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Oxidative addition chemistry of tetrathiocines: Synthesis, structures and properties of Group 10 dithiolate complexes.

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Oxidative addition of the electron-rich tetra-methoxy-dibenzo-1,2,5,6-tetrathiocine $[(MeO)_2C_6H_2S_2]_2$ to zero-valent group 10 transition metal complexes in the presence of diphenylphosphinoethane (dppe) affords the corresponding dithiolate complexes, [(DMOBD)M(dppe)] (DMOBD = dimethoxybenzenedithiolato, $(MeO)_2C_6H_2S_2^{2^-}$; M = Ni, Pd, Pt) in high yield which were characterized by single crystal X-ray diffraction. Whereas the Pd and Pt complexes exhibit two quasi-reversible 1e⁻ oxidation processes, the nickel species undergoes a quasi-reversible 1e⁻ reduction.

Introduction

Transition metal dithiolene chemistry has continued to be an active field of study since it first originated in the early 1960s.¹ Recent studies have focused on their potential applications in the areas of non-linear optics,² dyes,³ catalysis⁴ and as conducting⁵ and magnetic materials.⁶ In particular the potential to tailor the electronic properties of the dithiolene ligand through modification of the substituents is central to future applications.¹ Such dithiolene complexes are typically prepared from ligand exchange reactions of *s*-block metal dithiolates with *d*-block metal salts or *via* condensation of the free thiol with transition metal oxo, alkoxo, and amido precursors.¹ Alternative strategies include reaction of 1,2-dithietes (RC)₂S₂ and dithiins to low-valent metals.⁸

Despite the potential for π -delocalisation and conjugation, few benzo-fused derivatives have been reported and the chemistry of benzo-fused-1,2-dithiolato complexes focuses extensively on derivatives of commercially available 1,2benzenedithiol and toluene-3,4-dithiol,⁹ though a small number of other derivatives have been crystallographically characterised.¹⁰⁻¹³ Our recent studies on the chemistry of tetrathiocines¹⁴ prompted us to examine the oxidative addition chemistry of such tetrathiocines to low oxidation state transition metals as an alternative strategy to synthesise transition metal dithiolate complexes. In particular, ready access to a range of alkoxy-functionalised tetrathiocines in multi-gram quantities in





Scheme 1. Two-step synthesis of group 10 dithiolenes.

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Compound	1	2	3
Chemical formula	$C_{34}H_{32}O_2P_2S_2Ni$	$C_{34}H_{32}O_2P_2S_2Pd\cdot CH_2Cl_2$	C34H32O2P2S2Pt·CH2Cl
Formula weight	657.37	789.98	878.67
Crystal System	Orthorhombic	Tetragonal	Tetragonal
Space group	$P2_{1}2_{1}2_{1}$	I-42d	I-42d
a (Å)	11.9151(12)	20.8660(21)	20.864(6)
b (Å)	12.7964(11)	20.8660(21)	20.864(6)
<i>c</i> (Å)	20.0546(19)	15.5435(16)	15.544(5)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00
$V(Å^3)$	3057.7(5)	6767.5(15)	6766(3)
Z	4	8	8
D_{calcd} (g cm ⁻³)	1.428	1.551	1.725
μ (mm ⁻¹)	0.907	0.956	4.556
θ range (deg)	2.55 to 30.03	1.95 to 24.99	1.38 to 28.46
Reflns collected	20051	32531	39594
Unique reflns	8721	4126	4142
Data/restraints/parameters	8721/0/373	4126/6/205	4142/0/205
R_1 , w R_2 ($I > 2\sigma(I)$)	0.0426, 0.0881	0.0289, 0.0666	0.0172, 0.0407
Residual electron density (e^{-1}/A^3)	+0.527/-0.346	+0.596/-0.538	+0.647/-0.487

Experimental Section

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General Considerations.

