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Para-Functionalised Molybdenum Aryl–Imido Complexes $[Mo(NAr)(S_2CNEt_2)_2Cl_2]$ and Diimido Complexes $[{Mo(S_2CNEt_2)_2Cl_2}_2(\mu-1,5-NC_{10}H_6N)]$ and $[{Mo(S_2)(S_2CNEt_2)_2}_2(\mu-p-NC_6H_4N)]$

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Abstract

A range of *para*-substituted aryl–imido complexes $[Mo(NAr)(S_2CNEt_2)_2Cl_2]$ has been prepared upon reaction of $[MoO(S_2CNEt_2)_2Cl_2]$ with substituted anilines. With diamines similar mononuclear complexes result containing a pendant amino group which is deactivated towards further addition of molybdenum. This is attributed to the significant reduction in basicity of the remaining amine functionality upon coordination of the first to the electron-deficient molybdenum(VI) centre, and suggests that the two centres communicate strongly via the π -conjugated organic linking group. Diimido-bridged [$\{Mo(S_2CNEt_2)Cl_2\}_2(\mu-1,5-NC_{10}H_6N)$] was isolated from the reaction with naphthalene-1,5-diamine, while reaction of [$MoO_2(S_2CNEt_2)_2$] with *para*-phenylene diisocyanate afforded [$\{Mo(S_2)(S_2CNEt_2)_2\}_2(\mu-P-NC_6H_4N)$]. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Interest in the chemistry of the imido ligand continues unabated [1]. While a wide-range of synthetic approaches to this class of complex have been established, use of amines as the imido source is most appealing as their variety and easy accessibility offer an almost unlimited potential for imido functionalisation. One of our recent research goals has been the preparation of diimido-bridged complexes in which metal centres are linked via a strongly π -conjugated diimido ligand, such that there is potential for strong electronic communication between the two [2]. Such complexes are relatively rare, although a number of para-phenylene diimido complexes have been reported [2–10]. Our strategy has been to vary the π -conjugated organic moiety linking the imido metal centres together and investigate the effects that this has on the communication between metal centres. In this respect, we have prepared a wide-range of tungsten(IV) diimido-bridged complexes of the type [{W(CO)Cl2(Ph2PMe)2}2(N-link-N)], via oxidative-addition of two equivalents of [WCl₂(Ph₂PMe)₄] to diisocyanates [2,11]. It is noteworthy that in this system no evidence is found for the intermediate formation of monoimido complexes with pendant isocyanate functionalities, suggesting that coordination of the first imido group leads to activation of the second towards further oxidative-addition.

While the oxidative-addition of diisocyanates to $[WCl_2(Ph_2PMe)_4]$ afforded a simple clean route to tungsten(IV) diimido-bridged complexes, it was restricted with respect to the range of commercially available or easily prepared diisocyanates. Thus, in extending our studies to the molybdenum(VI) centre, we looked for simple preparations of such complexes which utilised amines. One such synthesis is that developed by Minelli and coworkers for the preparation of aryl-imido complexes $[Mo(NAr)(S_2CNEt_2)_2Cl_2]$ via reaction of $[MoO(S_2CNEt_2)_2Cl_2]$ with anilines in methanol [12]. This synthetic route to substituted imido complexes is especially appealing as the precursor oxo-complex is easily prepared, in high yield, from inexpensive starting materials. Herein we describe our attempts to prepare diimido-bridged complexes via this route utilising aromatic diamines. Two new diimido-bridged complexes of molybdenum(VI) have been prepared and characterised, including the first naphthalene-bridged complex of this type. We have also, however, noted for other aromatic diamines a significant and general deactivation of the pendant amino function-

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ality upon coordination of the first to the electron-deficient molybdenum(VI) centre, an effect which suggests that the nitrogen lone-pair is significantly delocalised in these systems.

2. Results and discussion

2.1. Para-substituted complexes 1a-c

Our initial experiments were aimed at extending Minelli's synthesis of molybdenum(VI) aryl-imido complexes to simple para-substituted derivatives. These proved successful, for example, addition of para-iodoaniline to a suspension of yellow $[MoO(S_2CNEt_2)_2Cl_2]$ in methanol resulted in the slow formation of an orange solution, from which a yellow precipitate was deposited. Dissolution of the latter in dichloromethane and addition of light-petroleum resulted in the isolation of $[Mo(p-NC_6H_4I)(S-$ ₂CNEt₂)₂Cl₂] **1a** as yellow crystals in 68% yield. The beige para-nitro 1b (54%) and orange para-dimethylamino 1c (46%) complexes were prepared in an analogous fashion, but being more soluble, did not precipitate from solution. Characterisation was straight-forward, each displaying two doublets in the aromatic region of the ¹H NMR spectrum, that shifted to higher-field being associated with the aromatic protons adjacent to the imido functionality. A number of related seven-coordinate molybdenum(VI) complexes have previously been characterised crystallographically [12-14] and the imido ligand always occupies an axial site.



