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Multinuclear Magnetic Resonance (^{31}P , ^{77}Se , ^{199}Hg) and Electrochemical Studies of Nonlabile Mercury(II) Complexes with Group 15/Group 16 Donor Ligands

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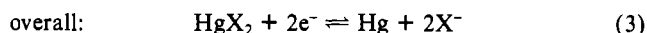
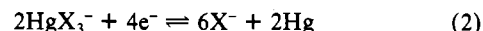
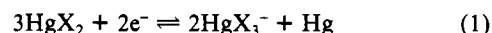
Multinuclear magnetic resonance (^{31}P , ^{77}Se , ^{199}Hg) and electrochemical studies have been carried out on Hg(II) perchlorate complexes of $\text{Ph}_2\text{PCH}_2\text{P}(\text{E})\text{Ph}_2$ [$\text{E} = \text{S}$ (dpmS), Se (dpmSe)] and $\text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{P}(\text{E})\text{Ph}_2$ [$\text{E} = \text{S}$ (dpmS₂), Se (dpmSe₂)] as well as the free ligands. These studies were conducted in dichloromethane, acetonitrile, and acetone with all results being independent of solvent. In all cases a single complex, $[\text{Hg}(\text{dpmE})_2]^{2+}$ or $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$, is formed, which is static at room temperature on the NMR time scale. Addition of excess ligand causes ligand exchange, but cooling slows the rate of ligand exchange, allowing observation of separate signals due to the mercury complex and free ligand. Coordination of selenium to mercury leads to a reduction of the phosphorus-selenium coupling constant relative to that in the free ligand, and mercury-selenium coupling is observed in some cases. Competitive exchange studies clearly show that mercury favors coordination to dpmE rather than dpmE₂. The electrochemical reduction of both $[\text{Hg}(\text{dpmE})_2]^{2+}$ and $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ at a mercury electrode occurs via a Hg(I) intermediate as in $[\text{Hg}(\text{dpmE})_2]^{2+} + \text{Hg} \rightleftharpoons 2[\text{Hg}(\text{dpmE})]^+$ and $2[\text{Hg}(\text{dpmE})]^+ + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{dpmE}$. With the dpmE complexes, the processes are both chemically and electrochemically reversible, but in marked contrast, the dpmE₂ complexes exhibit chemical reversibility but electrochemical irreversibility, which is highly unusual for mercury complexes at a mercury electrode. This difference is explicable in terms of the preference of mercury for phosphorus rather than group 16 donor atoms. The reversible processes for the dpmE systems occur under conditions where both the mercury complex and the free ligand are present simultaneously at the electrode surface and mimic the NMR experiments where rapid exchange reactions occur. At platinum electrodes all the complexes are reduced to elemental mercury and free ligand in an overall irreversible two-electron process.

Introduction

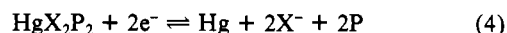
There have been many reported examples of Hg(II) complexes with monodentate group 15 donor ligands that have been investigated by a variety of physical methods.³⁻⁷ Much less study has been made of analogous derivatives of group 16 monodentate ligands.⁸⁻¹⁰ Lusser and Peringer¹¹ have recently reported the low temperature in situ syntheses and NMR properties of the unstable $\text{Hg}(\text{Ph}_2\text{PCHP}(\text{E})\text{Ph}_2)_2$ ($\text{E} = \text{S}$, Se , Te). The only group 16 bidentate ligands that have been extensively studied with mercury are the dithiocarbamates and closely related ligands. Studies include the application of electrochemical, NMR, and X-ray crystallographic methods.¹²⁻¹⁵ A feature of the dithiolate chemistry is the labile nature of the complexes in solution as shown by NMR spectroscopy and electrochemical studies.

In the majority of electrochemical investigations of inorganic compounds, the redox process involves two oxidation states and the observed electrochemical response is a function of the chemistry of both oxidation states. However, in the special case of the reduction of mercury complexes at a mercury electrode, the product is usually elemental mercury, and so a common product is formed irrespective of the initial complex. Thus the thermodynamic data derived from the electrochemical experiment directly reflect the free energy of formation of the complex. This provides a substantial simplification in the interpretation of electrochemical experiments.

There are numerous pathways to achieve an overall two-electron reduction of a mercury(II) complex. For example, HgX_2 ($\text{X} = \text{Cl}$, Br , I) is reduced in two steps¹⁶



and the complex $\text{Hg}(\text{S-S})_2$ with the chelating xanthate ligand follows a similar mechanism.¹² On the other hand, the mixed halophosphine complexes HgX_2P_2 reduce in a single two-electron process¹⁷



and other mechanisms are known.^{6,13} Despite the complexity of these systems, they all show chemical and electrochemical reversibility, which can only occur if the above equilibria are established very rapidly. Crowe¹⁸ has summarized the wide variety of metal-ligand interactions that can be studied at mercury electrodes.

It has become apparent from our previous reports^{13-15,17} that, for the special case of mercury, the combination of ^{199}Hg NMR spectroscopy and electrochemical studies is particularly apposite in the study of solution processes of mercury compounds. In this paper we report the reactions of mercuric perchlorate with the bidentate mixed group 15/group 16 ligands $\text{Ph}_2\text{PCH}_2\text{P}(\text{E})\text{Ph}_2$ [$\text{E} = \text{S}$ (dpmS), Se (dpmSe)] and the bidentate group 16 ligands $\text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{P}(\text{E})\text{Ph}_2$ [$\text{E} = \text{S}$ (dpmS₂), Se (dpmSe₂)]. The stable complexes $[\text{Hg}(\text{dpmE})_2]^{2+}$ and $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ are nonlabile on the NMR time scale at room temperature, in contrast to some other tetrahedral species containing only group 15 or group 16 ligands.^{6,14,15} Extensive NMR and electrochemical studies on these compounds leads to a more detailed understanding of the factors that are important in the electrochemical processes.

