Ready Displacement of Dithiolene Ligands from Electron-poor Dithiolene Complexes by Weak Nucleophiles

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Summary The 'reduction' of electron-poor bis-dithiolene metal complexes (one-electron reduction potentials >0 V *vs.* SCE) by halide and pseudohalide anions, unhindered amines, and common weakly Lewis basic solvents such as acetonitrile, proceeds by initial nucleophilic displacement of a dithiolene ligand, which induces rapid consequent reactions leading to overall disproportionation stoicheiometry.

Among the transition-metal–dithiolene complexes[1] are many highly oxidised electron-deficient compounds with unusually high positive reduction potentials. The following isolable species,† listed with their electrochemical (thermodynamic) one-electron reduction potentials *vs.* SCE, are examples: $[Fe(tfd)_2]_2^0$, +1·1; $[Co(tfd)_2]_2^0$, +1·1; $[Ni(tfd)_2]^0$, +0·92; $[Pt(tfd)_2]^0$, +0·82; $[Pd(mnt)_2]^-$, +0·46; $[Cu(mnt)_2]^-$, +0·34; $[Ni(mnt)_2]^-$, +0·23; $[Ni(S\text{–}S,Ph)_2]^0$, +0·12 V. The literature describing the homogeneous one-electron reduction of these complexes is puzzling in that electron abstraction from the 'reductants' is very unfavourable at the potentials in question. For example, $[Ni(tfd)_2]^0$ is rapidly reduced to $[Ni(tfd)_2]^-$ by MeCN, Me_2CO, and $HCONMe_2$, even though the anodic potential limits for electrochemistry in these solvents[2] are 0·7—0·9 V more positive than the reduction potential of $[Ni(tfd)_2]^0$.

We report here that the properties of these reactions all indicate a mechanism sequence in which the 'reducing reagent,' generally denoted L, functions only as a substituting nucleophile, and not as an electron-transfer reagent.

The stoicheiometry of these reactions is a diagnostic characteristic; the conversion of the oxidised dithiolene complex into the reduced dithiolene complex is always <100 mol %, while the remainder of the metal is converted into a conventional complex with L, and the remainder of the dithiolene ligand appears in a free oxidised form. For instance, when $[Ni(tfd)_2]^0$ reacts with Lewis base solvents such as MeCN, $HCONMe_2$, Me_2CO, or halides Cl^- and Br^- in the inert solvent CH_2Cl_2, $[Ni(tfd)_2]^-$ is formed invariably in 66—68 mol % yield, together with either $[Ni(solvent)_6]^{2+}$ or $[NiX_4]^{2-}$ (X = Cl, Br), and $(tfd)^0$ or its degradation products. Similar results for a variety of these reactions are summarized in the Table. This overall product distribution, which is essentially disproportionation, is clearly distinct from the 100 mol % formation of reduced dithiolene complex observed in pure electron-transfer reactions, such as those of $[Ni(mnt)_2]^-$ with excess of $Pr^n{}_3N$[3] or with wet PPh_3,[4] and $[Ni(tfd)_2]^0$ with I^-. The disproportionation is severely inhibited by steric bulk in the nucleophile L. Experiments using selected alkyl, aryl, and heterocyclic amines have revealed that disproportionation is kinetically very competitive with electron transfer for unhindered nucleophiles, but is kinetically noncompetitive for hindered tertiary amines.