2.2. Para-Substituted phenylene amine complexes 2a-g

Extending this preparative method to prepare paraphenylene bridged diimido complexes we reacted two equivalents of $[MoO(S_2CNEt_2)_2Cl_2]$ with a range of commercially available para-phenylene diamines. For all however, whatever the reaction conditions used, only a single amine functionality reacted to produce an imido ligand, the second remaining unreacted. Thus, addition of para-phenylenediamine of to а suspension $[MoO(S_2CNEt_2)_2Cl_2]$ in methanol at room temperature, resulted over 4h in the formation of a deep red solution with dissolution of all molybdenum-oxo starting material. After work-up, an oily red solid was isolated which proved difficult to purify, requiring three recrystallisations from dichloromethane and light-petroleum, yielding red [Mo(p- $NC_6H_4NH_2$)(S₂CNEt₂)₂Cl₂] **2a** in 63% yield. Minelli has

previously prepared the *ortho* isomer of **2a**, namely [Mo(o-NC₆H₄NH₂)(S₂CNEt₂)₂Cl₂] via the same preparative route and spectroscopic data are similar [12]. The uncoordinated amine was clearly seen as a broad resonance at δ 4.27 in the ¹H NMR spectrum, while in the mass spectrum peaks associated with loss of one and two chlorides were evident. Other *para*-phenylene diamines reacted with [MoO(S₂CNEt₂)₂Cl₂] in an analogous fashion leading to the formation of complexes **2b–g** in moderate yields. Most were oily red solids and in many cases we failed to isolate analytically pure solids.



With asymmetric diamines mixtures of isomers are potentially possible. For 2b, 2f-g, however, only a single isomer was observed by ¹H NMR spectroscopy, being assigned on the basis of the chemical shift of the uncoupled proton(s) adjacent to the substituent on the aryl ring. For example, in **2b** this appears as a singlet at δ 6.47, the high-field shift being indicative of its close-proximity to the free amine group. Thus, here the more sterically hindered amine has reacted preferentially. In contrast, 2f is assigned as the isomer in which the least hindered amine has reacted since the proton adjacent to the nitro group appears at δ 8.19. This may be an electronic effect as the nitro group will deactivate the amine ortho to it. Assignment of 2g is less ambiguous with the aryl protons appearing as a singlet at δ 7.39. This can be compared to their chemical shift of δ 6.60 in the free amine, suggesting that they are now located away from the molybdenum(VI) centre.

2.3. Biaryl and alkynyl diamine derived complexes 3a-b

The deactivation of the second amine group on paraphenylene diamines described above is ascribed to the delocalisation of the nitrogen lone-pair via the π -conjugated aryl group to the electron-deficient molybdenum(VI) centre. This, then, suggests that there is a strong degree of communication between the metal centre and the pendant amine as a result of extensive π -conjugation. In order to further probe the extent of this communication we carried out reactions of $[MoO(S_2CNEt_2)_2Cl_2]$ with more extended diamines. Addition of biaryldiamines 3,3',5,5'-tetramethylbiphenylene diamine and 3.3'-dimethoxybiphenylene diamine suspensions to of $[MoO(S_2CNEt_2)_2Cl_2]$ in methanol resulted in the isolation of **3a** (56%) and **3b** (47%) respectively as oily red solids after work-up. Attempts to prepare diimido-bridged complexes upon further reaction of either 3a-b with [MoO(S₂CNEt₂)₂Cl₂] were not successful.



2.4. naphthalene-1,5-diamine complexes 4a-b

Unlike all reactions detailed above, the outcome of the reaction of naphthalene-1,5-diamine with $[MoO(S_2CNEt_2)_2Cl_2]$ was dependent upon the relative stoichiometry of reactants. Thus, addition of one equivalent of the oxo complex resulted in the formation of a purple solution from which the expected mononuclear product, $[Mo(1,5-NC_{10}H_6NH_2)(S_2CNEt_2)_2Cl_2]$ 4a, in ca. 70% yield. Pure samples of 4a were not obtained as ¹H NMR analysis indicated that it was contaminated with a second minor and symmetrical species, namely the diimido-bridged complex 4b. Thus, addition of two equivalents of [MoO(S2CNEt2)2Cl2] to the diamine resulted in the isolation of dimeric $[{Mo(S_2CNEt_2)_2Cl_2}_2(1,5 NC_{10}H_6N$] **4b** as a purple crystalline solid in 78% yield. Elemental analysis supported this formulation, while in the mass spectrum peaks due to successive loss of four chlorines were observed. The aromatic region of the ¹H NMR spectrum was diagnostic, consisting of three signals at δ 7.48 (t, J 8.6), 7.91 (d, J 8.6) and 8.69 (d, J 8.6). The formation of diimido-bridged 4b demonstrates that the second amine is much less deactivated (if at all) than those in the linear systems.



