Redox-active Planar Complexes. Electrochemical Investigations of Palladium and Platinum Bis(dithioacetylacetonate) Complexes and their Structural Analogues

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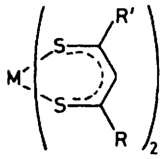
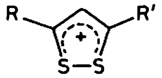
Direct- and alternating-current voltammetric investigations in CH_2Cl_2 of 17 variously substituted planar bis(dithio-β-diketonate) complexes $[M(S_2C_3RHR')_2]$ (M = Ni, Pd, or Pt and R,R' = Bu^t,CF_3, Me, or Ph), including many new palladium and platinum complexes, confirm two reversible reductions in each case. The rapid rearrangement reported for $[M(S_2C_3MeHMe)_2]^-$ is largely suppressed in the other derivatives, apparently for steric rather than electronic reasons. The successive one-electron transfers are found to be ligand-centred in $[M(S_2C_3RHR)_2]$, as in the metal 'dithienes' $[M(S_2C_2R_2)_2]$, despite their difference in topology. An orderly and comparable dependence of reduction potentials on substituent influence (σ^*_R) is displayed by all such systems. The isostructural diketonates, $[M(O_2C_3RHR')_2]$ (M = Pd or Pt), show a parallel trend in first reduction potential and are systematically *ca.* 0.4 V more difficult to reduce than their dithio-analogues.

Dithioacetylacetone (like other hypothetical dithio-β-diketones) is known only as a chemically inert tetrathia-adamantane dimer;[1] however, Martin and Stewart[2] prepared the planar monomeric co-ordination complexes $[M(SacSac)_2]$ (I; M^{II} = Co, Ni, Pd, or Pt; R = R' = Me; SacSac = dithioacetylacetonate), by elegant metal-ion template or ligand-trapping reactions of the diketone and H_2S in the presence of the appropriate metal salt. This principle has been extended to other metal centres, *e.g.* M^{III} = Co, Rh, or Ir,[3] and Fe, Ru, or Os,[4] and to alternatively substituted ligands. In particular, an extensive range of nickel complexes has been established, namely $[Ni(S_2C_3RHR')_2]$, structure (I) with R,R' = Bu^t,Bu^t; Me,Ph; Ph,Ph; Me,CF_3; CF_3,Ph;[2,5,6] Meuller-Westerhoff and Alscher[7] have isolated the attractive parent complexes $[M(S_2C_3H_3)_2]$ (M = Ni, Pd, or Pt) by the procedure of Martin and Stewart. Reduction of the structurally related ions (II) provides an interesting route to the Cr^{III} and Zn^{II} complexes as well as an alternative synthesis of $[Ni(S_2C_3H_3)_2]$ and the other Ni^{II} complexes.[8]



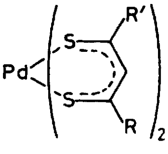
(I)



(II)

The monomeric CoS_4 and NiS_4 complexes differ strikingly from the corresponding β-diketonates which generally adopt oligomeric octahedral structures, but the palladium and platinum systems provide a true isostructural sequence of planar resonance-stabilized chelates; for example (III)—(V).

A particular aim of the present work is to remedy the relative neglect of the palladium and platinum bis(dithio)-systems, and to provide a useful range of substituted PdS_4 and PtS_4 complexes capable of detailed comparison with their isostructural MS_2O_2 and MO_4 analogues, which are readily available. This paper describes the orderly and informative electrochemical behaviour of these complexes and the implications for their electronic structure. The preparation, properties, and spectroscopic characterisation of the new compounds will be described in detail elsewhere.[9]



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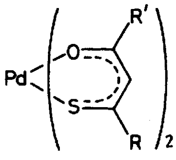

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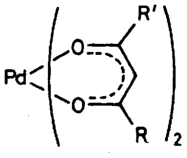
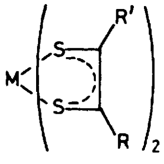


(V)

The bis(1,2-dithiene) metal complexes (VI) have made a considerable contribution to the recognition of ligand-based electron-transfer processes of co-ordination complexes.[10]



(VI)