 $Ni(COD)_2$ was obtained commercially from Sigma Aldrich and used as received. Pd_2dba_3 and $Pt(dppe)_2$ were prepared according to the literature methods^{16,17} using starting materials acquired from Strem. The *bis*-(dimethoxybenzo)-tetrathiocine (**T**) was prepared according to the literature method.¹⁵ Standard solvents were dried and deoxygenated using an Innovative Technology Solvent Purification System and manipulation of air-sensitive materials carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and a dry-nitrogen glove box (Braun Labmaster). Microwave syntheses were carried out in sealed vessels using a Biotage Initiator 1 microwave.

Physical Measurements.

NMR spectra were recorded on a Bruker DPX300 UltraShield 300MHz spectrometer with a Broadband AX Probe using CDCl₃ (¹H δ = 7.26 ppm, s) as an internal reference point relative to Me₄Si (δ = 0 ppm). ³¹P NMR spectra were referenced to 85% H₃PO₄ (δ = 0 ppm). IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. Elemental compositions were determined on a PerkinElmer 2400 Series II Elemental Analyzer. Mass spectra were recorded on a Waters Micromass LCT Classic Electrospray Ionization Time of Flight (ESI-TOF) mass spectrometer operated in positive mode.

Synthesis of 1 – 3 (Scheme 1)

Synthesis of [(DMOBD)Ni(dppe)], 1. Ni(COD)₂ (0.150 g, 0.545 mmol), dppe (0.218 g, 0.545 mmol) and tetrathiocine T (0.109 g, 0.273 mmol) were combined in an oven dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 40 min at 150 °C. The resultant dark brown solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.320 g, 89% yield). The solid was recrystallized from a saturated CH₂Cl₂ solution layered with hexanes to produce dark purple needle-shaped crystals suitable for X-ray diffraction. NMR: $\delta_{\rm H} = 7.83$ (8H, 7.86-7.80, m, *m*-H), 7.47 (12H, 7.54-7.43, m, o,p-H), 6.95 (2H, s, benzo C-H), 3.74 (6H, s, CH₃), 2.36 (4H, d, J = 17.4 Hz, PCH₂); $\delta_P = 59.83$. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{34}H_{33}O_2P_2S_2Ni^+$ 657.0745; found 657.0723. Elemental Analysis calcd for C₃₄H₃₂O₂P₂S₂Ni: C 62.12; H 4.91%; found: C 61.59; H 4.71%. IR v_{max} (cm⁻¹): 3052(w), 2997(w), 2929(w), 2829(w), 1584(w), 1483(s), 1469(s), 1434(vs), 1343(m), 1244(vs), 1199(s), 1174(m), 1100(s), 1043(s), 815(m), 782(m), 746(m), 690(vs), 531(vs), 482(m).

Synthesis of [(DMOBD)Pd(dppe)], 2. Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocine T (0.044 g, 0.109 mmol) were combined in an oven dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension heated in the microwave for 30 min at 150 °C. The resultant bright pink solid was isolated from the clear-yellow solution by filtration. The precipitate was washed with a small amount of hexanes and dried in air (0.131 g, 85% yield).

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The solid was recrystallized from a saturated CH₂Cl₂ solution layered with toluene and hexanes to produce red-purple needles suitable for X-ray diffraction. NMR: $\delta_{\rm H} = 7.83$ (8H, 7.86-7.79, m, *m*-H), 7.46 (12H, 7.51-7.44, m, *o*,*p*-H), 6.91 (2H, s, *benzo* C-H), 3.75 (6H, s, CH₃), 2.50 (4H, d, *J* = 20.7 Hz, PCH₂); $\delta_{\rm P} =$ 51.94. HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₃₄H₃₃O₂P₂S₂Pd⁺ 705.0427; found 705.0462. Elemental Analysis calcd for C₃₄H₃₂O₂P₂S₂Pd·CH₂Cl₂: C 53.20; H 4.87%; found: C 53.26; H 4.39%. IR vmax (cm-1): 3358(w), 3050(w), 2922(m), 2850(w), 2829(w), 1483(s), 1470(s), 1434(vs), 1339(m), 1240(vs), 1198(s), 1174(m), 1100(s), 1039(s), 846(m), 744(m), 703(s), 690(vs), 524(vs), 486(m).