2.5. Synthesis of $[\{Mo(S_2)(S_2CNEt_2)_2\}_2(\mu-p-NC_6H_4)]$ 5

In earlier work, we showed that thermolysis of $[MoO_2(S_2CNEt_2)_2]$ with phenylisocyanate yielded the imido-disulfur complex $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ in moderate yield [15,16]. This results from both oxo substitution by the imido group, and the formal double sulfurcarbon bond cleavage of a dithiocarbamate ligand. As an extension to this chemistry, we were interested in utilising diisocyanates towards the synthesis of diimido-bridged molybdenum(VI) complexes. Thermolysis of two equiva- $[MoO_2(S_2CNEt_2)_2]$ with *para*-phenylene lents of diisocyanate in toluene for 3d resulted, after chromatography, in the isolation of a green diimido-bridged $[{Mo(S_2)(S_2CNEt_2)_2}_2(\mu-p-NC_6H_4)]$ 5 in 26% yield; also prepared (18%)yield) upon thermolysis of $[MoO(S_2)(S_2CNEt_2)_2]$ with *para*-phenylene diisocyanate in toluene for 1d. Characterisation was made on the basis of analytical and spectroscopic data, the aryl protons appearing as a singlet at δ 7.06 in the ¹H NMR spectrum. A number of other products were also isolated from these reactions but eluded full characterisation. Attempts to extend the scope of this reaction to other diisocyanates were generally unsuccessful; in all cases reactions did occur but product separation and characterisation proved difficult and was inconclusive.



2.6. Attempted coupling of $[Mo(N-p-C_6H_4I)(S_2CNEt_2)_2Cl_2]$ **1a** to prepare diimido-bridged complexes

Thus far the synthetic approach adopted towards the formation of diimido-bridged complexes has been to link the metal centres via coordination to the preformed organic bridge. An alternative strategy involves the linking of mononuclear imido complexes via carbon-carbon bond formation. Sharp and co-workers [17] have recently reported the successful application of this strategy. Thus, oxidation of $[(\mu-dppm)_2(CO)_2Rh_2(\mu-NPh)]$ by half an equivalent of ferricinium resulted in formation of the benzidine derivative $[{(\mu-dppm)_2(CO)_2Rh_2}_2(\mu-p NC_6H_4-C_6H_4N$)] via coupling of the initially formed cationic radicals. Our approach is somewhat different, being based on the well-established Ullman coupling of bromo- and iodo-arenes [18] which has previously been successfully applied to the coupling of low-valent metal centres.

Treatment of yellow 1a with activated copper in dimethylformamide at high temperatures, resulted in the formation of a bright red solution and the deposition of copper iodide. Filtration and removal of solvent left an oily red solid. The ¹H NMR spectrum was poorly resolved but appeared to contain a number of products, all attempts at separation and purification of which were unsuccessful. Some evidence for carbon-carbon bond formation was seen in the mass spectrum, as envelopes of peaks at 646 and 611 mass units relate to the molecular ion of $[Mo(NC_6H_4-C_6H_4NH_2)(S_2CNEt_2)_2Cl_2]$ and subsequent loss of chlorine respectively. Other higher mass peaks were, however, also observed which should not easily be accounted for. A further coupling reaction was attempted between two equivalents of 1a and para-diiodo benzene, which again lead to the formation of an oily red solid. Here, the mass spectrum contained an envelope of peaks at 1116 mass units, corresponding to diimido-bridged terphenyl complex $[{Mo(S_2CNEt_2)_2Cl_2}(\mu-p-NC_6H_4-$ $C_6H_4-C_6H_4N$] after loss of two chlorines. Again, the ¹H NMR spectrum was uninformative and all attempts to isolate a pure product were unsuccessful.

These results suggest that, at least to some extent, carbon–carbon bond formation may occur under these conditions. Reactions are not, however, clean and thus it is not a suitable synthetic method towards the preparation of high-valent diimido-bridged complexes. The contrast between the high yield coupling of free aryl halides and also those linked to low-valent metal centres is striking. One explanation of this is that metal reduction may also take place under the reaction conditions. In support of this, a preliminary cyclic voltammetry study of **1a** revealed an irreversible reduction at 0.7 V [19], a value similar to that of the Cu(0)/Cu(I) couple. Thus, it appears that reduction of the aryl iodide are in competition.