McCleverty[11] first suggested that compounds of structure (I) might possess similar redox activity. Schrauzer[12] drew attention to the important topological distinction between 'even' (1,2-dithio) and 'odd' (1,1-dithio and 1,3-dithio) resonance-stabilized ligands and concluded that the remarkable redox properties conferred by dithiene ligands would not be shared by the 'odd' systems. In fact, the planar dithiodiacetylacetonate complexes were soon shown as a class to undergo two successive one-electron reductions by polarography in acetone [equation (1)].[13]

$$[M(SacSac)_2]^0 \Leftrightarrow [M(SacSac)_2]^- \Leftrightarrow [M(SacSac)_2]^{2-} \quad (1)$$

For $[Co(SacSac)_2]$, the first reduction is relatively easy and evidently a favoured Co^{II}/Co^{I} process in the planar environment. The basis of redox activity in the d^8 complexes, however, is an area of some dispute. Schrauzer's criterion would require successive M^{II}/M^{I} and M^{I}/M^{0} assignments for the whole series. Indeed, true metal-based reductions have been identified recently for the 'odd-membered' 1,1-dithiocarbamate complexes,[14] and even for the nickel 1,2-dithiene complexes themselves beyond the second ligand-based reduction.[15] Despite similar formal assignments for the

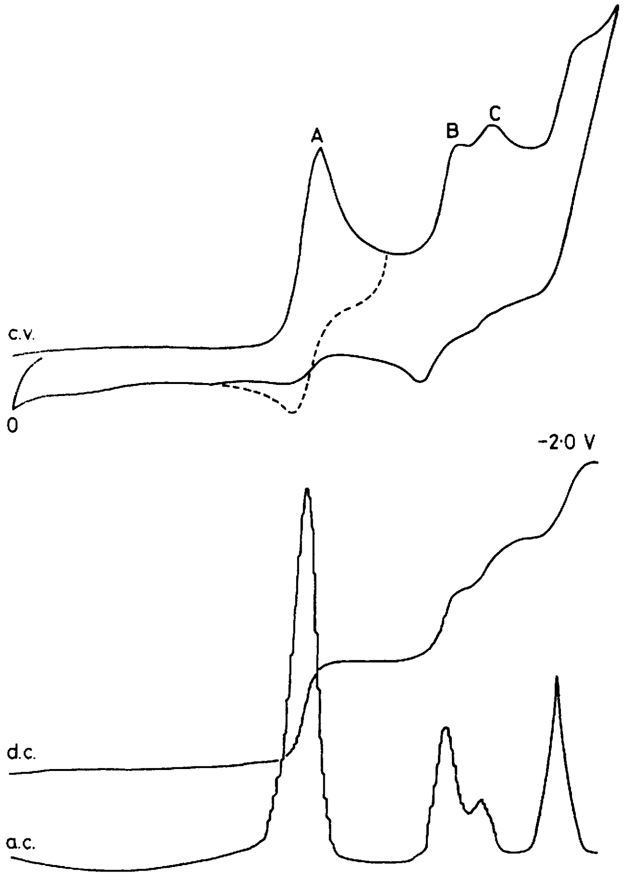


Figure 1. Reductions of [Pd(SacSac)$_2$]: c.v. = cyclic voltammogram on Pt (dashed line, $E\lambda = -1.2$ V); d.c. = d.c. polarogram; a.c. = a.c. polarogram; waves A, B, and C are as designated in the text

d^8 1,3-dithioacetylacetonates, Bond *et al.*[13] described the acceptor orbitals as substantially delocalized over the whole molecule.

Martin and co-workers [16] found an orderly variation in E^0 with changing substituent within the nickel series (I) suggesting ligand participation, and Geiger and co-workers [17] noted a corresponding shift in the parent compound (I; R = R′ = H). This substituent effect is clearly informative, but requires ‘ calibration ’ for proper assessment since, for example, the unquestionably metal-based reductions of [Ru(O$_2$C$_3$RHR)$_3$] show a qualitatively similar trend.[18]

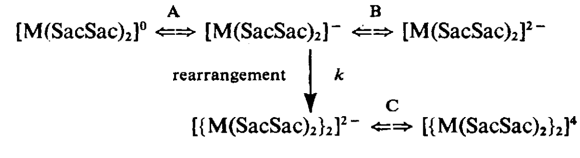
An extended Hückel molecular orbital calculation for [Ni(SacSac)$_2$] attributed largely metal-based character to the lowest unoccupied orbital.[19] However, recently a more elaborate analysis reached the striking conclusion that the redox-active orbital has virtually no metal character.[20]