Synthesis of [(DMOBD)Pt(dppe)], 3. Pt(dppe)₂ (0.100 g, 0.101 mmol) and tetrathiocine T (0.020 g, 0.050 mmol) were combined in an oven dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added to the vial and the suspension heated in the microwave for 30 min at 150 °C. The resultant bright yellow microcrystalline solid was isolated from a clear-yellow solution by gravity filtration. The precipitate was washed with a small amount of hexanes dried in air (0.062 g, 77% yield). The solid was recrystallized from a saturated CH₂Cl₂ solution layered with hexanes to produce bright yellow plate-like crystals suitable for X-ray diffraction. NMR: $\delta_{\rm H}$ = 7.84 (8H, 7.87-7.81, m, m-H), 7.45 (12H, 7.46-7.44, m, o, p-H), 7.07 (2H, s, benzo C-H), 3.76 (6H, s, CH₃), 2.47 (4H, 2.54-2.39, m, PCH₂); $\delta_{\rm P} = 45.90 ({}^{1}J_{\rm Pt-P} = 3427$ Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{34}H_{33}O_2P_2S_2Pt^+$ 794.1039; found 794.1037. Elemental Analysis calcd for C₃₄H₃₂O₂P₂S₂Pt·CH₂Cl₂: C 47.84, H 3.90%; found: C 47.53, H 3.66%. IR v_{max} (cm⁻¹): 3053(w), 2988(w), 2900(w), 2830(w), 1485(s), 1435(vs), 1341(m), 1241(vs), 1200(m), 1103(s), 1042(m), 748(m), 691(vs), 531(vs), 481(m).

X-Ray Crystallography

Crystals were mounted on a cryoloop with paratone oil and examined on a Bruker SMART or Bruker APEX-II diffractometer equipped with a CCD area detector and an Oxford Cryostream cooler. Data were measured at 150(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the APEX-II software.¹⁸ Final cell constants were determined from full least squares refinement of all observed reflections. The data were collected for absorption (sadabs)¹⁹ and the structures solved by direct methods to reveal most non-H atoms. Remaining heavy atom positions were located in subsequence difference maps and the structure refined with full least squares refinement on F^2 within the SHELXTL suite.²⁰ Hydrogen atoms were placed at calculated positions and refined isotropically with a riding model. In the case of 2 and 3 both the complex and the CH₂Cl₂ solvate lay about a crystallographic 2fold axis with the CH₂Cl₂ exhibiting some evidence for disorder which was modeled over two sites. In addition all three complexes crystallized in acentric space groups. In all cases there was some degree of merohedral twinning. In the case of 2 and 3 the twin was ca. 50:50 making assignment of the absolute structure meaningless. However, in the case of 1, the crystal chosen exhibited a 90:10 twin and the Flack parameter

(0.094(10)) permitted the correct absolute structure to be determined (as *S* for the crystal selected for the crystallographic study).



Figure 1. Crystal structure and selected atom labelling of complexes 1 - 3. Hydrogen atoms (and solvate molecules for 2 and 3) have been omitted for clarity. Thermal ellipsoids are drawn at the 75% probability level. In all cases the twinning was treated with the appropriate TWIN law and BASF parameter to refine the twin components. Structure solution, refinement and preparation of final cif files were undertaken using the SHELXTL package. Crystallographic data are summarized in Table 1. CCDC 965075 – 965077.

Electrochemistry

Cyclic voltammetry measurements were made on solutions of **1** – **3** in CH₂Cl₂ using 0.1 M [^{*n*}Bu₄N][PF₆] as the supporting electrolyte (electrochemical grade, Fluka) using a BAS 100B Electrochemical Analyzer with BAS 100W software using a sweep rate of 100 mVs⁻¹ with glassy carbon working electrode, Pt wire auxiliary electrode and a Ag/AgCl reference electrode against which the Fc/Fc⁺ couple appeared at +0.73 V.

