feasible. We are currently examining a series of 5-substituted phenyltetrazolato complexes in an effort to separate electronic contributions should they exist.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. N_1-bonded (5-methyltetrazole)pentaamminecobalt(III), 84943-93-1; N_2-bonded (5-methyltetrazole)pentaamminecobalt(III), 84927-27-5; N_1-bonded (5-methyltetrazolato)pentaamminecobalt(III), 84927-29-7; N_2-bonded (5-methyltetrazolato)pentaamminecobalt(III), 84927-31-1.

Contribution from the Department of Chemistry,
University of Auckland, Auckland, New Zealand

Electrochemical and ESR Studies of the Redox Reactions of Nickel(II), Palladium(II), and Platinum(II) Complexes of 1,2-Diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′

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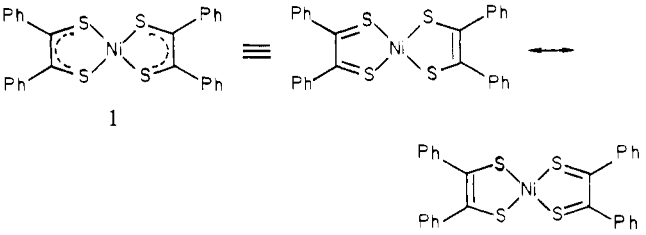
Received July 2, 1982

The electron spin resonance (ESR) spectra of the one-electron-reduction products of the 1,2-diphenyl-1,2-ethenedithiolate complexes $M(Ph_2C_2S_2)_2$ (M = Ni, Pd, Pt) support the view that these reductions are mainly ligand based. Dc cyclic voltammetric studies of the above complexes also show an apparently quasi-reversible oxidation process in each case. ESR studies indicate that several species with slightly differing *g* values are formed in this process under the longer time scale of controlled-potential electrolysis. The 1,2-diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′ complexes $M(dpe)(Ph_2C_2S_2)$ (M = Ni(II), Pd(II), Pt(II); dpe = 1,2-bis(diphenylphosphino)ethane) and $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd(II)) were prepared, as described by previous workers, by ligand substitution reactions between the metal dithiolene complexes and the appropriate phosphine ligand. $Ni(dpe)(Ph_2C_2S_2)$ undergoes a reversible one-electron reduction to the corresponding nickel(I) complex and a reversible one-electron oxidation to give a long-lived species that is characterized by ESR spectroscopy as a complex of the previously unknown dithioketyl $(Ph_2C_2S_2)^{-}\cdot$. The palladium and platinum 1,2-diphenyl-1,2-ethenedithiolate(2−)-*S*,*S*′ complexes do not undergo reversible reduction but like the above nickel complex undergo reversible oxidation to give dithioketyl complexes.

Introduction

The compound bis[1,2-diphenyl-1,2-ethenedithiolato(1−)-*S*,*S*′]nickel, $Ni(Ph_2C_2S_2)_2$ (**1**), first discovered by Schrauzer and Mayweg,[1-3] was one of the first of a large class of transition-metal complexes, known as dithiolene complexes, which have attracted considerable interest over the last 20 years because of their unusual chemical properties.[4-8] One of these properties is the ability of the complexes to undergo a sequence of reversible electron-transfer reactions, and these have been the subject of many chemical, electrochemical, structural, and spectroscopic studies.[4-8] As a result of these studies, it has been concluded that the accessibility of a range of oxidation states of the complex is the result of the accessibility of a number of formal oxidation states for the ligand and that the electron density in the metal orbitals does not change significantly as the oxidation state is changed.[4-8] Thus the redox processes for the Ni-group dithiolenes $M(R_2C_2S_2)_2$ (M = Ni, Pd, Pt; R = CN, CF_3, Ph, etc.)[5,8-10] can be represented in the following way:



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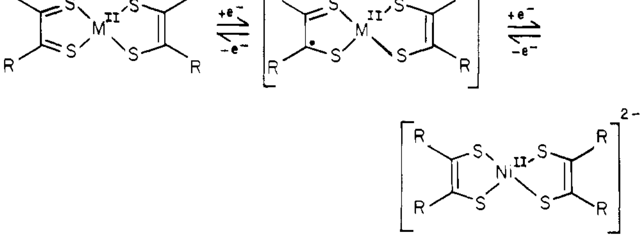

The most highly reduced member of the series involves coordinated dithiolate ligands. The others formally contain in addition coordinated dithioketones, $R_2C_2S_2$, or dithioketyls, $R_2C_2S_2^{-}\cdot$, neither of which are stable as isolated molecules. The true electronic structures of these complexes are of course resonance hybrids involving several different valence-bond structures, as shown for **1** above.[4,7,8] Only one such structure is shown for each of the members of the electron-transfer series in eq 1. In principle, further redox processes for these complexes could exist that involve more highly oxidized states of the ligands.

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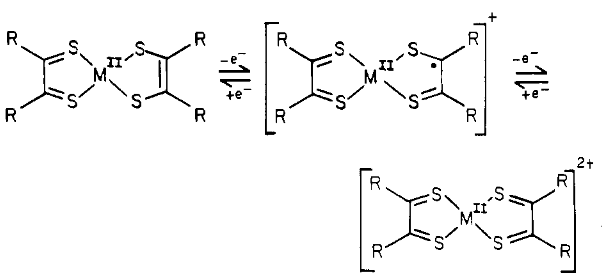

(1)

The oxidized members of this series formally contain coordinated dithioketyl and/or dithioketone molecules. These oxidation processes have not yet been reported for any Ni group dithiolenes. However, several closely related 1,2-diolate transition-metal complexes undergo electron-transfer processes in which the ligands are formally converted to the semidione or quinone forms.[11-13]

Complexes of the type $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd, Pt) and $M(dpe)(S_2C_2Ph_2)$ (M = Ni, Pd, Pt; dpe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$) have been prepared by reaction of $M(Ph_2C_2S_2)_2$ with PPh_3 or dpe.[14] The IR and electronic spectra of these complexes indicate that the sulfur ligand is present in the dithiolate form,[5] but the redox properties of these complexes have not yet been reported. We have previously shown that Ni complexes containing phosphine and dithiolate ligands undergo reversible one-electron reductions, and the ESR spectra of the products show that they are best described as nickel(I) complexes.[15,16] None of the complexes studied were found to undergo reversible oxidation processes, however.