We present here a summary of comparative a.c. and d.c. voltammetric studies on the electroreduction of the nickel, palladium, and platinum complexes [M(S$_2$C$_3$RHR′)$_2$] (I; R,R′ = Bu^t, Me, Ph, or CF$_3$) in non-aqueous media at temperatures in the range −60 to +20 °C. Remarkably consistent electrode-potential/inductive-parameter correlations emerge for the uncomplicated successive one-electron transfer steps, and these trends are assessed in relation to the behaviour of variously substituted metal dithienes, (VI), and (non-metallated) dithiolylium ions, (II). Similar extended comparisons show that the planar [M(O$_2$C$_3$RHR′)$_2$] systems parallel their dithio-congeners much more closely than might be expected from cursory observation of their generally irreversible electrochemical behaviour.

Results and Discussion

A. Comparative Voltammetry of [M(SacSac)$_2$] (I; R = R′ = Me).—The original polarographic results demonstrated that these complexes exhibit two successive one-electron reductions, although there was clear evidence of a competing rearrangement of electrogenerated [M(SacSac)$_2$]$^-$ to form a new complex also capable of reduction.[13] Subsequent cyclic voltammetric data firmly established this behaviour for M = Ni and Pt and provided cogent evidence that the rearrangement involved dimerisation, though Geiger and co-workers [17] found difficulty in preparing [Pd(SacSac)$_2$] and their study was restricted by having none of this compound.

We have now re-examined the complete triad of complexes. Complementary a.c., d.c., and cyclic voltammetric data for [Pd(SacSac)$_2$] are shown in Figure 1. Three reduction waves are apparent which may be assigned in each case according to the Scheme. A fourth wave near −2.0 V is also present.



Scheme. ($k_{Pt} > k_{Pd} \gg k_{Ni}$)

Comparison of the three complexes (Figure 2) makes it apparent that at conventional scan rates the nickel complex undergoes negligible rearrangement, whereas the voltammogram for the platinum complex is dominated by this pathway, with wave C growing at the expense of wave B and the return wave A. Thus the palladium complex is particularly instructive, because of its intermediate rate of rearrangement, so that routine voltammetric reduction leads to comparable concentrations of the monoanion and its rearranged (presumed dimerised) form at the electrode surface. Voltammograms of [Pt(SacSac)$_2$] recorded at progressively faster scan rates show the simultaneous growth of return wave A, consolidation of wave B, and disappearance of wave C.

A parallel and striking observation is that for both Pd and Pt complexes the dimerisation is fully or largely suppressed at lower temperatures. This has enabled secure determination of the relevant E^0 values at −50 °C. The possibility of bulk generation and characterisation of the monoanions is receiving further attention.

B. Substituted Complexes (I; R, R′ = Bu^t, CF$_3$, Me, *or* Ph).—Several substituted complexes of palladium and platinum have been synthesised with the bulkier groups Bu^t, Ph, or CF$_3$ replacing one or both methyl groups on each ligand. These complexes all show two one-electron reductions satisfying the standard criteria for rapid charge transfer. In each case the mono-anion rearrangement discussed above is found to be largely suppressed. Thus the palladium complexes have two fully reversible waves only. Conventional voltammograms of the Pt complexes show, in addition, evidence of dimerisation as a minor pathway (<10%), as confirmed by their characteristic response to changes in scan rate and temperature.

It appears that the tendency to dimerisation is controlled simply by steric factors since the rearrangement is effectively suppressed for derivatives with E^0 values both less negative and more negative than the ‘ SacSac ’ complexes {for example,

