*ii*) $[Ni(dppe)_2]^{2+}$ (1.0×10^{-3} mol dm^{-3}) after addition of equimolar $acac^-$ (– – – –); the full line corresponds to the same solution as above at 1 V s^{-1} and with a sensitivity reduced to one-half

175 Universal Programmer. The recorder device was either an Hewlett-Packard model 7040 A X-Y recorder or a Tracor-Northern NS-570A digital storage oscilloscope/waveform digitizer with analogue output for X-Y recorders, depending on the scan rate applied. In the controlled-potential generation of copper(I), an Amel model 552 potentiostat was used and the associated coulometer was an Amel model 731 integrator.

In spectrophotometric measurements a Perkin-Elmer Lambda 5 spectrometer was employed.

All measurements were performed at 25 °C.

Results and Discussion

The System Ni^{II}–dppe–$acac^-$.—It is known that $[Ni(dppe)_2]^{2+}$ in acetonitrile exhibits a cyclic voltammetric behaviour characterized by two one-electron cathodic–anodic reversible systems [see Figure 1(*i*)] corresponding to the processes[6] (1) and (2). Addition of equimolar amounts of $acac^-$

$$[Ni^{II}(dppe)_2]^{2+} + e^- \rightleftharpoons [Ni^{I}(dppe)_2]^{+} \quad (1)$$

$$[Ni^{I}(dppe)_2]^{+} + e^- \rightleftharpoons [Ni^{0}(dppe)_2] \quad (2)$$

to $[Ni(dppe)_2]^{2+}$ solutions results in a fast significant change in the voltammetric picture leading to the pattern in Figure 1(*ii*), which is displayed also by an authentic sample of $[Ni(acac)(dppe)]^+$ dissolved in acetonitrile.

The height of the cathodic peak a compared with that of the parent complex $[Ni(dppe)_2]^{2+}$ [Figure 1(*i*)] indicates that a one-electron process is involved in the reduction of the heteroleptic species. This conclusion is based on the reasonable assumption that the diffusion coefficients characterizing these two fairly similar complexes do not differ appreciably. The relevant process appears to be reversible and uncomplicated at scan rates higher than *ca.* 1 V s^{-1} [Figure 1(*ii*), full line], in that the peak potential is unaffected by the potential sweep rate and the peak separation $E_{pb} - E_{pa}$ as well as the peak width $E_{p/2} - E_p$ are equal to 60 mV. On the contrary, a chemical reaction following the charge transfer becomes apparent by lowering the scan rate [Figure 1(*ii*), dashed line], as indicated by the progressive decrease in the ratio i_{pb}/i_{pa}. This (e.c.) process leads to the appearance of the same anodic–cathodic systems c–f and d–e for pure $[Ni(dppe)_2]^{2+}$ [see Figure 1(*i*)].

These data allow us to conclude that the cathodic–anodic system a–b is attributed to the occurrence of the simple electron-transfer reaction (3) followed by the very fast decay of

$$[Ni^{II}(acac)(dppe)]^{+} + e^- \rightleftharpoons [Ni^{I}(acac)(dppe)] \quad (3)$$

the mixed-ligand nickel(I) species. In such a decay, a redox step has to be involved (in the homogeneous phase), which affords the species $[Ni^0(dppe)_2]$ responsible for the anodic–cathodic systems c–f and d–e [see redox processes (1) and (2)]. The instability of the β-diketonate diphosphine nickel(I) complex is not unexpected in that a mixed hard–soft co-ordination sphere is not likely to stabilize a basically soft centre like nickel(I).[6–8]

A further proof of the remarkable stability of the nickel(II) mixed-ligand species is the observation that a quantitative and rapid ligand conproportionation reaction occurs between equimolar amounts of $[Ni(acac)_2]$ and $[Ni(dppe)_2]^{2+}$ in acetonitrile [equation (4)]. Voltammetric tests show the rapid

$$[Ni(dppe)_2]^{2+} + [Ni(acac)_2] \rightleftharpoons 2[Ni(acac)(dppe)]^{+} \quad (4)$$

conversion of the profile reported in Figure 1(*i*) into that in Figure 1(*ii*); at the same time a fast colour change from light yellow, $[Ni(dppe)_2]^{2+}$, to yellow-orange, $[Ni(acac)(dppe)]^+$, is observed.