Experimental Section

Materials. All solvents and reagents used were of AR grade. Tetrabutylammonium perchlorate, Bu_4NClO_4 , used as the supporting electrolyte for electrochemical studies in CH_2Cl_2 , was obtained wet with water from South Western Analytical and was dried under vacuum at 70 °C. The dpmE and dpmE₂ ligands were prepared as described previously.¹⁹⁻²¹

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Preparations. *Caution!* Although no difficulties have been experienced in the preparation and handling of these complexes, care should always be exercised in the use of perchlorate salts. The complexes $[\text{Hg}(\text{dpmE})_2](\text{ClO}_4)_2$ and $[\text{Hg}(\text{dpmE}_2)_2](\text{ClO}_4)_2$ were prepared by stirring the ligands in approximately 1:1 proportions with solid $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in dichloromethane at room temperature. This procedure ensures that the final product does not contain excess ligand. After reaction, the solution was filtered to remove excess $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and evaporated to dryness, and the resulting solid was recrystallized from dichloromethane/*n*-hexane.

Instrumentation. NMR spectra of approximately 0.1 M solutions were recorded by using a JEOL FX 100 spectrometer with external ^7Li lock. Phosphorus-31 NMR spectra were recorded at 40.26 MHz (reference external 85% H_3PO_4 , selenium-77 at 18.99 MHz (external 1 M H_2SeO_3 in H_2O^{22} used as a secondary reference) and mercury-199 at 17.76 MHz (external 1 M phenylmercury acetate in $\text{Me}_2\text{SO}^{23}$ used as a secondary reference). The convention used is that chemical shifts to high frequency are positive. A JEOL NM 5471 controller was used for temperature control, and temperatures in the probe were measured with a calibrated platinum resistance thermometer.

Infrared spectra were recorded on a Jasco A-320 instrument.

Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer with a dropping-mercury electrode or a polished platinum-disk electrode. For cyclic voltammetry at a mercury electrode, a sweep delay of 1 s was introduced to allow uniform growth of the mercury drop. A platinum wire served as the auxiliary electrode while the reference electrode was Ag/AgCl (saturated LiCl in CH_2Cl_2) separated from the test solution by a salt bridge containing the appropriate solvent. The $[(\text{C}_5\text{H}_5)_2\text{Fe}]^+ / (\text{C}_5\text{H}_5)_2\text{Fe} (\text{Fc}^+/\text{Fc})$ redox couple was measured frequently, and all data are reported relative to this couple. Unless otherwise stated all measurements were made at 25 °C in CH_2Cl_2 (0.1 M Bu_4NClO_4), CH_3CN (0.1 M Et_4NClO_4), or acetone (0.1 M Et_4NClO_4).

Results and Discussion

NMR Studies. In all cases the NMR spectra of complexes prepared *in situ* in the NMR tube were identical with those of the isolated products.

(a) dpmSe and dpmS Complexes. The proton-decoupled phosphorus-31 NMR spectrum of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ at room temperature in dichloromethane solution consists of two triplets of equal intensity, one with selenium-77 satellites ($J_{\text{P,Se}} = 595$ Hz) and the other with mercury-199 satellites ($J_{\text{P,Hg}} = 3750$ Hz). The phosphorus-selenium coupling constant is less than that in the free ligand ($J_{\text{P,Se}} = 732$ Hz). This has been shown¹⁹ in other systems to be indicative of selenium coordination, and this is confirmed by the ^{77}Se NMR spectrum (below). The phosphorus chemical shift for this resonance is close to that of the free ligand since this phosphorus is not the donor atom upon coordination. The other phosphorus resonance is well shifted from the P(III) resonance of free dpmSe and together with the typically large coupling constant to mercury indicates phosphorus coordination. The appearance of both resonances as triplets shows that two ligands are chelated to mercury on the NMR time scale (confirmed below), and the phosphorus atoms constitute an $\text{AA}'\text{XX}'$ spin system,²⁴ which in practice simplifies to an A_2X_2 system. All NMR data are given in Table I.

Although the phosphorus-31 NMR spectrum showed the molecule to be rigid on the NMR time scale, it was found that, for the mercury-199 NMR spectrum, better resolution of the couplings was obtained at -50 °C than at room temperature. The mercury-199 NMR spectrum of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ recorded at -50 °C in dichloromethane is a triplet of triplets, as required for chelation of two dpmSe ligands, with the larger coupling constant being equal to that observed in the phosphorus spectrum. The small 2J coupling of 27 Hz to the P(Se) atoms is not detectable in the phosphorus spectrum since the weak mercury-199 satellites are lost in the foot of the phosphorus triplet. Selenium-77 satellites

Table I. NMR Data for $[\text{Hg}(\text{dpmE})_2]^{2+}$ and $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ (E = S, Se) in Dichloromethane Solution^a