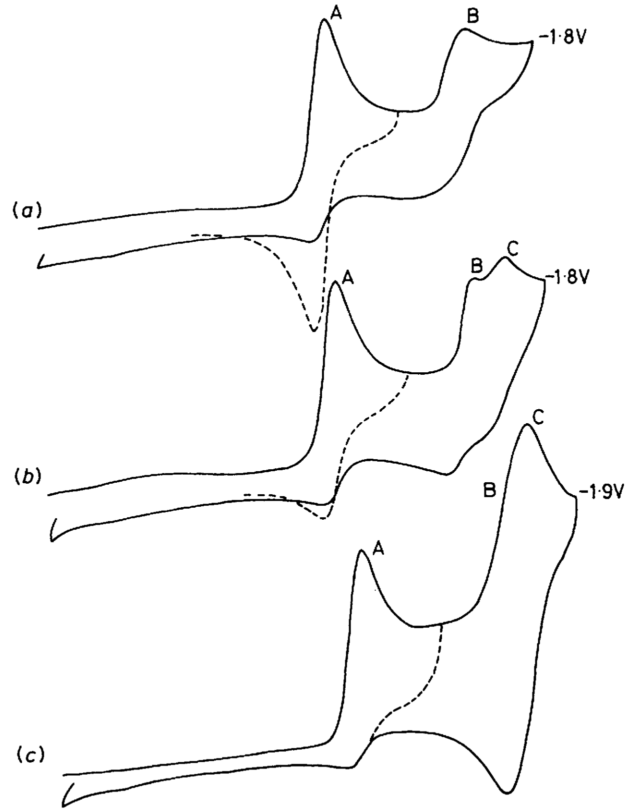


Figure 2. Comparison of [M(SacSac)$_2$] reductions for M = (*a*) Ni, (*b*) Pd, and (*c*) Pt: waves A, B, and C are as designated in the text; dashed line, E_λ prior to wave (*b*)

Table 1. Electrode potentials for the complexes [M(S_2C_3RHR')$_2$] [a]

R,R′	Ni	Pd	Pt
Bu^t,Bu^t	−1.07	−1.06	—
	−1.58 [b]	—	—
Me,Me	−0.94	−0.96	−0.96
	−1.42	−1.44	−1.41
Me,Ph	−0.75	−0.72	−0.80
	−1.16	−1.13	−1.24
Ph,Ph	−0.61	−0.60	—
	−1.02	−1.01	—
CF_3,Me	−0.43	−0.38	−0.46
	−0.93	−0.90	−0.9
CF_3,Ph	−0.25	−0.24	−0.23
	−0.73	−0.73	−0.69
CF_3,CF_3	—	+0.17	—
	—	−0.38	—

[a] $E^0_{red}(1)$ and $E^0_{red}(2)$ *versus* Ag–AgCl. [b] By a.c. voltammetry on platinum.

[Pd($S_2C_3CF_3HCF_3$)$_2$] and [Pd($S_2C_3Bu^tHBu^t$)$_2$]}. We also note that [Pt($S_2C_3H_3$)$_2$]$^-$ rearranges even more rapidly than [Pt(SacSac)$_2$]$^-$ itself.[17]

The substituted complexes exhibit a marked gradation in their characteristic electrode potentials. The extensive data collected here (Table 1) for various permutations of substituents on three metal centres allow a systematic analysis of the substituent influence. Superimposed in Figure 3 are the E^0_{red} (1) and E^0_{red} (2) values for all available [M(S_2C_3RHR')$_2$] complexes, plotted against the one-ligand sum of the Taft inductive parameters ($\sigma^*_R + \sigma^*_{R'}$). We note that the successive reduction potentials are virtually independent of the identity of the metal and are determined by the substituents in a manner which maintains an almost constant gap (*ca.* 0.45 ± 0.05 V) between the successive couples. The faithful linear correlation justifies our conclusion that the substituent influence is truly inductive in nature, and accords with the successful choice of the *meta*-Hammett parameter in an earlier analysis restricted to [Ni(S_2C_3RHR')$_2$].[16]