In the present work we have studied the reduction and oxidation properties of the complexes $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd, Pt) and $M(dpe)(Ph_2C_2S_2)$ (M = Ni, Pd, Pt), and the products of several reversible redox reactions have been characterized by ESR spectroscopy. We have also carried out similar studies on the parent dithiobenzil complexes, $M(Ph_2C_2S_2)_2$, since the ESR spectra of the one-electron-reduction products of the Pd and Pt complexes and the oxidation properties of these compounds do not appear to have been previously reported.

Experimental Section

Materials. The bis[1,2-diphenyl-1,2-ethenedithiolato(1−)-*S*,*S*′]metal(II) complexes $M(Ph_2C_2S_2)_2$ (M = Ni, Pd, Pt), were prepared by literature methods[2] and characterized by their melting points.

[1,2-Diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′][1,2-ethanediylbis(diphenylphosphine)-*P*,*P*′]nickel, Ni(dpe)($Ph_2C_2S_2$). To a solution of $Ni(Ph_2C_2S_2)_2$ (0.4 g, 0.74 mmol) in dichloromethane (30 mL), under a N_2 atmosphere, was added an excess of dpe (1.0 g, 2.5 mmol). The solution was stirred for 3 h and then filtered and ethanol (15 mL) added. The bulk of the solvent was then slowly removed by suction until crystallization was complete. The dark green solid was then filtered, washed with diethyl ether, and recrystallized again from dichloromethane/ethanol; mp 165–167 °C. Anal. Calcd for $C_{40}H_{34}NiP_2S_2$: C, 68.68; H, 4.90. Found: C, 68.21; H, 5.37.

[1,2-Diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′][1,2-ethanediylbis(diphenylphosphine)-*P*,*P*′]palladium, Pd(dpe)($Ph_2C_2S_2$). To a solution of $Pd(Ph_2C_2S_2)_2$ (0.25 g, 0.42 mmol) in dichloromethane (30 mL), under a N_2 atmosphere, was added an excess of dpe (0.5 g, 1.25 mmol). The solution was stirred for 3 h and then filtered and ethanol (15 mL) added. The bulk of the solution was then slowly removed by suction until crystallization was complete. The pink solid was then filtered, washed with diethyl ether, and recrystallized from CH_2Cl_2/ethanol; mp 180 °C. Anal. Calcd for $C_{40}H_{34}P_2PdS_2$: C, 64.30; H, 4.59. Found: C, 64.18; H, 4.94.

Bis[1,2-diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′][1,2-ethanediylbis(diphenylphosphine)-*P*,*P*′]platinum, Pt(dpe)($Ph_2C_2S_2$)$_2$. To a solution of $Pt(Ph_2C_2S_2)_2$ (0.25 g, 0.37 mmol) in dichloromethane (30 mL), under a N_2 atmosphere, was added an excess of dpe (0.5 g, 1.25 mmol). The solution was stirred for 1 h and then filtered and ethanol (15 mL) added. The bulk of the solvent was slowly removed by suction until crystallization was complete. The very dark purple crystalline solid was then filtered and washed with diethyl ether; mp 167–168 °C. Anal. Calcd for $C_{54}H_{44}P_2PtS_4$: C, 60.15; H, 4.11; S, 11.89. Found: C, 60.21; H, 4.44; S, 12.01.

[1,2-Diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′][1,2-ethanediylbis(diphenylphosphine)-*P*,*P*′]platinum, Pt(dpe)($Ph_2C_2S_2$). A solution of $Pt(dpe)(Ph_2C_2S_2)_2$ (0.1 g, 0.09 mmol) in dichloromethane (50 mL) was left to stand for 24 h, during which time the color of the solution changed from dark purple to yellow. The solution was filtered, ethanol (15 mL) was added, and then the bulk of the solvent was slowly removed by suction until crystallization was complete. The yellow solid was then filtered, washed with diethyl ether, and recrystallized from dichloromethane/ethanol; mp 182 °C. Anal. Calcd for $C_{40}H_{34}P_2PtS_2$: C, 57.48; H, 4.09; S, 7.67. Found: C, 58.3; H, 4.56; S, 7.88.

[1,2-Diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′]bis(triphenylphosphine)palladium, Pd(PPh_3)$_2$($Ph_2C_2S_2$). To a solution of $Pd(Ph_2C_2S_2)_2$ (0.25 g, 0.42 mmol) in dichloromethane (30 mL), under a N_2 atmosphere, was added a large excess of triphenylphosphine (2.0 g, 7.6 mmol). The solution was stirred for 3 h and then filtered and ethanol (15 mL) added. The bulk of the solution was slowly removed by suction until crystallization was complete. The solution was then filtered and washed with a large volume of hot *n*-hexane to remove the triphenylphosphine which cocrystallized with the product. The remaining purple solid was recrystallized from CH_2Cl_2/ethanol. The solid decomposes above 190 °C. Anal. Calcd for $C_{50}H_{40}P_2PdS_2$: C, 68.76; H, 4.61; S, 7.34. Found: C, 68.34; H, 4.85; S, 7.77.

[1,2-Diphenyl-1,2-ethenedithiolato(2−)-*S*,*S*′]bis(triphenylphosphine)platinum, Pt(PPh_3)$_2$($Ph_2C_2S_2$). To a solution of $Pt(Ph_2C_2S_2)_2$ (0.25 g, 0.37 mmol) in dichloromethane (30 mL), under a N_2 atmosphere, was added a large excess of triphenylphosphine (2.0 g, 7.6 mmol). The solution was stirred for 3 h during which time the color of the solution changed from dark red to yellow. The solution was filtered, ethanol (15 mL) was added, and then the bulk of the solvent was removed by suction until crystallization was complete. The solution was then filtered and washed with a large volume of hot *n*-hexane to remove the triphenylphosphine which cocrystallized with the product. The remaining yellow solid was recrystallized from CH_2Cl_2/ethanol; mp 300–302 °C. Anal. Calcd for $C_{50}H_{40}P_2PtS_2$: C, 62.42; H, 4.19; S, 6.66. Found: C, 62.43; H, 4.65; S, 7.03.