compd	$\delta(^{31}\text{P})$	$\delta(^{77}\text{Se})^a$	$\delta(^{199}\text{Hg})^b$	J , Hz
dpmSe ^c	30.4 (d)	-343 (d)		$^2J(\text{P,P}) = 85$ $^1J(\text{P,Se}) = 732$
$[\text{Hg}(\text{dpmSe})_2]^{2+}$	-27.7 (d) 44.1 (t) 23.2 (t)	-330 (d)	-177 (tt)	$^3J(\text{P,P}) = 24$ $^1J(\text{P,Se}) = 595$ $^1J(\text{P,Hg}) = 3750$ $^2J(\text{P,Hg}) = 27$ $^1J(\text{Se,Hg}) = 855$ $^2J(\text{P,P}) = 78$
dpmS	40.0 (d)			$^2J(\text{P,P}) = 20$
$[\text{Hg}(\text{dpmS})_2]^{2+}$	-28.5 (d) 49.5 (t) 23.4 (t)		<i>d</i>	$^1J(\text{P,Hg}) = 4516$ $^1J(\text{P,Se}) = 753$
dpmSe ^c	24.2 (s)	-302 (d)		$^1J(\text{P,Se}) = 592$
$[\text{Hg}(\text{dpmSe}_2)_2]^{2+}$	29.6 (s)	-280 (d)	-785 (q)	$^2J(\text{P,Hg}) = 125$ $^1J(\text{Se,Hg}) = 908$
dpmS ₂	34.5 (s)			
$[\text{Hg}(\text{dpmS}_2)_2]^{2+}$	41.4 (s)		-479 (q)	$^2J(\text{P,Hg}) = 109$

^a Versus Me_2Se , assuming δ for Na_2SeO_3 is +1253 ppm. ^b Versus Me_2Hg , assuming δ for $\text{PhHg}(\text{O}_2\text{CMe})$ is -1437 ppm. ^c NMR data have been reported previously: Carr, S. W.; Colton, R. *Aust. J. Chem.* **1981**, *34*, 35. ^d Not observed due to solubility problems. ^e Key: s, singlet; d, doublet; t, triplet; tt, triplet of triplets; q, quintet.

are not observed in the mercury spectrum due to an insufficient signal to noise ratio. The chemical shift for mercury in $[\text{Hg}(\text{dpmSe})_2]^{2+}$ of -177 ppm may be compared with the value of -292 ppm^{25,26} for $[\text{Hg}(\text{dpe})_2]^{2+}$ ($\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and -422 ppm⁷ for $\text{HgCl}_2(\text{PBu}_3)_2$, both of which are known to contain tetrahedrally coordinated mercury.

The selenium-77 NMR spectrum of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ in dichloromethane at -50 °C is a doublet with mercury-199 satellites ($J_{\text{Se,Hg}} = 855$ Hz), which compares with values of 750–960 Hz for some mercury complexes containing tributylphosphine selenide.²⁷ The chemical shift of the doublet is well removed from that of the free ligand (Table I) and together with the observation of mercury satellites confirms the coordination of both selenium atoms.

The ^{31}P NMR spectrum of $[\text{Hg}(\text{dpmS})_2]^{2+}$ is similar to that of $[\text{Hg}(\text{dpmSe})_2]^{2+}$, and numerical data are shown in Table I. For both systems identical spectra are obtained in dichloromethane, acetone, and acetonitrile solutions demonstrating that the same species are produced in all these solvents.

Addition of some excess dpmSe to $[\text{Hg}(\text{dpmSe})_2]^{2+}$ causes ligand exchange at room temperature in dichloromethane solution, but cooling to -80 °C slows the exchange on the NMR time scale to give separate phosphorus-31 NMR signals for $[\text{Hg}(\text{dpmSe})_2]^{2+}$ and free dpmSe, showing that coordination of additional ligand does not occur.

(b) dpmSe₂ and dpmS₂ Complexes. The phosphorus-31 NMR spectrum of $[\text{Hg}(\text{dpmSe}_2)_2]^{2+}$ in dichloromethane at 0 and -50 °C consists of a singlet with both selenium and mercury satellites. The selenium-77 NMR spectrum is a doublet with mercury-199 satellites, and the mercury-199 NMR spectrum is a quintet with selenium-77 satellites. In all cases coupling constants were equal in the appropriate spectra. All of the NMR data are given in Table I and indicate chelation of two dpmSe₂ ligands to mercury. The ^{31}P and ^{199}Hg NMR spectra for $[\text{Hg}(\text{dpmS}_2)_2]^{2+}$ at 0 °C are similar to those of its selenium analogue. Identical spectra are observed in CH_3CN and acetone solutions.

Addition of free dpmSe₂ to $[\text{Hg}(\text{dpmSe}_2)_2]^{2+}$ in dichloromethane causes rapid exchange between free and coordinated ligand at room temperature, but cooling the solution to -80 °C slows the rate of exchange to allow observation of separate signals for the complex and free ligand; however, no new complexes are observed.

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Table II. Infrared Data^a for the Complexes [Hg(dpmE)₂]²⁺ and [Hg(dpmE₂)₂]²⁺ and the Ligands dpmE and dpmE₂

complex	$\nu(\text{P}=\text{E}), \text{cm}^{-1}$	
	ligand	complex
[Hg(dpmSe) ₂] ²⁺	529	510
[Hg(dpmS) ₂] ²⁺	600	580
[Hg(dpmSe ₂) ₂] ²⁺	520	515
[Hg(dpmS ₂) ₂] ²⁺	592	560

^a KBr disk.

Mixing of equimolar proportions of [Hg(dpmSe)₂]²⁺ and [Hg(dpmSe₂)₂]²⁺ in dichloromethane at room temperature leads to ligand exchange. However, when the sample is cooled to -80 °C, the phosphorus-31 NMR spectrum is resolved into a number of overlapping resonances, which suggest the presence of a mixture of the starting materials and the mixed-ligand complex [Hg(dpmSe)(dpmSe₂)]²⁺. This was fully confirmed by the mercury-199 NMR spectrum at -80 °C, which clearly shows the presence of the quintet and triplet of triplets of [Hg(dpmSe₂)₂]²⁺ and [Hg(dpmSe)₂]²⁺, respectively, and an apparent doublet of triplets due to the mixed-ligand complex. The large Hg-P coupling constant (3765 Hz) is very similar to that seen in [Hg(dpmSe)₂]²⁺ and being a doublet indicates that only one phosphorus is coordinated to mercury. The magnitude of the smaller triplet coupling constant (122 Hz) is likewise very similar to that observed in [Hg(dpmSe₂)₂]²⁺ and indicates a chelated dpmSe₂ ligand. The P(Se) atom of the chelated dpmSe would be expected to couple with a rather small coupling constant (cf. [Hg(dpmSe)₂]²⁺, Table I), and this coupling is not observed with the large spectral window necessary to observe the complete spectrum. The mercury chemical shift for the mixed-ligand complex is, as expected, intermediate between those of the parent compounds.