Computational studies

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Single point DFT calculations were undertaken on the structures of 1 - 3 determined by X-ray diffraction using the LACVP3* basis set and both B3LYP and BP86 functionals²¹ within Jaguar.²² The LACVP3* basis set uses an effective core potential for the metal atom and provides triple split-valence zeta quality (6-311+G*) for all atoms with an additional polarization function.²³ Such basis sets have been previously employed to study a range of organometallic/coordination chemistry complexes including Pd and Ru phosphines.²⁴ Changes in the functional did not lead to significant changes to the energies of the HOMOs and LUMOs or indeed the nature of the frontier orbitals.

Results and Discussion

Ligand exchange of dithiolate anions with simple metal salts has proved to be the most common route to dithiolate complexes.¹ However oxidative addition of dithietes and disulfides to lower oxidation state metals has proved an alternative if not extensively used synthetic strategy.^{8,25} For example, recent studies by Corrigan and co-workers revealed oxidative addition of cyclic disulfides to Pt(PPh₃)₄ occurred in moderate isolated yield (ca. 50%) after stirring at ambient temperature for 20 h.²⁵ In our current studies we have investigated tetrathiocines as a readily accessible alternative to dithiete and disulfides.¹⁵ However the low solubility of the tetrathiocines in a range of organic solvents led to very slow reactivity with zero-valent group 10 transition metals in the presence of dppe under ambient conditions and, disappointingly, yielded a mixture of products (³¹P NMR) upon heating. Conversely microwave irradiation has been shown to afford higher selectivity and fast reaction times in many transformations²⁶ and we found that reaction of tetrathiocine T with the zero-valent group 10 metal complexes $Ni(COD)_2$ or $Pd_2(dba)_3$ in the presence of 1 equivalent of dppe per metal centre or with Pt(dppe)₂ in toluene at 150 °C under microwave irradiation for 30-40 min afforded 1, 2 and 3 respectively in very good (77 – 89%) recovered yields (Scheme 1). The ${}^{31}P$ NMR spectra of the resultant solids dissolved in CDCl₃

revealed singlet spectra (with satellites from ${}^{1}J_{Pt-P}$ coupling in the case of **3**) consistent with a unique ${}^{31}P$ environment and ${}^{31}P$ NMR chemical shifts comparable with other square-planar group 10 M^{II} complexes with MP₂S₂ ligand sets.^{27,28}

e 2. Structural and electrochemical data				
	1	2	3	
M-P bond length (Å)	2.1619(7) 2.1661(7)	2.2739(6)	2.2552(7)	
M-S bond length (Å)	2.1490(7) 2.1613(7)	2.2977(6)	2.3042(7)	
P-M-P bond angle (°)	86.64(3)	84.98(3)	85.31(4)	
S-M-S bond angle (°)	92.88(3)	88.85(3)	88.46(4)	
$E_{1/2}(V)^{red}$	-1.61	n	ⁿ	
$E_{1/2}$ (V) ^{ox}	$+0.73^{i}$	+0.51,	+0.58,	
		+1.35	+1.36	
ΔE_{pp} (V)	0.37	0.33,0.29	0.29,0.26	



Figure 2. CV scans of complexes 1-3 using 0.1 M $[^nBu_4N][PF_6]$ supporting electrolyte in CH_2Cl_2 (scan rate 100 mV/s)

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Complexes 1 - 3 all revealed $[M+H]^+$ ions by positive ion ESI-TOF mass spectroscopy and were further characterized by X-ray diffraction and compositions confirmed by elemental analysis.

X-Ray Crystallographic studies.

In all cases crystals of 1, 2 and 3 were grown by slow diffusion of hexane into a concentrated CH_2Cl_2 solution and their structures determined by X-ray diffraction (Figure 1). Whilst 1 crystallises in the orthorhombic space group $P2_12_12_1$ without any solvent molecules, 2 and 3 are isomorphous (tetragonal *I-42d*), crystallizing as CH_2Cl_2 solvates with half a molecule in the asymmetric unit. The crystal structures of 1 - 3 each reveal square-planar coordination geometries at the group 10 metal with unexceptional bond lengths (Figure 1, Table 2). In particular the lengths of the M-S, C-S and aryl C-C bonds coupled with the square-planar geometries at the metal centres confirms that the best representation for these complexes is as an M^{2+} -dithiolate complex as opposed to the alternative representation as a M^0 -dithioketone.