Attempts to prepare the complex $Ni(dpe)(Ph_2C_2O_2)$, for comparison with the complex $Ni(dpe)(Ph_2C_2S_2)$, failed to give a compound with the correct elemental analysis.

Electrochemical Measurements. Cyclic voltammograms and controlled-potential electrolyses were performed with a PAR 173 potentiostat, PAR 179 digital coulometer with *iR* compensation, ECG 175 universal programmer, and HP 7046A X-Y recorder. For scan rates faster than 500 mV/s a Techtronix 5223 digital storage oscilloscope was used. Reference electrodes were either Ag-AgCl (0.1 M LiCl in acetone) or Ag-Ag (LiCl-saturated CH_2Cl_2) separated from the voltammetric cell by an appropriate salt bridge. Measurements were performed mainly in CH_2Cl_2 (0.1 M NBu_4ClO_4 supporting electrolyte). Reported potentials are all referenced to ferrocene/ferrocenium couple taken as 0.46 V vs. Ag/AgCl (0.1 M LiCl) couple as described previously.[15,16]

Electron Spin Resonance Spectra. X-Band electron spin resonance spectra were recorded with a Varian E 4 spectrometer. The electrochemical generation of species for spectral studies and spectral simulations were carried out as reported previously.[15,16]

Results and Discussion

Reduction and Oxidation of $M(Ph_2C_2S_2)_2$ (M = Ni, Pd, Pt). Cyclic voltammetric studies confirm that each of the above complexes undergo two reversible or quasi-reversible reduction steps.[9,10] The voltammetric parameters for these processes are shown in Table I. In addition to these reductions, an ap-

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Table I. Cyclic Voltammetry Parameters for the Reversible or Quasi-Reversible Oxidations and Reductions of the Complexes $[M(Ph_2C_2S_2)_2]^n$, $[M(dpe)(Ph_2C_2S_2)]^n$, and $[M(PPh_3)_2(Ph_2C_2S_2)]^n$ (M = Ni, Pd, Pt) in CH_2Cl_2 at ~290 K

	reductions								oxidations			
	n: $2- \rightleftharpoons 1-$				n: $1- \rightleftharpoons 0$				n: $0 \rightleftharpoons 1+$			
	$E_{1/2}$, V[a]	ΔE_{pp}, V[b]	ΔE_{pp}, V[c]	i_p^r/i_p^f [b]	$E_{1/2}$, V[a]	ΔE_{pp}, V[b]	ΔE_{pp}, V[c]	i_p^r/i_p^f [b]	$E_{1/2}$, V[a]	ΔE_{pp}, V[b]	ΔE_{pp}, V[c]	i_p^r/i_p^f [b]
$Ni(Ph_2C_2S_2)_2$	−0.80	0.12	0.13	1.0	0.02	0.10	0.11	1.0	1.15	0.17	0.19	0.6
$Pd(Ph_2C_2S_2)_2$	−0.61	0.09	0.10	1.0	0.02	0.09	0.10	1.0	1.17	0.15	0.16	0.6
$Pt(Ph_2C_2S_2)_2$	−0.80	0.08	0.09	1.0	−0.06	0.07	0.07	1.0	1.20	0.11	0.13	0.9
$Ni(dpe)(Ph_2C_2S_2)$					−1.68	0.26	0.30	0.9	0.48	0.08	0.10	1.0
$Pd(dpe)(Ph_2C_2S_2)$									0.43	0.06	0.07	1.0
$Pt(dpe)(Ph_2C_2S_2)$									0.45	0.08	0.09	1.0
$Pd(PPh_3)_2(Ph_2C_2S_2)$									0.40	0.10	0.11	1.0
$Pt(PPh_3)_2(Ph_2C_2S_2)$									0.43	0.06	0.06	1.0
$Pt(Ph_2C_2S_2)_2 \cdot dpe$									0.33	0.06	0.06	1.0
									0.86[d]	0.06[d]	0.06[d]	1.0[d]

[a] Potential measured halfway between the potentials of the peak cathodic and anodic currents. [b] At scan rate of 100 mV s^{-1}. [c] At scan rate of 200 mV s^{-1}. [d] n: $1+ \rightleftarrows 2+$.

Table II. ESR Parameters for the One-Electron-Reduction and -Oxidation Products[f]

complex	g	g_1	g_2	g_3	A[a]	A_1[a,e]	A_2[a,e]	A_3[a,e]
$[Ni(Ph_2C_2S_2)_2]^-$	2.052	2.000	2.043	2.119				
$[Pd(Ph_2C_2S_2)_2]^-$	2.022	1.960	2.041	2.051	b	5.0	6.6	9.2
$[Pt(Ph_2C_2S_2)_2]^-$	2.039	1.845	2.065	2.169	c	84	109	32
$[Ni^I(dpe)(Ph_2C_2S_2)]^-$ [d]	2.061	2.151	2.040	2.033		94	102	112
$[Ni(dpe)(Ph_2C_2S_2)]^+$	2.014	1.992	2.023	2.023	4.7	5.4 ± 0.3	4.0 ± 0.3	4.0 ± 0.3
$[Pd(dpe)(Ph_2C_2S_2)]^+$	2.006	1.989	2.010	2.015	3.9	4.3 ± 0.3	4.7 ± 0.3	5.4 ± 0.3
$[Pt(dpe)(Ph_2C_2S_2)]^+$	1.991	1.957	2.009	2.022	5.1			
					18.1[c]	33 ± 1[c]	41 ± 1[c]	30 ± 1[c]
$[Pd(PPh_3)_2(Ph_2C_2S_2)]^+$	2.007	1.987	2.015	2.017	4.0	4.2 ± 0.5[c]	5.5 ± 0.3[c]	5.3 ± 0.3[c]
$[Pt(PPh_3)_2(Ph_2C_2S_2)]^+$	1.991	1.943	2.008	2.032	5.1			
					18.6[c]	28 ± 1	42 ± 1	−14 ± 1

[a] Hyperfine coupling constants are in 10^{-4} cm^{-1}. Unless otherwise indicated, coupling is to ^{31}P. [b] ^{105}Pd coupling. [c] ^{195}Pt coupling. [d] ESR parameters as defined in Figure 8 of ref 16. [e] Due to the poor resolution of some of these spectra an estimate of the error of the hyperfine values is included. [f] Isotropic parameter from solution spectra at ~20 °C. Anisotropic parameters from frozen-solution spectra at −160 °C.

parently quasi-reversible, oxidation process was observed, with anodic to cathodic peak separations only slightly greater than those for the reduction processes in the same complex. The ratio of the peak cathodic and anodic currents i_p^r/i_p^f for the oxidation process was found to be less than unity (Table I). When the scan rate was increased from 100 to 200 mV s^{-1}, the ratio i_p^r/i_p^f improved for the process (Figure 1).