Addition of a small quantity of dpmSe₂ to the solution whose spectra are discussed above causes changes in the phosphorus-31 NMR spectrum at -60 °C that are consistent with exchange between free and chelated dpmSe₂ but not between free dpmSe₂ and chelated dpmSe. Thus, the two triplets due to [Hg(dpmSe)₂]²⁺ are apparent together with two doublets due to the dpmSe ligand of the mixed-ligand cation. The remaining resonances are coalesced into a very broad signal that is only partially resolved at -80 °C. This result suggests that dpmSe is more strongly coordinated than dpmSe₂, presumably because mercury prefers phosphorus to selenium. This conclusion is confirmed by adding 2 mol of dpmSe to a solution of [Hg(dpmSe₂)₂]²⁺. The phosphorus-31 NMR spectrum at -60 °C clearly reveals the two triplets due to [Hg(dpmSe)₂]²⁺ and a singlet due to free dpmSe₂.

The important conclusions from the NMR data that are relevant to the electrochemical studies below are as follows: (i) Only one complex is observed in the interactions of each ligand with Hg(ClO₄)₂ and its formation is independent of solvent. (ii) At room temperature the complexes are static on the NMR time scale in contrast to [HgP₄]²⁺ (P = monodentate phosphine)⁵ or Hg-(S₂CNRR')₂ species.^{6,14,15,28} However, it should be noted that addition of free ligand does cause rapid exchange between coordinated and free ligand. (iii) The coordination of dpmE to mercury is much stronger than the coordination of dpmE₂.

Infrared Studies. The infrared spectra of all of the compounds isolated were examined in the P=S or P=Se region. In all cases the frequency observed was lower than that for the free ligand, and this is confirmation of coordination of the group 16 donor atoms.¹⁹ Infrared data are given in Table II.

Electrochemical Studies. (a) **dpmSe and dpmS Systems.** Figure 1 shows the dc polarograms, differential-pulse polarograms, and cyclic voltammograms for solutions of [Hg(dpmSe)₂]²⁺ at (a) 1 × 10⁻³ and (b) 2.5 × 10⁻⁴ M concentration in dichloromethane (0.1 M Bu₄NClO₄). At the higher concentration the limiting

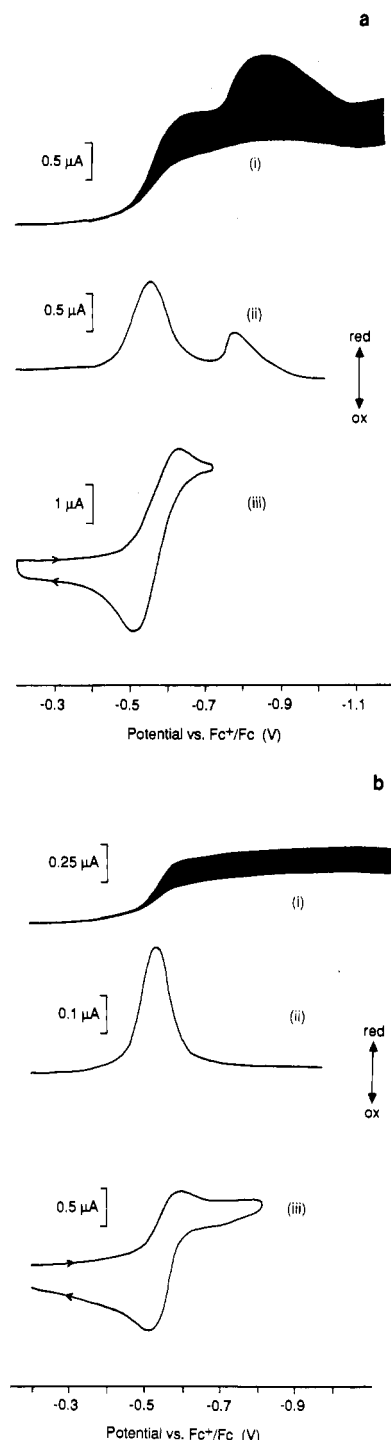


Figure 1. Reduction of (a) 1 × 10⁻³ and (b) 2.5 × 10⁻⁴ M [Hg(dpmSe)₂]²⁺ at the mercury electrode in CH₂Cl₂ (0.1 M Bu₄NClO₄) at 25 °C: (i) dc polarogram; (ii) differential-pulse polarogram; (iii) cyclic voltammogram.

current region in the dc polarogram is complicated at negative potentials by a maximum that indicates adsorption effects and uncompensated resistance effects are observed. In the more dilute solution the redox process is clearly reversible and uncomplicated by surface phenomena. Polarograms in acetone and acetonitrile are less complicated by adsorption phenomena over the concentration range 2.5 × 10⁻⁴ to 2 × 10⁻³ M. Electrochemical data in all three solvents are summarized in Tables III and IV. $E_{1/2}$ is essentially independent of solvent (CH₂Cl₂, CH₃CN, acetone) and only slightly dependent on concentration, although some distortion of wave shape does occur below 10⁻⁴ M. The solvent independence of $E_{1/2}$ for reversible processes leading to reduction to the metal implies that Hg(II) complexes are nonsolvated, as is suggested by the NMR data, which are also solvent independent.