In order to estimate the thermodynamics of equation (4), we carried out a parallel spectrophotometric investigation. The continuous-variation method was used to plot the absorbance values obtained from spectra recorded at 425 nm (where the mixed-ligand complex exhibits its absorption maximum) for a series of acetonitrile solutions containing various concentrations of both $[Ni(acac)_2]$ and $[Ni(dppe)_2]^{2+}$, wherein their sum is kept constant. The resulting curve allowed us to confirm the 1:1 ratio of $acac^-$ to dppe for the mixed-ligand complex, but no reliable information concerning the relevant conproportionation constant could be obtained, owing to its relatively high value. Such a constant could however be estimated to be higher than 10^3 by the molar ratio method.[9]

The reaction between $[Ni(acac)_2]$ and dppe results in a rather complex pattern. Voltammetric tests reveal that the addition of equimolar amounts of dppe to the neutral nickel(II) species causes a rapid although not quantitative formation of the mixed-ligand derivative $[Ni(acac)(dppe)]^+$, together with small amounts of reduced nickel species, namely $[Ni(dppe)_2]^+$ and $[Ni(dppe)_2]$. The concentrations of the last complexes increase with time at the expense of the heteroleptic complex whose concentration is concomitantly decreased. This conversion, which is almost complete in about 3 h, is also observed upon addition of free $acac^-$ to the mixed-ligand nickel(II) complex, thus indicating that the reduction of nickel(II) accompanying

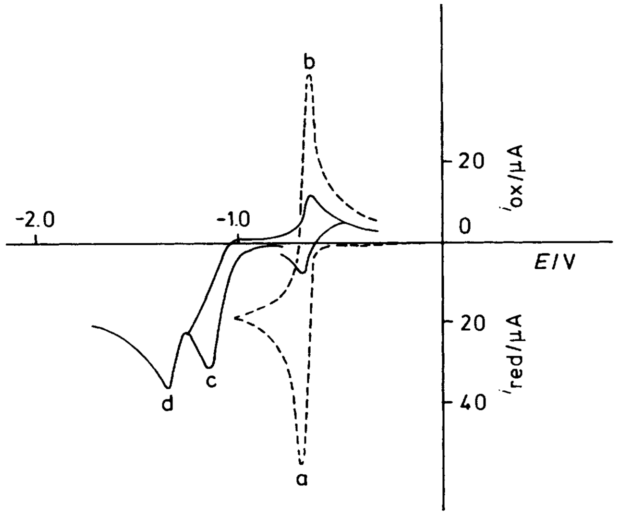


Figure 2. Voltammograms recorded with a glassy-carbon electrode for 0.1 mol dm^{-3} NBu_4ClO_4–acetonitrile solutions containing (– – – –) $[Pd(dppe)_2]^{2+}$ (8.0 × 10^{-4} mol dm^{-3}) and (——) $[Pd(dppe)_2]^{2+}$ (8.0 × 10^{-4} mol dm^{-3}) after addition of equimolar acac$^-$ and equilibration. Scan rate 0.1 V s^{-1}

the above ligand-exchange reaction is caused by the acac$^-$ ion displaced by the added phosphine ligand. No detailed investigation of this reaction pathway has been performed. However, the ability of the acetylacetonate anion to act as a reducing agent towards metal complexes has been noted previously.[10]

The System Pd^{II}–dppe–acac$^-$.—A solution of $[Pd(dppe)_2]^{2+}$ in acetonitrile exhibits the cyclic voltammetric behaviour depicted in Figure 2 (dashed line), from which it is apparent that this complex undergoes a two-electron appreciably reversible reduction. It yields the corresponding palladium(0) complex which is reoxidized to Pd^{II} in the associated anodic peak b, according to the literature.[11]

When acac$^-$ is added in a 1:1 molar ratio to $[Pd(dppe)_2]^{2+}$ solutions a slow reaction takes place yielding the final voltammetric profile in Figure 2 (full line) after about 2 h. Reduction peak a disappears completely in favour of two more cathodic peaks c and d, the second of which has been identified as due to the reduction of $[Pd(acac)_2]$ by comparison with the behaviour exhibited by an authentic sample. Cathodic peak c is associated with a one-electron process and with the anodic–cathodic system b–a (see Figure 2), thus indicating that it leads to the formation of $[Pd(dppe)_2]$. Moreover, the final voltammetric picture in Figure 2 (full line) is identical to that displayed by solutions of independently prepared[2] $[Pd(acac)(dppe)]^+$. All these findings enable us to infer that the equimolar addition of acac$^-$ to $[Pd(dppe)_2]^{2+}$ leads to the formation of the heteroleptic palladium(II) complex which is reduced at peak c according to equation (5), thus yielding the species responsible for the associated peaks b (Pd^0) and d (Pd^{II}).