The reduction processes each involve the transfer of one electron, and the ESR spectra of the products obtained during controlled-potential electrolysis in the in situ ESR cell at the potential of the first reduction have isotropic g values that are close to the free-electron value (2.0023) (Table II). In the ESR spectra of the complexes $[M(Ph_2C_2S_2)_2]^-$ (M = Pd, Pt), no ^{105}Pd ($I = 5/2$, 22.23%) or ^{195}Pt ($I = 1/2$, 33.8%) hyperfine satellite lines were resolved. The frozen-solution spectra are anisotropic and have three distinct g values (Table II) as has been found previously for the one-electron-reduction products of complexes of the type $M(R_2C_2S_2)_2$ (M = Ni, Pd, Pt; R = CN, CF_3). In the case of the platinum complex, anisotropic hyperfine coupling to ^{195}Pt ($I = 1/2$, 33.8%) is clearly resolved (Figure 2). The anisotropic g values are distributed about the free-electron value, and the spread of values increases progressively from the Ni to the Pt complex. These results are consistent with the view that the reduction involves the transfer of an electron to an orbital in the complex that is mainly ligand based. This accounts for the small spread of g values (2.00–2.119) for the nickel complex, compared with the much larger spread (2.034–2.321) observed for the nickel(I) complexes, in which the unpaired electron occupies an orbital that is mainly metal based.[15-17] The unpaired electron orbital has a degree of metal-orbital character, however, as the g values are spread over a larger range than expected for organic radicals (even in sulfur-containing organic radicals, which generally have a g value range greater than that of

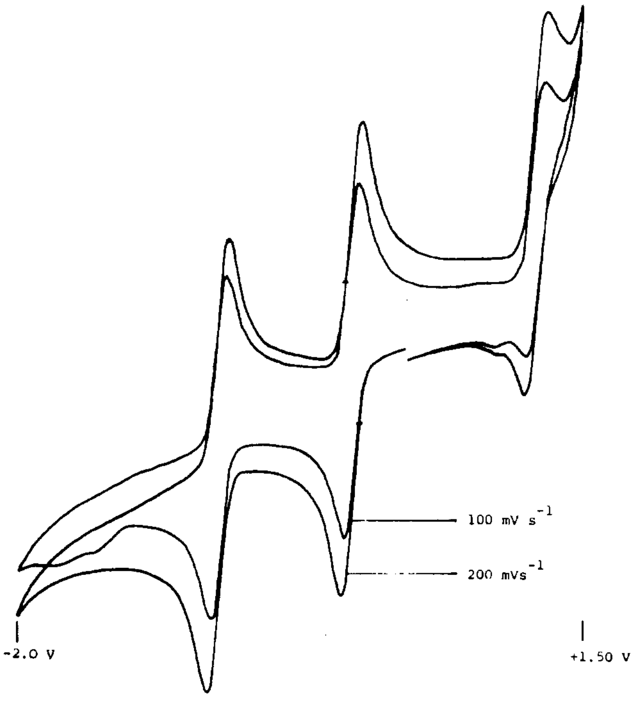

Figure 1. Cyclic voltammogram of the redox process for $Ni(Ph_2C_2S_2)$ (CH_2Cl_2 solvent at ca. 290 K) at (a) 100 mV s^{-1} scan rate and (b) 200 mV s^{-1} scan rate.

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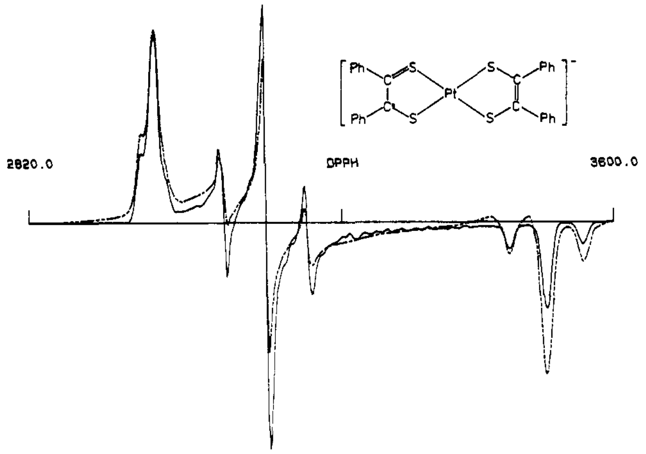

Figure 2. ESR spectrum of $[Pt(Ph_2C_2S_2)_2]^-$ in frozen dichloromethane at -160 °C, simulated with $g_1 = 1.845$, $g_2 = 2.065$, $g_3 = 2.169$; $A_1(^{195}Pt) = 84$, $A_2(^{195}Pt) = 109$, $A_3(^{195}Pt) = 32 \times 10^{-4}$ cm^{-1}; and $\sigma_1 = \sigma_3 = 5.5$, $\sigma_2 = 3.0$ G: ---, experimental spectrum; —, simulated spectrum.

radicals containing first-row elements only).[18] This is due to the magnitude of the spin-orbit coupling constant of the nickel atom. As expected, this effect increases from the nickel to the platinum complex, since the metal atom spin-orbit coupling constant increases considerably from Ni to Pt.[19]

The frozen-solution hyperfine parameters for the Pd and Pt complexes are very comparable to those reported previously for the complexes $[M((CN)_2C_2S_2)_2]^-$ (M = Pd, Pt) (Table II).[5] As the solution ESR spectra of the complexes $[M(Ph_2C_2S_2)_2]^-$ (M = Pd, Pt) showed no ^{105}Pd or ^{195}Pt hyperfine structure, the signs of the hyperfine parameters obtained from the frozen solution cannot be absolutely assigned, and this excludes the possibility of unambiguously determining the ground-state orbital as has been done previously for the complexes $[M((CN)_2C_2S_2)_2]^-$ (M = Pd, Pt). For the Pd complex $A_1 \simeq A_2 > A_3$ (Table II), and this qualitatively indicates a ground state of different symmetry for the two complexes.