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Table III. Concentration Dependence of Dc Polarographic^a Data in Different Solvents for [Hg(dpmSe)₂]²⁺ (Reduction Process) and dpmSe (Oxidation Process) at 25 °C

solvent	compd	concn = 2 × 10 ⁻³ M		concn = 1 × 10 ⁻³ M		concn = 5 × 10 ⁻⁴ M		concn = 2.5 × 10 ⁻⁴ M		concn = 1.25 × 10 ⁻⁴ M	
		E _{1/2} , ^b V	E _{1/4} - E _{3/4} , mV	E _{1/2} , V	E _{1/4} - E _{3/4} , mV	E _{1/2} , V	E _{1/4} - E _{3/4} , mV	E _{1/2} , V	E _{1/4} - E _{3/4} , mV	E _{1/2} , V	E _{1/4} - E _{3/4} , mV
CH ₂ Cl ₂	[Hg(dpmSe) ₂] ²⁺	-0.60 ^c	60	-0.56 ^c	60	-0.54	55	-0.54	50	-0.53	60
	dpmSe	-0.56	50	-0.56	60	-0.55	60	-0.54	50	-0.53 ^d	<i>d</i>
CH ₃ CN	[Hg(dpmSe) ₂] ²⁺	-0.56 ^c	60	-0.54 ^c	60	-0.54	55	-0.52	65	-0.45 ^d	<i>d</i>
	dpmSe	-0.54 ^c	40	-0.55	50	-0.53	55	-0.52	50	-0.53 ^d	50
acetone	[Hg(dpmSe) ₂] ²⁺	-0.58 ^c	60	-0.58	55	-0.57	60	-0.56	60	-0.53 ^d	65
	dpmSe	-0.57	50	-0.57	50	-0.56	50	-0.55	50	-0.50 ^d	<i>d</i>

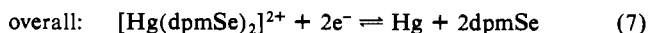
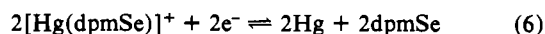
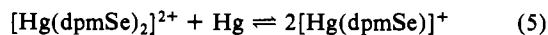
^a Dropping mercury electrode; *t* = 0.5 s. ^b All potentials are relative to E_{1/2}[(C₅H₅)₂Fe]^{+/0}/(C₅H₅)₂Fe. E_{1/2}[(C₅H₅)₂Fe]^{+/0}/(C₅H₅)₂Fe vs Ag/AgCl (saturated LiCl in CH₂Cl₂) = 0.50 V in CH₂Cl₂, 0.38 V in CH₃CN, and 0.42 V in acetone. ^c Maxima present. ^d For these dilute solutions the response is distorted.

Table IV. Polarographic Data in Different Solvents for [Hg(dpmE)₂]²⁺ and [Hg(dpmE₂)₂]²⁺ (Reduction Processes) and dpmE and dpmE₂ (Oxidation Processes) at 25 °C

solvent	compd ^a	dc polarography ^b	
		E _{1/2} , ^c V	E _{1/4} - E _{3/4} , mV
CH ₂ Cl ₂	[Hg(dpmSe) ₂] ²⁺	-0.56 ^d	60
	dpmSe	-0.56	60
CH ₃ CN	[Hg(dpmSe) ₂] ²⁺	-0.54 ^d	60
	dpmSe	-0.55	50
acetone	[Hg(dpmSe) ₂] ²⁺	-0.58	55
	dpmSe	-0.57	50
CH ₂ Cl ₂	[Hg(dpmSe ₂) ₂] ²⁺	-0.52 ^d	90
	dpmSe ₂	-0.31 ^d	60
CH ₃ CN	[Hg(dpmSe ₂) ₂] ²⁺	-0.46	110
	dpmSe ₂	-0.29 ^d	60
acetone	[Hg(dpmSe ₂) ₂] ²⁺	-0.51	100
	dpmSe ₂	-0.27 ^d	75
CH ₂ Cl ₂	[Hg(dpmS) ₂] ²⁺	-0.44 ^d	<i>d</i>
	dpmS	-0.47 ^d	40
CH ₃ CN	[Hg(dpmS) ₂] ²⁺	-0.44 ^d	<i>d</i>
	dpmS	-0.45 ^d	50
acetone	[Hg(dpmS) ₂] ²⁺	-0.48 ^d	<i>d</i>
	dpmS	-0.48 ^d	50
CH ₂ Cl ₂	[Hg(dpmS ₂) ₂] ²⁺	-0.32 ^d	150
	dpmS ₂	-0.17 ^d	60
CH ₃ CN	[Hg(dpmS ₂) ₂] ²⁺	-0.27	120
	dpmS ₂	-0.16 ^d	50
acetone	[Hg(dpmS ₂) ₂] ²⁺	-0.23	130
	dpmS ₂	-0.17 ^d	50

^a All compounds are 1 × 10⁻³ M. ^b Dropping mercury electrode; *t* = 0.5 s. ^c All potentials are relative to E_{1/2}[(C₅H₅)₂Fe]^{+/0}/(C₅H₅)₂Fe. E_{1/2}[(C₅H₅)₂Fe]^{+/0}/(C₅H₅)₂Fe vs Ag/AgCl (saturated LiCl in CH₂Cl₂) = 0.50 V in CH₂Cl₂, 0.38 V in CH₃CN, and 0.42 V in acetone. ^d Complicated by adsorption and maxima.