$$[Pd^{II}(acac)(dppe)]^+ + e^- \longrightarrow \tfrac{1}{2}[Pd^0(dppe)_2] + \tfrac{1}{2}[Pd^{II}(acac)_2] \quad (5)$$

The voltammetric pattern of Figure 2 (full line) for the heteroleptic complex is also observed after equilibration when equimolar amounts of dppe are added to solutions of $[Pd(acac)_2]$. In this case, no chemical reduction of palladium(II) is observed in contrast with the analogous reaction of the corresponding nickel species reported above. On the other hand, the heteroleptic palladium(II) complex is indefinitely stable towards reduction even when large amounts of acac$^-$ are present. Finally, $[Pd(acac)(dppe)]^+$ can also be obtained upon reaction of equimolar amounts of the two homoleptic palladium(II) complexes. In contrast with the case of nickel(II), both these last ligand substitution and ligand conproportionation reactions are relatively slow, requiring some hours to go to completion.

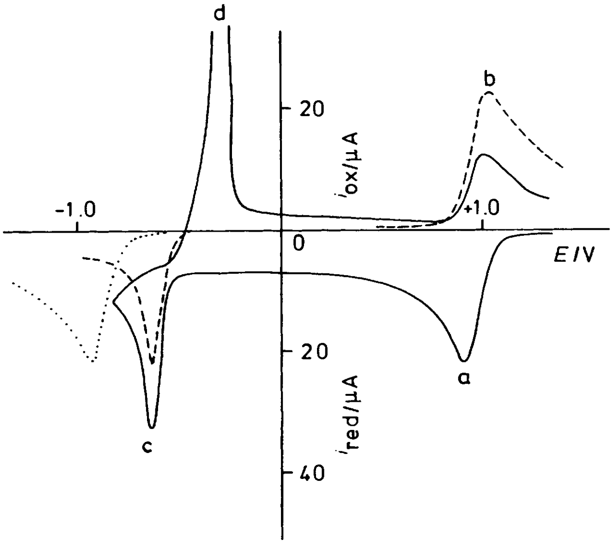
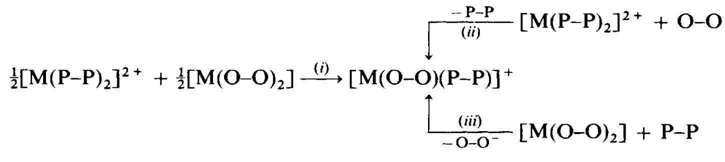


Figure 3. Voltammograms recorded with a glassy-carbon electrode for 0.1 mol dm^{-3} NBu_4ClO_4–acetonitrile solutions containing (——) $Cu(ClO_4)_2$ (1.0 × 10^{-3} mol dm^{-3}), (– – – –) $Cu(ClO_4)_2$ (1.0 × 10^{-3} mol dm^{-3}) after addition of dppe (5.0 × 10^{-4} mol dm^{-3}), and (· · · ·) $Cu(ClO_4)_2$ (1.0 × 10^{-3} mol dm^{-3}) after addition of dppe (2.5 × 10^{-3} mol dm^{-3}). Scan rate 0.1 V s^{-1}

A parallel spectrophotometric investigation made possible an estimate of the equilibrium constant for the ligand conproportionation reaction. Thus, the continuous-variation method applied to the $[Pd(acac)_2]$—dppe system in acetonitrile gave a value of 60 ± 20. The equilibration reaction is slow (some hours), in contrast to that observed for the nickel(II) system under comparable conditions, thus confirming the electrochemical findings.