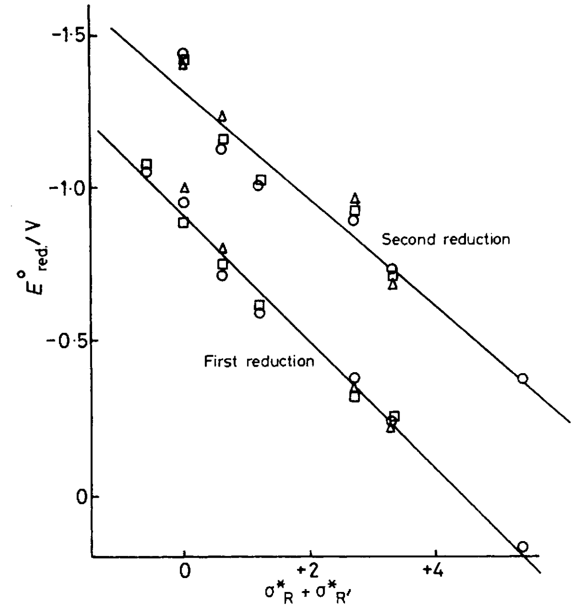


Figure 3. Reduction potential/substituent effect correlations for [M(S_2C_3RHR')$_2$] with M = Ni (□), Pd (○), and Pt (△): R,R′ = Bu^t,Bu^t; CH_3,CH_3; CH_3,Ph; Ph,Ph; CF_3,CH_3; CF_3,Ph; and CF_3,CF_3. Graph shows line of best fit (using least-squares analysis)

Closer inspection shows that the small but discernible deviations of, for example, the [Pd(S_2C_3RHR')$_2$] $E^0_{red}(1)$ data from a least-squares line of best fit are not random, since they are also reflected in the $E^0_{red}(2)$ *versus* σ^* profile, and faithfully reproduced for nickel and platinum. Thus, the substituent effects determined in this study are meaningful to a precise degree (±10 mV) and the deviations from the classical Taft plot indicate the inevitable limitations of applying the kinetically determined 'linear free energy' parameter in such a remote context. A consequence of this is that the least-squares analysis of the present data for [Pt(S_2C_3RHR')$_2$] might suggest a spurious distinction in substituent sensitivity compared to nickel and palladium, due to the bias in the limited set of platinum derivatives presently available.*

For the present purpose we therefore find it justified to establish a new scale of electrochemically derived induction parameters. This scale, designated σ^e, is based on the first reduction potentials for the [Pd(S_2C_3RHR')$_2$] (R = R′) family, which provides the widest range of symmetrically substituted derivatives. New values are obtained by horizontally 'smoothing' the measured points onto a line precisely parallel to the least-squares fitted $E^0_{red}(1)$ *versus* σ^* line previously established (Figure 3), in order strictly to retain a correlation

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* Matched subsets of compounds can be validly compared using literature σ^* values of course, with the disconcerting result that the characteristic 'sensitivity' appears to vary according to the bias in σ^* for the subset selected. This problem would be more pronounced in comparisons with available dithiene and dithiolylium systems (see later).

Table 2. Substituent inductive parameters

R	Taft [a] (σ^*_R)	Electrochemical [b] (σ^e_R)
Bu^t	−0.30	−0.25
Me	0	0
Ph	+0.60	+0.90
CF_3	+2.70	+2.80

[a] R. W. Taft, ' Steric effects in organic chemistry,' Wiley, New York, 1956. [b] See Results and Discussion section.

Table 3. Linear E^0/inductive parameter correlations [a] in $[M(X_2C_3RHR')_2]$

	NiS_4	PdS_4	PtS_4	PdO_4 [b]	NiS_2O_2
$k_{red}(1)$/mV	190	198	206	208	166
	(1.00)	(1.00)	(1.00)	(0.96)	(0.99)
$k_{red}(2)$/mV	172	176	186	—	—
	(0.98)	(0.99)	(0.99)		

[a] Least-squares fitted gradients, 1 000k/mV, with correlation coefficients in parentheses, for $E^0 = k(\sigma^e_R + \sigma^e_{R'})$. [b] See Table 4.

of unaltered physical significance. Thus the appropriate $2\sigma^e_R$ value for each $[Pd(S_2C_3RHR)_2]$ complex is simply read off the line at the experimentally measured potential. The modified and classical Taft parameters are compared in Table 2.

The worth of the new procedure is confirmed by the fact that the originally excluded asymmetric palladium complexes fit well on the modified scale, and by the observation that analogous ($\sigma^e_R + \sigma^e_R$) plots of E^0_{red} (2) for $[Pd(S_2C_3RHR')_2]$, and of both $E^0_{red}(1)$ and $E^0_{red}(2)$ for $[Ni(S_2C_3RHR')_2]$ and $[Pt(S_2C_3RHR')_2]$, show significantly improved correlation coefficients. As a result, certain slight, but significant, trends in gradient become apparent. For all six redox couples, the least-squares analyses, based on the modified σ^e parameters, are listed in Table 3.