The ESR spectra of solutions of these complexes during controlled-potential electrolysis in the in situ ESR cell at the potential of the oxidation process indicated that several species with slightly different g values were present. The spectra run on solutions electrolyzed at -40 °C in dichloromethane solvent each contained a strong line at $g = 2.0151$, but several weaker additional lines at lower g values appeared as well, particularly in the case of the Ni complex. With variation of the temperature, it was evident that three distinct paramagnetic species were present in the solution: the main peak at $g = 2.0151$, a weaker peak at 2.0080, and a third species that exhibited two lines due to the coupling of an $I = {}^1/_2$ nucleus to an unpaired electron, $g = 2.0076$; $A = 6.7 \times 10^{-4}$ cm^{-1}. No satisfactory frozen-solution spectra could be obtained for these species. Thus, despite the appearance of quasi-reversible oxidation waves in the cyclic voltammetry experiments, no clear evidence for the presence of simple one-electron-oxidation products of the type $[M(Ph_2C_2S_2)_2]^+$ could be obtained from the ESR spectra.

The low values for the ratio i_p^r/i_p^f (Table I) for the oxidation process and the variation of the ratio with scan rates indicate that the oxidized species are very reactive and, from the ESR experiments, apparently decompose in the time scale of the in situ controlled-potential electrolysis to give other radical species even at -40 °C. This is indicated by the scheme in Figure 3 for the case of the nickel complex, where the transition between **1** and **4** is shown as irreversible.

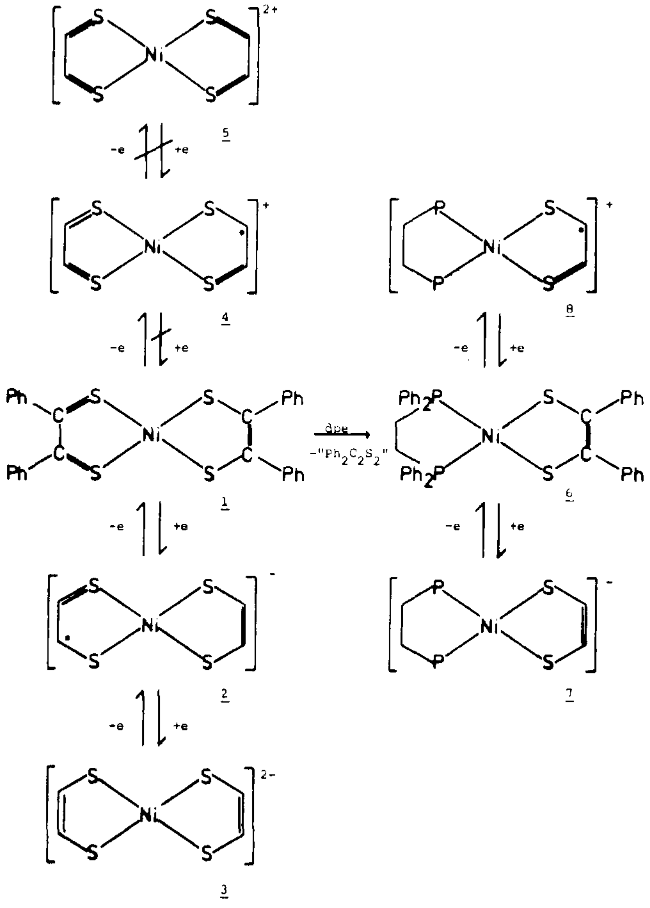

Figure 3. Redox reaction scheme for nickel–dithiobenzil complexes.

Synthesis and Investigation of the Redox Behavior of the Complexes $M(dpe)(Ph_2C_2S_2)$ (M = Ni, Pd, Pt) and $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd, Pt). Schrauzer and Mayweg reported the synthesis of the complexes $M(dpe)(Ph_2C_2S_2)$ (M = Ni, Pd, Pt) and $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd, Pt) by the reaction of $M(Ph_2C_2S_2)_2$ with dpe or PPh_3.[14] These complexes were originally formulated as adducts of the type $M(Ph_2C_2S_2)_2{\cdot}dpe$ and $M(Ph_2C_2S_2)_2{\cdot}2PPh_3$,[2] but subsequent work showed that these reactions formally involve the elimination of dithiobenzil and so can be formulated as mixed-ligand complexes involving phosphine and *cis*-1,2-diphenyl-1,2-ethenedithiolate ligands.[14,20] This reaction is shown in the scheme of Figure 3 for the case of the nickel–dpe complex as the transition from **1** to **6**. The structure of **6** is proposed to be similar to that of several other mixed-ligand nickel(II) complexes involving phosphine and 1,2-dithiolate ligands.[16] The existence of adducts of the type mentioned above was established by Schrauzer and Mayweg in the case of $Pt(Ph_2C_2S_2)_2$, which reacts with dpe to initially form the adduct $Pt(Ph_2C_2S_2)_2{\cdot}dpe$. On irradiation with light, this adduct was converted into the substitution product $Pt(dpe)(Ph_2C_2S_2)$ and the condensation products of dithiobenzil.[14] In this work it was found that this transformation took place when a solution of the adduct was allowed to stand with no special provision for irradiation.