The System Cu^{II}–dppe–acac$^-$.—The existence of the complex $[Cu(dppe)_2]^{2+}$ is not expected in view of the tendency of copper(II) to oxidize phosphines in the presence of even trace amounts of oxygenated species (like water) to give copper(I).[12] In order to confirm this expectation, we have recorded the voltammetric pattern displayed by anhydrous copper(II) electrogenerated in acetonitrile prior to and after the addition of dppe. Figure 3 shows that, in the absence of this ligand, copper(II) is reduced stepwise to copper(I) and copper(0) in correspondence to the one-electron cathodic peaks a and c with which the anodic peaks b and d (for the reverse charge transfers) are associated. The addition of a half equivalent of dppe (Figure 3, dashed line) results in the rapid disappearance of peak a, while peaks b and c can be now recorded directly in positive and negative scans respectively, thus indicating that the chemical reduction of Cu^{II} to Cu^{I} is indeed occurring under our experimental conditions. Surprisingly, in this redox reaction the diphosphine acts as a two-electron reducing agent, that is as a monophosphine. Further addition of dppe leads to a further change in the voltammetric picture (Figure 3, dotted line) which is complete after about 2.5 equivalents of dppe have been added, thus suggesting the formation of a copper(I) complex of the type $[Cu(dppe)_2]^+$.



Scheme. M = Ni or Pd

Consequently, in an attempt to gain information on the mixed-ligand complex $[Cu(acac)(dppe)]^+$, we were forced to study only the reaction of $[Cu(acac)_2]$ with dppe. The cathodic behaviour of the acetylacetonate complex on a glassy-carbon electrode in acetonitrile is known to involve two one-electron irreversible reduction processes at *ca.* -0.9 and -1.3 V *vs.* s.c.e. affording copper(I) and metallic copper respectively.[13] Addition of 0.5 mol of dppe per mol of Cu^{II} results in a quite fast change of the voltammetric picture leading to the final one depicted in Figure 3 (dashed line). The presence of the relevant anodic and cathodic peaks clearly indicates that also in this case dppe is able to reduce copper(II) to the solvated [14,15] copper(I) complex. Once again, further addition of dppe (to a dppe to copper molar ratio of 2.5:1) converts this profile into that (Figure 3, dotted line) corresponding to the dppe-complexed copper(I) species.

It is concluded that the heteroleptic complex $[Cu(acac)(dppe)]^+$ does not exist under the conditions which make possible the existence of the analogous nickel(II) and palladium(II) species. On the contrary, copper appears to be stable as $[Cu^I(MeCN)_4]^+$ or $[Cu^I(dppe)_2]^+$ depending upon the dppe to copper molar ratio.

Conclusions

The replacement of one dppe molecule by one acetylacetonate ligand per metal atom appears to be possible inside the co-ordination spheres of nickel(II) and palladium(II). Apparently, the formation of a β-diketonate–diphosphine (*i.e.* hard–soft) co-ordination sphere is thermodynamically favoured on starting from (*i*) a mixture of the relevant $[M(P–P)_2]^{2+}$ and $[M(O–O)_2]$ complexes, (*ii*) from $[M(P–P)_2]^{2+}$ and a stoicheiometric amount of acetylacetonate, and (*iii*) from $[M(O–O)_2]$ and a stoicheiometric amount of the diphosphine (see Scheme).

Interestingly, the ligand conproportionation constant is higher for nickel(II) (a borderline metal acceptor)[16] than for palladium(II) (a soft metal acceptor) and this finding fits nicely with the expected average borderline character of the mixed β-diketonate–diphosphine co-ordination sphere.

Copper(II) is reluctant [12] to accommodate phosphine ligands in its co-ordination sphere and our electroanalytical approach has provided evidence of its tendency to undergo inner-sphere reduction to copper(I), after the dppe has presumably entered its co-ordination sphere.

As to the stereochemistry of the complexes involved in the investigated systems, the square-planar [17] $[Ni(dppe)_2]^{2+}$ is converted into a mixed-ligand derivative which maintains the same geometry.[1,18] This is remarkable in that the presence of two acac$^-$ ligands per nickel atom imposes an exceptionally stable trimeric 'octahedral' structure.[19] Moreover, it should be noted that the mixed co-ordination sphere seems to favour an essentially planar ligand arrangement for the unstable electrochemically generated nickel(I) complex, as is suggested by the reversible character of the relevant process. The preservation of the square geometry in the mixed-ligand palladium(II) complex is not surprising in view of the known preference of this metal centre for such a stereochemistry. Conversely a change in geometry is involved in the copper(II) to copper(I) reduction in that the square planar [20] $[Cu(acac)_2]$ is converted into tetrahedral [15] $[Cu(MeCN)_4]^+$ in the absence of phosphine. The related $[Cu(dppe)_2]^+$ complex obtained in the presence of dppe is expected to exhibit the same geometry.[12]

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Received 31*st March* 1987; *Paper* 7/573