The shapes of the dc polarographic waves are consistent with a one-electron charge-transfer process; that is, a plot of *E* vs log ((*i*_d - *i*)/*i*) is linear with a slope of 60 mV (Figure 2a), and E_{1/4} - E_{3/4} = 55–60 mV. Similarly, peak to peak separations in the cyclic voltammograms (some *iR* drop terms present) and half-widths of differential-pulse polarograms are similar to those of the known one-electron oxidation of ferrocene at the same concentrations. However the limiting current, in contrast to the charge transfer step, is consistent with an overall two-electron diffusion-controlled process. These data indicate that the reduction proceeds through a one-electron charge-transfer step associated with coupled chemical reactions prior to or after electron transfer leading to an overall two-electron reduction. A mechanism consistent with the data is



which requires that the equilibria are very rapid, and it is the same

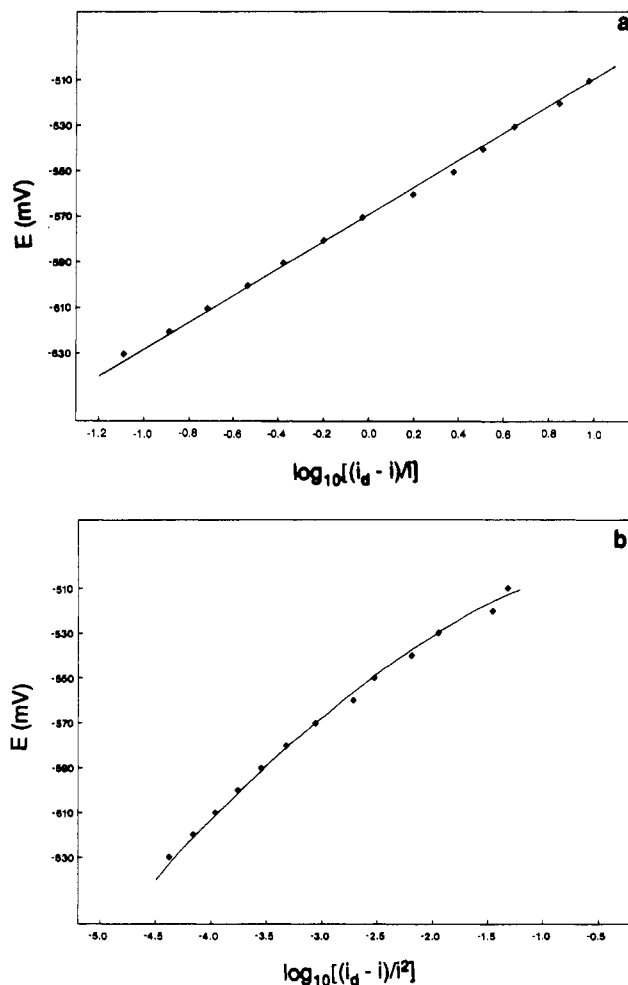
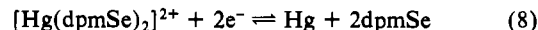
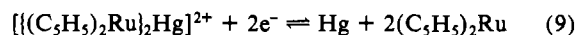


Figure 2. Analysis of polarograms for the reduction of 1 × 10⁻³ M [Hg(dpmSe)₂]²⁺ at the mercury electrode in acetone (0.1 M Et₄NClO₄) at 25 °C: (a) plot of *E* vs log ((*i*_d - *i*)/*i*); (b) plot of *E* vs log ((*i*_d - *i*)/*i*²).

mechanism that operates in the Hg(S₂CNR₂)₂ systems.¹³ An alternative mechanism could involve a direct reversible two-electron transfer as in (8). This kind of mechanism has been observed²⁹



for the reduction of a mercury ruthenium cyclopentadienyl complex according to (9). For this mechanism, a plot of *E* vs log



((*i*_d - *i*)/*i*²) should be linear with a slope of 2.303RT/2*F*. Furthermore, E_{1/2} should vary with concentration, and a 10-fold increase in concentration should shift the potential by 2.303RT/2*F* mV to more negative potential. There is a shift of potential with concentration in the dpmSe system. Unfortunately the potential shift could not be studied over a wider range of concentration

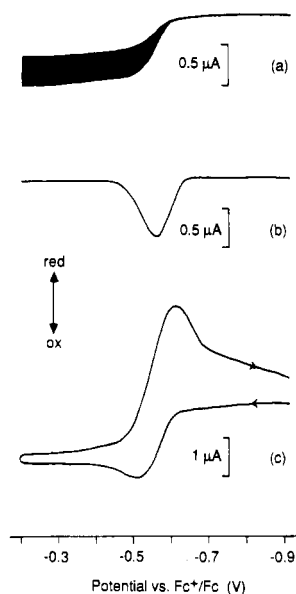


Figure 3. Polarograms of 1×10^{-3} M dpmSe (oxidation process) at the mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 25 °C: (a) dc polarogram; (b) differential-pulse polarogram; (c) cyclic voltammogram.

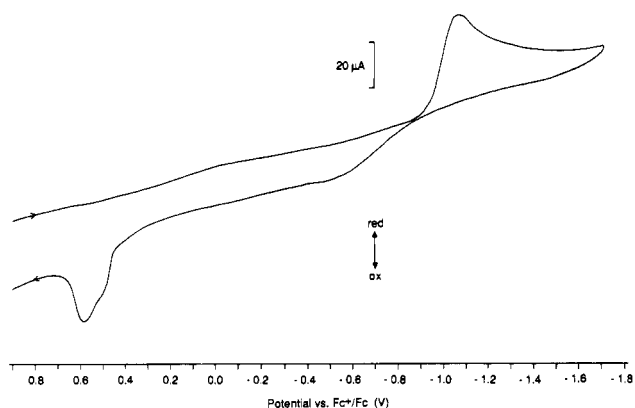


Figure 4. Reduction of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ at a platinum-disk electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 25 °C.

because at higher concentrations adsorption effects interfere and at low concentrations the waves are distorted, as noted earlier, for reasons that are not clear. Hence the best criterion to distinguish between the possible mechanisms is the plots in Figure 2, and these clearly favor a one-electron charge-transfer step since the plot of $\log((i_d - i)/i^2)$ is not linear (Figure 2b).