With PPh_3 the $Ni(Ph_2C_2S_2)_2$ complex was reported to give an adduct $Ni(Ph_2C_2S_2)_2{\cdot}2PPh_3$ in which the PPh_3 molecules are very weakly bound to the central nickel atom. $Pd(Ph_2C_2S_2)_2$ formed no corresponding adduct with PPh_3, the substitution product $Pd(PPh_3)_2(Ph_2C_2S_2)$ being formed in-

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stead.[14] In this work no evidence was found for the formation of an addition product (or a substitution product) of $Ni(Ph_2C_2S_2)_2$ with PPh_3. The substitution product $Pd(PPh_3)_2(Ph_2C_2S_2)$ formed readily as described above, and the corresponding platinum complex was prepared in a similar manner (see Experimental Section).

The complex $Ni(dpe)(Ph_2C_2S_2)$ showed both a single reduction process and a single oxidation process. The cyclic voltammetry parameters are listed in Table I. The reduction potential has a relatively high negative value. It is more negative than that for the maleonitriledithiolate complex $Ni(dpe)((CN)_2C_2S_2)$ (−1.20 V) but comparable to the value for the toluenedithiolate complex $Ni(dpe)(CH_3C_6H_3S_2)$ (−1.59 V).[16] The ESR spectrum of the product of the in situ electrolysis of $Ni(dpe)(Ph_2C_2S_2)$ at a potential below that of the reduction process shows *g* values and ^{31}P hyperfine coupling constants (Table II) that are similar in magnitude to those of the previously studied nickel(I) complexes, which were generated by one-electron reductions of nickel(II) complexes containing phosphine and other dithiolate ligands.[16] This result supports the proposal that the complex $Ni(dpe)(Ph_2C_2S_2)$ should be formulated as a nickel(II) complex containing a ditiholate ligand, and since the sulfur ligand is in its most reduced form in this complex, further reduction takes place primarily at the metal center to produce a nickel(I) complex. This process is shown as the reversible transformation between **6** and **7** in the scheme of Figure 3.

The most surprising feature of the cyclic voltammogram of $Ni(dpe)(Ph_2C_2S_2)$ is the reversible oxidation processes at 0.48 V (Table I). This process is shown as the reversible transformation between **6** and **8** in the scheme of Figure 3. In order to investigate the stability of the product of the oxidation process, bulk electrolysis of a dichloromethane solution of $Ni(dpe)(Ph_2C_2S_2)$ at a potential above that of the oxidation process was performed, followed by a cyclic voltammetry scan of the oxidized solution. The cyclic voltammetry scan exhibited no new features, indicating that the oxidation process forms a species that is stable for a long period of time. In contrast, it was found that the other mixed-ligand nickel(II) complexes such as the toluene–dithiolate complex $Ni(dpe)(CH_3C_6H_3S_2)$ all undergo completely irreversible oxidation reactions.[16]

The oxidation process can be formally regarded as an oxidation of nickel(II) to nickel(III) or as an oxidation of the coordinated dithiolate ligand to a coordinated dithioketyl radical ion. The ESR spectrum should distinguish between these two possibilities. The spectrum obtained of the product of a controlled-potential electrolysis in the in situ ESR cell at the oxidation potential of the complex showed a three-line pattern, which is assigned to coupling with two equivalent ^{31}P nuclei ($I = {}^1/_2$). The frozen-solution spectrum showed approximate axial symmetry with $g_\perp > g_\parallel$ and only barely resolved ^{31}P hyperfine coupling (Figure 4). The ESR parameters are listed in Table II. The species responsible for the spectrum was found to be very long-lived, with the spectrum still being observable at room temperature after a period of more than 1 week. For low-spin d^7 nickel(III) complexes with axial symmetry, theory predicts that $g_\perp > g_\parallel \simeq 2.00$.[21] This is found to be the case for most nickel(III) complexes that have been studied to date, which generally have $g_\parallel \simeq 2.0$ and $g_\perp \simeq 2.2$.[17,21] The lowest value for $g_\perp$ in such complexes is about 2.13. In contrast to this, the oxidation product found in this work gave $g_\perp = 2.023$. Thus, although the observed order of the *g* values, i.e. $g_\perp > g_\parallel$, is consistent with the nickel(III) formulation, the magnitude of the *g* values is not. The alternative formulation of **8** as the complex of a coordinated dithioketyl seems more reasonable, even though this is the first such complex that has been reported to date. In support of this formulation is the observation of corresponding palladium and platinum complexes (see below). Here the alternative formulation as metal(III) complexes seems chemically less reasonable. The *g* values and ^{31}P hyperfine coupling constants are similar in magnitude to those found in the nickel, palladium, and platinum complexes of the type $[Ni(dpe)(C_6H_4O_2)]^+$ and $[M(PPh_3)_2(C_6Cl_4O_2)]^+$ (M = Pd, Pt), which contain phosphine and coordinated semiquinone ligands.[16,22] The oxidation of **6** to **8** seems to be best described as an oxidation of the sulfur ligand to produce a nickel(II) dithioketyl complex (see scheme in Figure 3). Hence, the *cis*-1,2-diphenyl-1,2-ethenedithiolate complex of nickel(II) with