The electrochemically derived scale has the convenient property that, by chance, there is an electrode potential shift of almost exactly 100 mV per unit numerical change in an individual substituent σ^e value {one of the four contributing in $[Pd(S_2C_3RHR')_2]$}. Thus the new scale obeys within 1% the useful relationship (2) where δE^0 is the shift in $E^0_{red}(1)$

$$\delta E \text{ (in mV)} = 100\Sigma\sigma^e = 200\ (\sigma^e_R + \sigma^e_{R'}) \qquad (2)$$

between $[Pd(SacSac)_2]$ and any other $[Pd(S_2C_3RHR')_2]$ complex. Approximately the same numerical relationship extends to the nickel and platinum systems as well.

Several significant points emerge from the data presented in this way. Firstly, for a given metal ion, gradients for $E^0_{red}(1)$ and $E^0_{red}(2)$ plots are close to parallel, implying that the nature of the redox-active orbital is similar for first and second electron transfers (and apparently inconsistent, for example, with a hypothetical sequence of metal-based followed by ligand-based stepwise reduction). Secondly, the degree to which substituents influence the electrode potentials is consistent with substantial, or even exclusive, ligand participation in charge acceptance, and is relatively indifferent to the identity of the central ion.

Inevitable comparison arises with the metal dithienes (VI) which are accepted to have primarily ligand-based redox activity. We find that the series $[Ni(S_2C_2RR')_2]$, where $R = R' = CH_3$, Ph, or CF_3, gives a $E^0_{red}(1)$ gradient on the σ^e scale which is negligibly different from that of $[Ni(S_2C_3RHR')_2]$ (*i.e.* 186 mV *versus* 190 mV per unit, Figure 4). Furthermore, even the one-electron reduction potentials of the related metal-free dithiolylium ion series (II) are scarcely more sensitive to substitution than the present complexes, so that for example the distinction between $(S_2C_3RHR')^+$ and $[Pt(S_2C_3RHR')_2]$ (216 mV *versus* 206 mV per σ^e unit) is no greater than the differences between the isostructural Ni, Pd, and Pt systems (Table 3).

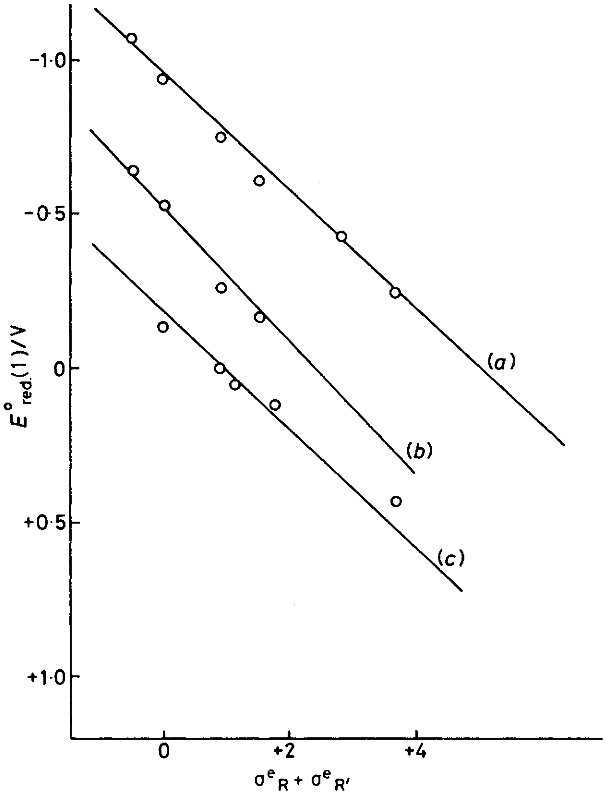

Figure 4. Reduction potential/substituent effect correlations for delocalised organosulphur systems: (*a*) $[Ni(S_2C_3RHR')_2]$, (*b*) $(S_2C_3RHR')^+$, and (*c*) $[Ni(S_2C_2RR')_2]$. R and R′ are various, see Figure 3

We note in passing that the good correlations associated with these structurally distinct species vindicate the modified inductive parameters in a broader context, since the correlation coefficients are of the order of 0.99.