Differential-pulse polarograms should be unsymmetrical if the two-electron transfer mechanism is applicable,^{6,30} but they are in fact symmetrical (Figure 1). In summary, the mechanism fits the scheme given in eq 5 and 6 much better than eq 8 over the concentration range 10^{-3} – 10^{-4} M. Undoubtedly, adsorption also accompanies the electron transfer process as evidenced by maxima and other nonidealities.

Definitive proof of the proposed mechanism at mercury is provided by recording polarograms and cyclic voltammograms for the oxidation of dpmSe at a mercury electrode. As shown in Figure 3 and Table III, the oxidative process observed at a mercury electrode is a reversible process which is identical with that for the reduction of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ except for the sign of the current. That is, the electrode process is both chemically and electrochemically reversible at a mercury electrode.

The proposed mechanism requires that all steps in the reduction process are extremely fast, so the chemical steps require reversible bond breaking and bond formation at rates close to diffusion control. There is an apparent anomaly in that the NMR spectra

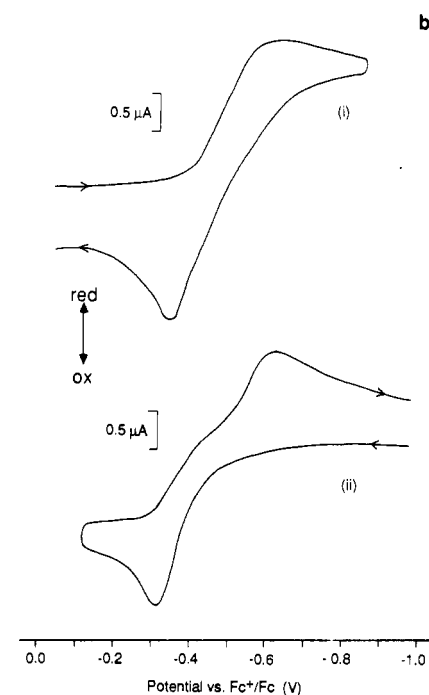
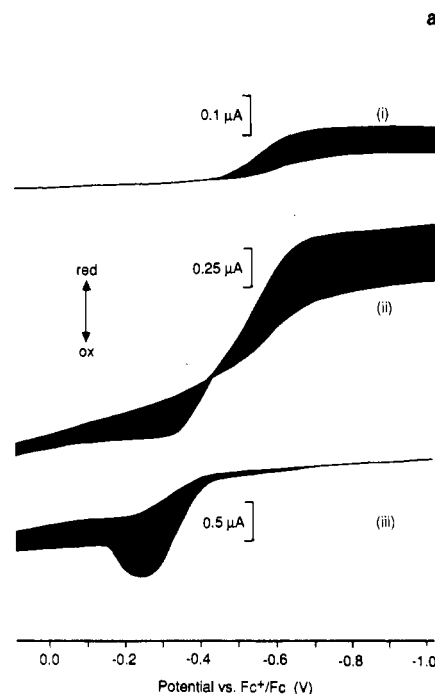


Figure 5. (a) Dc polarograms for (i) 5×10^{-4} M $[\text{Hg}(\text{dpmSe})_2]^{2+}$ (reduction process), (ii) an equimolar mixture (2.5×10^{-4} M) of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ (reduction process) and dpmSe₂ (oxidation process), and (iii) 5×10^{-4} M dpmSe₂ (oxidation process) in acetone (0.1 M Et_4NClO_4) at 25 °C. (b) Cyclic voltammograms at a mercury electrode for (i) 5×10^{-4} M $[\text{Hg}(\text{dpmSe})_2]^{2+}$ (reduction process) and (ii) 5×10^{-4} M dpmSe₂ (oxidation process) in acetone (0.1 M Et_4NClO_4) at 25 °C.

show that $[\text{Hg}(\text{dpmSe})_2]^{2+}$ is rigid on the NMR time scale, which is much slower than the rate of diffusion. However, this anomaly is resolved by noting that the moment reduction begins some free ligand is produced at the electrode surface and the NMR experiments show that the system becomes labile under these conditions. On the rising section of the dc polarogram there is a mixture of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ and free dpmSe at the electrode surface with the relative amounts being determined by the applied potential via the Nernst equation. That is, the electrochemical process takes place under conditions identical with those for the rapid exchange observed in the NMR experiments. Thus, reversible pathways not involving breaking of all the mercury-(II)-ligand bonds are then available, including interaction with

(30) Bond, A. M.; Hanck, K. W. *J. Electroanal. Chem. Interfacial Electrochem.* 1981, 129, 89.

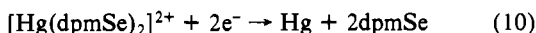
ligand and the mercury electrode.

A necessary condition for the proposed mechanism is that the lifetime of the Hg(I) intermediate must be short. Proof that Hg(I) disproportionates in the presence of dpmSe as expressed in eq 5 was obtained by reaction of $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ with the ligand. The rapid formation of elemental mercury was observed, and the ^{31}P NMR spectrum of the solution at low temperature shows the presence of $[\text{Hg}(\text{dpmSe})_2]^{2+}$.

The exact nature of the transient Hg(I) intermediate is unknown. Mercury(I) usually prefers a linear geometry so that insertion of a mercury atom into a mercury-phosphorus or mercury-selenium bond of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ followed by breaking of the chelate rings could generate a linear dimeric Hg(I) species, $[\text{Hg}_2(\text{dpmSe})_2]^{2+}$. A two-electron transfer would then give elemental mercury and free dpmSe.