Electrochemical Studies.

Cyclic voltammetry (CV) studies were carried out on complexes **1** - **3** in order to compare and contrast the effects of changing the metal centre on the redox properties of the complexes and to probe the nature of the frontier orbitals in conjunction with DFT studies. Cyclic voltammagrams for all three complexes are illustrated in Figure 2, and the resulting data in the form of half-wave potentials ($E_{1/2}$) relative to Ag/Ag⁺, and peak-to-peak potentials (ΔE_{pp}) are summarized in Table 2.

Previous studies on nickel dithiolate complexes has shown that the redox chemistry is sensitive to the dithiolate ligand.^{28a} For example [Ni(mnt)(dppe)] [mnt = maleonitrile dithiolato, $(NC)_2C_2S_2^{2-1}$ has an $E_{1/2}$ value of -1.20 V and a peak-to-peak potential of ca. 0.06 V, consistent with the 59 mV peak-to-peak separation expected for a 1e⁻ process and the [Ni(mnt)(dppe)] anion was detected by EPR spectroscopy. Conversely [Ni(tdt)(dppe)] [tdt = toluene-3,4-dithiolato, $MeC_6H_3S_2^{2-}$] was reported to have a $E_{1/2}$ of -1.50 V with a much larger peak-topeak potential which was scan-rate dependent (130 mV at 100 mV/s and 200 mV at 200 mV/s). The latter was assigned to electron transfer being a rate-limiting step in the redox process with the electro-generated product insufficiently stable to be detected by EPR, and undergoing rapid disproportionation at a rate comparable with the timescale of the electrochemical experiment.²⁹ Thus, whilst **1** was found to exhibit an apparently reversible one-electron reduction, the peak-to-peak potential (0.37 V) was consistent with a short-lived species, analogous to that generated from [Ni(tdt)(dppe)]. Attempts to identify a paramagnetic species by in situ EPR spectroscopy using either Cp₂Co or Mg as reducing agents also proved unsuccessful, supporting the transient nature of the electrochemically generated species.

Both complexes 2 and 3 exhibited two quasi-reversible oneelectron oxidations, the first of which appeared close to the

Computational Studies.

In order to evaluate the differing nature of the redox processes observed for 1 in relation to 2 and 3, a series of single point calculations on 1 - 3 were undertaken using hybrid density functional theory methods using both B3LYP and BP86 functionals and triple-zeta quality basis set with additional polarisation (LACV3P*) which implements an effective core potential for the *d*-block metal. No significant change to the relative energies or characteristics of the frontier orbitals were observed with changes to the functional employed.

In all three cases the LUMO is predominantly based around the metal-phosphine moiety Both the nickel and palladium LUMOs involve substantial metal-sulfur σ^* character (Figure 3a) with a metal $d_{x^2-y^2}$ contribution, whereas the Pt complex the LUMO comprises predominantly dppe π^* character. Conversely the HOMOs of the series are all highly dithiolate ligand-based, as shown for **2** (Figure 3b) with a small amount of electron density on the metal comprising a $d_{xz}-d_{yz}$ admixture. Thus reduction of **1** is likely to be a metal-based reduction and lead to weakening of the Ni-S bonds whereas oxidation of **2** and **3** are best considered to be ligand-based redox processes, consistent with conversion of the dithiolate DMOBDT²⁻ to the DMOBDT⁻⁻ radical anion, reflecting the non-innocent nature of this ligand. The similarity in $E_{y_2}^{0x}$ for both **2** and **3** is also consistent with a predominantly ligand based oxidation process.

Conclusions

We have shown that, under microwave conditions, oxidative addition of tetrathiocines to zero-valent group 10 metals occurs in very good yields. This is a potentially versatile route to a broad cross-section of *d*-block metal complexes, permitting tuning of phosphine, transition metal and tetrathiocine. Further systematic studies are underway to probe the effects of the tetrathiocine and co-ligand employed on such substitutions and will be the subject of future reports.

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Notes and references

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Electronic Supplementary Information (ESI) available: crystallographic data in cif format. See DOI: 10.1039/b000000x/

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