Table. Reactions of oxidised dithiolene complexes with common nucleophiles

	Oxidised dithiolene complex	Nucleophile[a]	Solvent	Metal complex products[b]		Reaction time scale[c]
				Reduced dithiolene complex	Metal-nucleophile complex	
A	$[Ni(tfd)_2]^0$	Donor solvents: MeCN, $HCONMe_2$, Me_2CO	None, CH_2Cl_2, toluene	$[Ni(tfd)_2]^-$ 0·66—0·68[d]	$[Ni(solvent)_6]^{2+}$	min
B	$[Ni(tfd)_2]^0$	X^-: X = Cl, Br	CH_2Cl_2	$[Ni(tfd)_2]^-$ 0·66—0·68[d]	$[NiX_4]^{2-}$	min
C	$[Cu(mnt)_2]^-$	Amines: Bu^nNH_2, piperidine	MeCN	$[Cu(mnt)_2]^{2-}$	Cu^{II}amine complexes	s
D	$[Cu(mnt)_2]^-$	X^-: X = Cl, Br	MeCN	$[Cu(mnt)_2]^{2-}$	Cu^{II} halide complexes	min
E	$[Ni(mnt)_2]^-$	Amines: NH_3, RNH_2	MeCN	$[Ni(mnt)_2]^{2-}$	$[Ni(NH_3)_6]^{2+}$ [e] $[Ni(en)_3]^{2+}$ [e]	s
F	$[Ni(mnt)_2]^-$	X^-: X = Cl, Br, NCS	MeCN, CH_2Cl_2	$[Ni(mnt)_2]^{2-}$	$[NiX_4]^{2-}$	h
G	$[Co(mnt)_2]_2^{2-}$	X^-: X = Cl, Br, NCS	MeCN	$[Co(mnt)_3]^{3-}$ 0·63[d]	$[CoX_4]^{2-}$	min

[a] In excess. [b] Oxidised forms of (tfd) or (mnt), or their degradation products, were identified spectrophotometrically or by isolation in some cases. [c] Approximate, for reactant complex concentrations 10^{-3}—10^{-1}M, at room temperature. [d] Mol fraction of reduced dithiolene complex produced, determined spectrophotometrically or by isolation. [e] The salts $[Ni(NH_3)_6]^{2+}[Ni(mnt)_2]^{2-}$, $[Ni(en)_3]^{2+}$-$[Ni(mnt)_2]^{2-}$ crystallise from the reaction solution; en = $NH_2CH_2CH_2NH_2$.

We propose the following generalised mechanism for the disproportionation. The first stage involves rate-deter-

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† We have used the abbreviation (S–S,R) or, generally, (S–S) to denote the ligand RC(S)=C(S)R; tfd = $F_3CC(S)=C(S)CF_3$ and mnt = NCC(S)=C(S)CN.

mining substitution of one dithiolene ligand from the oxidized dithiolene complex, as shown in equation (1).

$$[M(S\text{-}S)_2]^z + 2L \rightarrow L_2M(S\text{-}S) + (S\text{-}S) \qquad (1)$$

In a second stage, (2), the oxidised dithiolene complex is rapidly reduced by either the mixed-ligand intermediate $L_2M(S—S)$ or the displaced dithiolene ligand produced in equation (1). A third stage involves rapid nucleophilic

$$[M(S\text{-}S)_2]^z + \text{reductant} \rightarrow [M(S\text{-}S)_2]^{z-1} + \text{product} \qquad (2)$$

displacement of the dithiolene ligand remaining in intermediate mixed-ligand complexes, as shown in equation (3).

$$L_2M(S\text{-}S) + (n-2)L \rightarrow M^{II}L_n + (S\text{-}S) \qquad (3)$$

The distribution of charge between the intermediate mixed ligand complex and the displaced dithiolene ligand in equation (1) is uncertain, owing to the variable electron population ('non-innocence') characteristic of dithiolene complexes and ligands. For example, the reaction of ammonia with $[Ni(mnt)_2]^-$ may produce $[(NH_3)_n\,Ni(mnt)]^-$ and $(mnt)^0$, or $[(NH_3)_nNi(mnt)]^0$ and $(mnt)^-$, or $[(NH_3)_n\text{-}Ni(mnt)]^+$ and $(mnt)^{2-}$. Nevertheless, from a knowledge of the general trends in electron-transfer potentials of mixed-ligand dithiolene complexes[5] and dithiolate ligands[1b] it can be confidently estimated that one product of equation (1) is in all cases a one-electron reductant thermodynamically sufficient for reaction (2) to occur. Also, the mixed-ligand complex as it emerges from reactions (1) and (2) must be in an oxidised state which will favour further ready and complete substitution of the dithiolene ligand.[5]