The behavior of the dpmS system is similar to that of the dpmSe system in that reduction of $[\text{Hg}(\text{dpmS})_2]^{2+}$ and oxidation of dpmS at a mercury electrode constitute a chemically and electrochemically reversible couple. However, the $E_{1/2}$ value of the redox couple occurs at a significantly less negative potential as shown in Table IV. The same order of reduction $E_{1/2}$ potentials for sulfur and selenium ligand complexes is observed for $\text{Hg}(\text{S}_2\text{CNR}_2)_2$ and $\text{Hg}(\text{Se}_2\text{CNR}_2)_2$ ³¹ and, as expected, the opposite order for oxidation of $\text{Co}(\text{S}_2\text{CNR}_2)_3$ and $\text{Co}(\text{Se}_2\text{CNR}_2)_3$ ³². That is, it is easier to reduce sulfur derivatives and easier to oxidize selenium derivatives in all systems studied so far.

Figure 4 shows that the reduction of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ at platinum electrodes occurs at a more negative potential compared to mercury. The reduction is completely irreversible, in contrast to the situation at mercury, and on the reverse scan, the mercury stripping peak is observed at about 0.46 V. The process at platinum is represented by



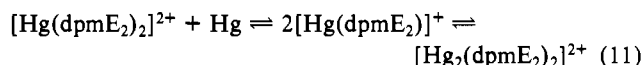
If successive cycles are performed without stripping off the mercury film from the platinum electrode, the cyclic voltammograms gradually assume the character of the responses at a mercury electrode. Although the overall reduction products are the same at both electrodes, clearly the mechanisms at the two electrodes are quite different. The reduction of $[\text{Hg}(\text{dpmS})_2]^{2+}$ at platinum is similar to that for $[\text{Hg}(\text{dpmSe})_2]^{2+}$ (eq 10).

(b) dpmSe₂ and dpmS₂ Systems. Figure 5 shows dc polarograms and cyclic voltammograms for the reduction of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ and for the oxidation of dpmSe₂ at a mercury electrode. Data are given in Table IV. Examination of the data shows a remarkable difference when compared to the results obtained in the Hg(dpmSe)₂²⁺ case. The reduction process for $[\text{Hg}(\text{dpmSe})_2]^{2+}$ occurs at a potential distinctly different from that for the oxidation of mercury in the presence of dpmSe₂. Furthermore, dc polaro-

grams of mixtures of $[\text{Hg}(\text{dpmSe}_2)_2]^{2+}$ and dpmSe₂ produce two well-resolved waves (Figure 5), unlike the case with mixtures of $[\text{Hg}(\text{dpmSe})_2]^{2+}$ and dpmSe where a single process is observed. That is, the process for reduction of $[\text{Hg}(\text{dpmSe}_2)_2]^{2+}$ is chemically reversible but electrochemically irreversible. This appears to be the first example of this class of reaction for a mercury complex at a mercury electrode.

The behavior of the dpmS₂ system is similar in that reduction of $[\text{Hg}(\text{dpmS}_2)_2]^{2+}$ and oxidation of dpmS₂ at a mercury electrode occur at quite different potentials as shown in Table IV. The system therefore is also chemically reversible but electrochemically irreversible. However the reduction potential is again less negative than for the selenium analogue.

Both the $[\text{Hg}(\text{dpmE})_2]^{2+}$ and $[\text{HgP}_2]^{2+}$ systems show electrochemically reversible behavior while the $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ cations, which have only selenium or sulfur coordinated to mercury, show electrochemically irreversible behavior. This suggests that the Hg(I) intermediate in the reduction of $[\text{Hg}(\text{dpmE})_2]^{2+}$ contains phosphorus-bonded dpmE, and subsequent reactions are rapid (to give electrochemical reversibility) in a manner analogous to the phosphine systems. In contrast, the Hg(I) intermediate in the reduction of $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ can only have sulfur or selenium bonded ligands. The observed electrochemical irreversibility of the reduction of $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ implies some kinetic stabilization of the Hg(I) intermediate so that the rate of the reaction



is no longer diffusion controlled. Alternatively, of course, the mechanism may be significantly modified to include new but unknown processes.

At platinum an irreversible two-electron-reduction process forming elemental mercury and free ligand is again observed in both $[\text{Hg}(\text{dpmE}_2)_2]^{2+}$ systems.

Conclusions

This study further emphasizes the complementary nature of NMR and electrochemical techniques, especially in mercury systems. The NMR data show that there is only one complex formed with each ligand and that it is nonlabile on the NMR time scale. However, in the presence of free ligand, which mimics the conditions at the electrode surface during reduction, exchange processes are rapid and enable reversible reductions to occur at a mercury electrode for the dpmE complexes. Both techniques provide evidence for the preference of mercury for phosphorus coordination rather than group 16 donor coordination.

Acknowledgment. J.E. thanks the Australian Government for a Commonwealth Postgraduate Award.

Registry No. dpmS, 54006-28-9; dpmS₂, 14633-92-2; dpmSe, 23176-19-4; dpmSe₂, 16675-12-0; Hg(dpmS)₂²⁺, 113703-97-2; Hg(dpmS₂)₂²⁺, 61460-10-4; Hg(dpmSe)₂²⁺, 113687-11-9; Hg(dpmSe₂)₂²⁺, 113687-12-0; Hg(dpmSe)(dpmSe₂)²⁺, 113687-13-1; Hg(dpe)₂²⁺, 93503-33-4; HgCl₂(PBu₃)₂, 41665-91-2; Bu₄NClO₄, 1923-70-2; CH₂Cl₂, 75-09-2; CH₃CN, 75-05-8; Hg, 7439-97-6; Pt, 7440-06-4; acetone, 67-64-1.

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