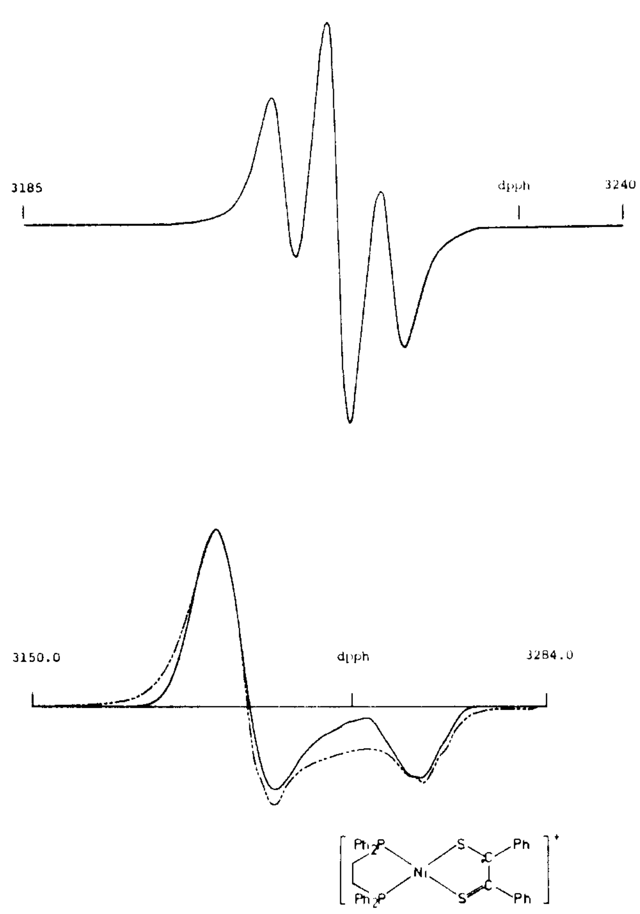

Figure 4. ESR spectra of electrogenerated $[Ni(dpe)(Ph_2C_2S_2)]^+$ in dichloromethane at ca. 20 °C: (a) solution spectrum; (b) frozen-solution spectrum, simulated with $g_1 = 1.992$, $g_2 = g_3 = 2.022$; $A_1(^{31}P) = 5.4$, $A_2 = A_3(^{31}P) = 4.0 \times 10^{-4}$ cm^{-1}; and $\sigma_1 = 2.8$, $\sigma_2 = \sigma_3 = 5.8$ G: - - -, experimental spectrum; —, simulated spectrum.

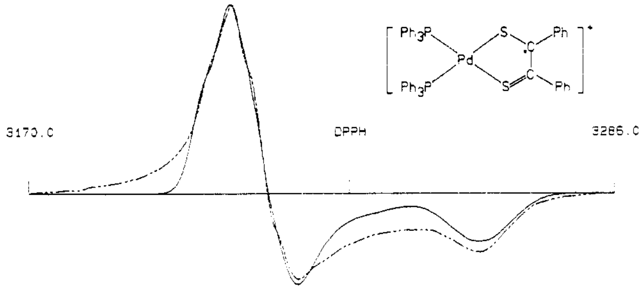

Figure 5. ESR spectrum of electrogenerated $[Pd(PPh_3)_2(Ph_2C_2S_2)]^+$, in frozen dichloromethane solvent at −160 °C, simulated with $g_1 = 1.987$, $g_2 = 2.015$, $g_3 = 2.107$; $A_1(^{31}P) = 4.2$, $A_2(^{31}P) = 5.5$, $A_3(^{31}P) = 5.3 \times 10^{-4}$ cm^{-1}; and $\sigma_1 = \sigma_2 = 4$, $\sigma_3 = 2.4$ G: —, experimental spectrum; - - -, simulated spectrum.

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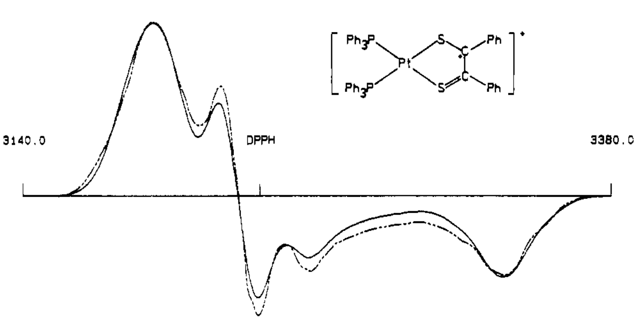

Figure 6. ESR spectrum of electrogenerated $[Pt(PPh_3)_2(Ph_2C_2S_2)]^+$ in frozen dichloromethane solvent at −160 °C, simulated with $g_1 = 1.943$, $g_2 = 2.008$, $g_3 = 2.032$; $A_1(^{195}Pt) = 28$, $A_2(^{195}Pt) = 42$, $A_3(^{195}Pt) = 14 \times 10^{-4}$ cm^{-1}; and $\sigma_1 = 8$, $\sigma_2 = 6$, $\sigma_3 = 9$ G: —, experimental spectrum; - - -, simulated spectrum.

dpe undergoes both one-electron reduction and one-electron-oxidation processes. This is similar to the situation previously found for the corresponding catecholate and substituted-catecholate complexes.[16] In both cases (i.e., with the (*cis*-1,2-diphenyl-1,2-ethenedithiolato)- and (catecholato)nickel(II)–dpe complexes) the oxidation appears to take place mainly on the dithiolate or diolate ligand.

The complexes $M(dpe)(Ph_2C_2S_2)$ and $M(PPh_3)_2(Ph_2C_2S_2)$ (M = Pd, Pt), unlike $Ni(dpe)(Ph_2C_2S_2)$, do not undergo reversible reductions. This reflects the relative instability of univalent Pd^I and Pt^I complexes compared with the corresponding Ni^I complexes. However, the above palladium and platinum complexes do undergo reversible oxidations at potentials similar to that for $Ni(dpe)(Ph_2C_2S_2)$ (Table I). The relative independence of the oxidation potentials on the metal ion or phosphine ligand supports the conclusion reached above that these oxidations are mainly sulfur ligand based, giving dithioketyl complexes.

The in situ electrolysis of the palladium and platinum complexes, $M(PPh_3)_2(Ph_2C_2S_2)$ and $M(dpe)(Ph_2C_2S_2)$, at a potential above that of the oxidation process, produced spectra that showed coupling to two equivalent phosphorus nuclei (Table II). In the case of the platinum complexes ^{195}Pt ($I = {}^1/_2$, 33.8%) hyperfine satellites were also observed. Frozen-solution spectra of the palladium complexes however exhibited poorly resolved phosphorus hyperfine splitting and an anisotropy of the g values similar to that observed for the $[Ni(dpe)Ph_2C_2S_2)]^+$ complex (Figure 4 and Table II). The frozen-solution spectra of the platinum complexes showed a greater g-value anisotropy (see Table II) but no resolvable phosphorus hyperfine splitting. Peaks due to the ^{195}Pt hyperfine satellites were, however, evident (Figure 6 and 7). The platinum hyperfine parameters were estimated by spectral simulation.[23] Comparison of the solution isotropic hyperfine coupling parameters with the average of the anisotropic coupling constants suggests that one of the principal hyperfine values must be negative in sign to give the isotropic platinum hyperfine coupling constant (i.e., $a = {}^1/_3(A_1 + A_2 + A_3)$). For the complex $[Pt(Ph_3P)_2(Ph_2C_2S_2)]^+$, $A_1 = 28 \times 10^{-4}$ cm^{-1} and $A_2 = 42 \times 10^{-4}$ cm^{-1}; hence, A_3 must be negative to average to the solution value, $a = 18.6 \times 10^{-4}$ cm^{-1}. The situation is less clear for the $[Pt(dpe)Ph_2C_2S_2)]^+$ complex. The magnitude of the phosphorus hyperfine coupling constants, and in the case of the platinum complexes the metal hyperfine coupling constant, and the range of g values confirm the conclusion that these oxidations are best considered to be mainly sulfur ligand based.