Details of the observed stoicheiometry depend on the relative rates of the reactions in the three stages. For example, we believe that the 66—68 mol % formation of $[Ni(tfd)_2]^-$ in reaction A of the Table most probably results from the specific processes in equations (4)—(7).

$$[Ni(tfd)_2]^0 + 2MeCN \xrightarrow[\text{det.}]{\text{rate}} [(MeCN)_2Ni(tfd)]^0 + (tfd)^0 \qquad (4)$$

$$[Ni(tfd)_2]^0 + [(MeCN)_2Ni(tfd)]^0 \xrightarrow{\text{fast}} [Ni(tfd)_2]^- + [(MeCN)_2Ni(tfd)]^+ \qquad (5)$$

$$[Ni(tfd)_2]^0 + [(MeCN)_2Ni(tfd)]^+ \xrightarrow{\text{fast}} [Ni(tfd)_2]^- + [(MeCN)_2Ni(tfd)]^{2+} \qquad (6)$$

$$[(MeCN)_2Ni(tfd)]^{2+} + 4MeCN \xrightarrow{\text{fast}} [Ni(MeCN)_6]^{2+} + (tfd)^0 \qquad (7)$$

$$\text{Overall: } 3[Ni(tfd)_2]^0 + 6MeCN \rightarrow 2[Ni(tfd)_2]^- + [Ni(MeCN)_6]^{2+} + 2(tfd)^0$$

The products of reaction G given in the Table are consistent with our general mechanism, since equilibria (8) and (9) are rapidly attained.

$$[Co(mnt)_2]^{2-} + \tfrac{1}{2}(mnt)_2{}^{2-} \rightleftharpoons [Co(mnt)_3]^{3-} \qquad (8)$$

$$\tfrac{1}{2}[Co(mnt)_2]_2^{2-} + (mnt)^{2-} \rightleftharpoons [Co(mnt)_3]^{3-} \qquad (9)$$

The substitution stage (1) is analogous to the substitution reactions of oxidized bis-dithiolene complexes by π-acidic bidentate di-imine ligands, reactions in which stable mixed-ligand dithiolene-di-imine complexes are formed.[5] However, the nucleophiles considered here are not π-acidic, and the reactions which follow substitution are not slower than substitution. In some cases the rate of the disproportionation increases as the temperature is decreased from ambient to *ca.* − 70 °C. This indicates the presence of an equilibrium with ΔH and ΔS both negative preceding the substitution stage (1). On the basis of these thermodynamic parameters and the strong nucleophile steric influence on rate, it seems probable that weak adduct formation (analogous to that known for iron and cobalt dithiolene complexes[6]) precedes the substitution given in equation (1).

Substitution-induced disproportionation with disruption of the bis-dithiolene $M(S\text{-}S)_2$ core[7] is a ready sequence not previously recognised.[8] Nevertheless this reaction is ubiquitous amongst oxidised dithiolene complexes. Our studies reveal that all bis-dithiolene complexes with positive (*vs.* SCE) reduction potentials are subject to this process. The effects of this reaction are usually undesirable. In redox catalysis by dithiolene complexes, nucleophilic reactants or products of the catalysed reaction can lead to catalyst decomposition.[9] In oxidative synthesis the use of halogen oxidants generates halide nucleophiles which then induce disproportionation of the desired oxidised complex product, resulting in autocatalysed decomposition. We have diminished the extent of these problems by decreasing the nucleophilic activity of anions *via* solvation. Thus reaction

$$Br_2 + 2[Ni(mnt)_2]^{2-} \rightarrow 2Br^- + 2[Ni(mnt)_2]^- \qquad (10)$$

(10) gives a poor yield in pure CH_2Cl_2 owing to the occurrence of reaction F in the Table but becomes a very satisfactory synthetic procedure with high yield when water (*ca.* 10 vol %) is added to the reaction mixture.

A generally valuable prescription for the synthesis and investigation of highly oxidised complexes with 'non-innocent' ligands is avoidance of nucleophilic conditions, or at least minimisation of nucleophilic activity by steric crowding, protonation, or solvation.

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