In relation to predictions based on molecular orbital calculations,[19,20] the present data clearly establish dominant ligand character in the redox-active orbital, since broadly speaking we encounter close to the maximum expected substituent influence and almost negligible (though consistent) metal ion effects. This must prompt a reappraisal of Schrauzer's [12] criterion. With the benefit of hindsight, it is clear that the correct inference from the topological distinction between resonance-stabilized 1,2-dithio- and 1,3-dithio-chelates is that the acceptor orbital in the latter lies to higher energy (by *ca.* 0.8 eV; eV ≈ 1.602×10^{-19} J), leading to relatively negative, reversible reduction potentials, rather than to an absence of ligand-mediated electron-transfer activity.

C. Comparison with the Oxo-systems.—We are not aware of any comparable voltammetric studies on the planar Pd and Pt bis(1,3-diketonate) complexes. However, the diamagnetic monomer $[Ni(O_2C_3Bu^tHBu^t)_2]$ shows irreversible electrode reductions,[21] in marked contrast to the dithio-chelates discussed above. Thus in the oxo-systems nothing is known of

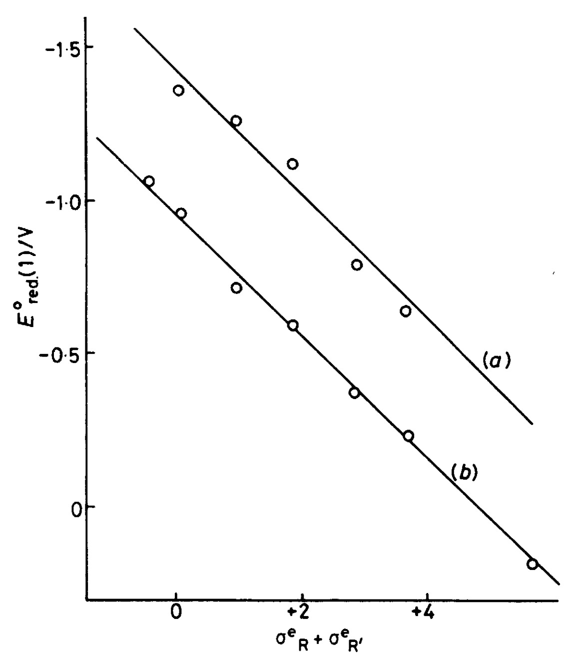

Figure 5. Reduction potential/substituent effect correlations for $[Pd(X_2C_3RHR')_2]$ systems: (*a*) X = O, (*b*) X = S. R and R′ are various, see Figure 3

Table 4. Electrode potentials[a] for diketonato- and monothiodiketonato-complexes

R,R′	$[Pd(O_2C_3RHR')_2]$[b]	$[Ni(SOC_3RHR')_2]$
Bu^t,Bu^t	—	−1.21
Me,Me	−1.37	−1.11
Me,Ph	−1.27	—
Ph,Ph	−1.24	−0.89
CF_3,Me	−0.80	—
CF_3,Ph	−0.65	−0.49

[a] $E^0_{red}(1)$–V *versus* Ag–AgCl. [b] $E_{red}(1)$ calculated as the potential at 85% of the cathodic peak current.

the thermodynamic implications, if any, of the measured electrode-potential data, or the nature of the reduced species.

We have extended the present investigation to complementary a.c. and cyclic voltammetric studies of a useful set of variously substituted palladium complexes $[Pd(O_2C_3RHR')_2]$ (R,R′ = Me, Ph, or CF_3) in non-aqueous media. Detailed analysis confirms that these complexes undergo an irreversible or quasi-reversible one-electron reduction and that the departure from ideality is due to sluggish heterogeneous charge-transfer kinetics. However, the opportunity to compare a *series* of such complexes, and in particular to consider these in relation to the isostructural and ideally behaved dithio-analogues (Figure 5), provides further insight. Clearly an orderly response to the inductive character of the substituents is again observed (with a respectable least-squares correlation coefficient, despite the difficulty of specifying $E_{\frac{1}{2}}$ in these non-reversible voltammograms). Moreover, the gradient of the $E^0_{red}(1)$ *versus* σ^e plot is notably close to that encountered in the corresponding $[M(S_2C_3RHR')_2]$ reductions (Figure 5) suggesting that the charge is similarly distributed in the two systems. The oxo-systems are seen to be systematically more difficult to reduce than their thio-analogues by *ca.* 0.45 V, reminding us that the antibonding (acceptor) molecular orbitals in particular may be destabilized by introduction of the ' harder ' more electronegative heteroatom.[22]

Limited data for the reversible first reductions of the monothio-chelates in the series $[Ni(SOC_3RHR')_2]$ show, not surprisingly, that the $E^0_{red}(1)$ values lie intermediate between those of the corresponding MS_4 and MO_4 complexes.