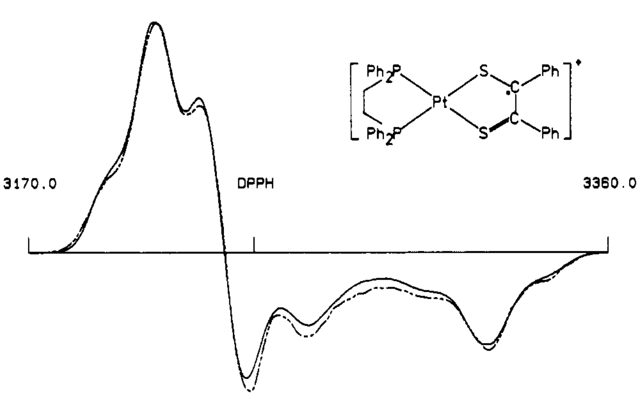

Figure 7. ESR spectrum of electrogenerated $[Pt(dpe)Ph_2C_2S_2)]^+$ in frozen dichloromethane solvent at −160 °C, simulated with $g_1 = 1.957$, $g_2 = 2.009$, $g_3 = 2.022$; and $A_1(^{195}Pt) = 33$, $A_2(^{195}Pt) = 41$, $A_3(^{195}Pt) = 30 \times 10^{-4}$ cm^{-1}: —, experimental spectrum; - - -, simulated spectrum.

The cyclic voltammetry parameters for the adducts $Pt(Ph_2C_2S_2)_2.dpe$ differ from those of the substituted complexes $(M(dpe)(Ph_2C_2S_2))$ in that two reversible oxidations are observed (Table I). Both oxidation potentials are considerably lower than those of the parent complex $Pt(Ph_2C_2S_2)_2$. A controlled-potential electrolysis of the adduct in the in situ ESR cell at the potential of the first oxidation step produced a spectrum identical with that for the oxidation of $Pt(dpe)(Ph_2C_2S_2)$. The first oxidation product appears to be the $[Pt(dpe)(Ph_2C_2S_2)]^+$ cation.

Conclusion

The one-electron-reduction products of the bis[1,2-diphenyl-1,2-ethenedithiolate(1−)-*S,S′*] $M(Ph_2C_2S_2)_2$ give species in which the unpaired electron is delocalized over both ligands and to some extent the central metal ion. The species $[M(Ph_2C_2S_2)_2]^-$ may be viewed as a resonance hybrid such as is shown in **2**. The "localized" dithioketyl $Ph_2C_2S_2^-$ ligand is found in the one-electron-oxidation products of the mixed-ligand complexes of $M(Ph_3P)_2(Ph_2C_2S_2)$, $M(dpe)(Ph_2C_2S_2)$ of 1,2-diphenyl-1,2-ethenedithiolate(2−)*S,S′*. A similar complex has recently been proposed in the mixed 1,2-dithio ligand complex $[Ni((CN)_2C_2S_2)(Ph_2C_2S_2)]^-$, where the $3b_{2g}$ orbital of the dithiolene is singly occupied.[24]

Acknowledgment. We thank the Auckland University Grants Committee and New Zealand University Grants Committee for financial assistance and Professor Graham Wright for the use of electrochemical equipment.

Registry No. **1**, 28984-20-5; **2**, 14879-11-9; **3**, 15683-67-7; **4**, 19582-99-1; **6**, 15133-70-7; **7**, 84836-60-2; **8**, 84836-61-3; $[Pd(Ph_2C_2S_2)_2]^{2-}$, 21246-00-4; $[Pd(Ph_2C_2S_2)_2]^-$, 30662-72-7; $Pd(Ph_2C_2S_2)_2$, 21954-15-4; $[Pd(Ph_2C_2S_2)_2]^+$, 84836-66-8; $[Pt(Ph_2C_2S_2)_2]^{2-}$, 21246-01-5; $[Pt(Ph_2C_2S_2)_2]^-$, 30662-73-8; $Pt(Ph_2C_2S_2)_2$, 15607-55-3; $[Pt(Ph_2C_2S_2)_2]^+$, 84836-67-9; $Pd(dpe)(Ph_2C_2S_2)$, 84836-58-8; $[Pd(dpe)(Ph_2C_2S_2)]^+$, 84836-62-4; $Pt(dpe)(Ph_2C_2S_2)$, 84836-59-9; $[Pt(dpe)(Ph_2C_2S_2)]^+$, 84836-63-5; $Pd(PPh_3)_2(Ph_2C_2S_2)$, 16037-99-3; $[Pd(PPh_3)_2(Ph_2C_2S_2)]^+$, 84836-64-6; $Pt(PPh_3)_2(Ph_2C_2S_2)$, 14403-63-5; $[Pt(PPh_3)_2(Ph_2C_2S_2)]^+$, 84836-65-7; $Pt(dpe)(Ph_2C_2S_2)_2$, 19582-32-2; $[Pt(dpe)(Ph_2C_2S_2)_2]^+$, 84836-68-0; $[Pt(dpe)(Ph_2C_2S_2)_2]^{2+}$, 84836-69-1.

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[23] Simulations for the mixed phosphine–thio ligand complexes were performed as described in ref 16, including effects of noncoincidence of the g tensor and P hyperfine coupling tensor principal axes. In the case of the dpe complex $2\alpha = 80°$ and for bis(triphenylphosphine) $2\alpha = 90°$.

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