Interestingly, the $E^0_{red}(1)$ *versus* σ^e plot is again closely linear, even for the asymmetrically substituted complexes, though it departs discernibly from the gradients encountered in the former systems. However, the profoundly lower symmetry of the $[M(SOC_3RHR')_2]$ systems should inhibit simple interpretation at this stage.

Experimental

(*i*) *Materials.*—All compounds were recrystallized and analytically pure.

$[M(S_2C_3RHR')_2]$ (M = Ni, Pd, *or* Pt). The Ni complexes were obtained by published methods,[2,5,6] and the Pd and Pt complexes were prepared similarly from the well known $[M(SOC_3RHR')_2]$ complexes,[22] by treatment with H_2S in acidified alcohol. Details of the preparation and general characterisation of the new compounds will be described separately.[9]

$[Pd(O_2C_3RHR')_2]$. These complexes were obtained from $PdCl_2$ and the appropriate diketone by standard procedures.[23]

(*ii*) *Instrumentation.*—Voltammetric studies in CH_2Cl_2–$[NBu^n_4][BF_4]$ (0.5 mol dm^{-3}) employed a PAR 170 Electrochemistry System (potentiostat and programmer), interfaced with a Metrohm E505 cell-stand and three-electrode configuration, with full positive feed back resistance compensation and phase-sensitive detection in a.c. measurements. A non-aqueous Ag,AgCl|Cl^-,CH_2Cl_2 reference electrode (against which ferrocene was oxidised at +0.58 V), separated by a further fritted salt bridge, and a platinum counter electrode were used in a 5-cm^3 jacketted glass cell. The polarographic dropping mercury electrode (d.m.e.) functioned at electronically controlled drop times (t_d normally 0.5 s). Other a.c. and cyclic voltammograms employed Pt wire and micro-disc working electrodes, whereas d.c. voltammograms and diffusion current measurements were obtained with a Tacussel EDI rotating platinum electrode (r.p.e.) in the range 1 000—6 000 r.p.m. Routine scan rates were 100 mV s^{-1} in cyclic voltammetry and 10 mV s^{-1} in other modes.

Cell solutions, normally 1.0×10^{-3} mol dm^{-3} in complex, were degassed with CH_2Cl_2-saturated argon, and cell temperatures in the range 225—295 K were maintained (±0.1°) by a digitally controlled Haake F3Q circulating bath.

(*iii*) *Voltammetric Analysis.*—Each compound's electrode response has been examined in detail; representative data for a typical system are provided below.

In CH_2Cl_2, at both d.m.e. and r.p.e., $[Pd(S_2C_3MeHCF_3)_2]$ shows two cathodic waves of equal height, and logarithmic analysis confirms d.c. Nernstian behaviour appropriate to stepwise reversible reductions. Diffusion currents are directly proportional to concentration in the range 1×10^{-5} to 5×10^{-3} mol dm^{-3}, with a measured diffusion coefficient D(293 K) = 6.8×10^{-6} cm^2 s^{-1}, at the r.p.e. Similar D values (within 5%) are obtained for the Ni and Pt analogues, and for $[Pd(SOC_3MeHCF_3)_2]$. A.c. waves are symmetric with half-height peak widths of 90 ± 5 mV and a linear I_p *versus* $\omega^{\frac{1}{2}}$ plot (passing through origin), in the frequency range ω = 20—1 000 Hz, with phase angle φ = 45°. Cyclic voltammograms in the scan-rate range v = 50 to 2 000 mV s^{-1} have ΔE_p = 60 ± 5 mV, I_p(reverse)/I_p(forward) ratios of unity, and linear I_p *versus* $v^{\frac{1}{2}}$

dependence. $E_{\frac{1}{2}}$/V(d.c.,c.v.) and E_p/V(a.c.) values are negligibly altered by concentration or other experimental parameters in the range 225—295 K.

The [M(SacSac)$_2$] systems, in particular, show deviations attributed to reactions following charge transfer, as described in the text. Detailed study of their electrode kinetics is in hand, and will be reported subsequently.[9]

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