3. Conclusions

This study reveals the strong deactivation of an aminofunctionality in a para-site on an arylimido ligand when bound to the molybdenum(VI) centre. It appears that this is due to the delocalisation of the amine lone-pair via the π -conjugated aryl group(s) onto the electron-deficient metal centre. This in turn suggests that in such high-valent diimido-bridged complexes, the metal centres communicate strongly through the full π -conjugated linking unit. Such deactivation may be a general phenomenon. As long ago as 1964, Chatt and co-workers noted a similar effect during their pioneering studies on the synthesis of rhenium(V) imido complexes, which utilised the addition of anilines to [ReOCl₃(PEt₂Ph)₂]. For example, while addition of aniline itself afforded the phenylimido complex $[Re(NPh)Cl_3(PEt_2Ph)_2]$, reaction with *para*-phenylene diamine afforded only the para-amino-substituted imido complex $[\text{Re}(p-\text{NC}_6\text{H}_4\text{NH}_2)\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$ [20]. These observations are in marked contrast to the oxidative-addition of isocyanates to the tungsten(II) centre, where the second isocyanate is activated upon coordination of the first to a tungsten(IV) centre [11]. At the molybdenum(VI) centre, it is only with 1,5-naphthalene diamine that a diimido-bridged complex was isolated. Here the rate of reaction of both amines to the molybdenum-oxo moiety appear to be similar, suggesting that little deactivation occurs through this organic spacer group, despite that fact that it is fully π -conjugated.

A molybdenum(VI) *para*-phenylene diimido complex, $[{Mo(S_2)(S_2CNEt_2)_2}_2(\mu-p-NC_6H_4)]$ **5**, was isolated from the slow, high temperature, reaction of $[MoO_2(S_2CNEt_2)_2]$ with *para*-phenylene diisocyanate. Here it is difficult to say anything about the relative rates of the reactions of the two ends of the isocyanate. Circumstantial evidence points to the activation of the second isocyanate. Thus, reaction with phenylisocyanate proceeds at a similarly slow rate;

while further, the mono-substituted complex was not observed. Such an activation might be expected as the delocalisation of electron density away from the isocyanate will render it more susceptible to nucleophilic attack by the a second metal-bound oxo moiety.

4. Experimental

All reactions were carried out using standard schlenk techniques under a nitrogen atmosphere, but sample separation and purification were carried out in air. Unless otherwise stated in the text, substituted anilines, diamines and para-phenylene diisocyanate were purchased from standard suppliers and used as supplied. Molybdenum-oxo complexes $[MoO(S_2CNEt_2)_2Cl_2]$ [21], $[MoO_2(S_2CNEt_2)_2]$ [21] and $[MoO(S_2)(S_2CNEt_2)_2]$ [22] were prepared by literature methods. Chromatography was carried out using deactivated alumina as the stationary phase. Infrared spectra were recorded on a Nicolet 205 FTIR spectrometer, NMR spectra on Varian XL-200 or VXR-400 spectrometers and mass spectra on VG 7070 high resolution and VG Analytical ZAB2F spectrometers. Elemental analyses were performed in house.

4.1. Synthesis of para-substituted complexes 1a-c

Iodoaniline (0.22 g, 1.00 mmol) in methanol (20 cm³) added suspension vellow was to а of $[MoO(S_2CNEt_2)_2Cl_2]$ (0.50g, 1.04mmol) in methanol (20 cm³) and the reaction was stirred overnight. A yellow precipitate formed within an orange solution. The volume of solvent was reduced to ca. 5 cm³ and the precipitate was isolated by filtration and washed with light-petroleum. Slow diffusion of light-petroleum into a saturated dichloromethane solution afforded $[Mo(p-NC_6H_4I)(S_2CNEt_2)_2-$ Cl₂] **1a** as small yellow crystals (0.46g, 68%).

1a: IR (KBr) 1560 s, 1521 vs, 1459 s, 1441 m, 1381 w, 1355 m, 1278 s, 1208 m, 1148 m, 1052 w, 1002 s, 817 m cm⁻¹; ¹H NMR (CDCl₃) δ 7.67 (d, J 8.7, 2H, Ar), 7.20 (d, J 8.7, 2H, Ar), 3.85 (m, 4H, CH₂), 3.76 (m, 4H, CH₂), 1.35 (t, J 7.2, 6H, CH₃), 1.34 (t, J 7.2, 6H, CH₃); ¹³C NMR (CDCl₃) 198.0 (CN), 137.8, 129.1, 113.0, 43.9, 43.0, 12.7, 12.6 ppm; mass spectrum (FAB⁺) m/z 646 (M⁺ – Cl), 611 (M⁺ – 2Cl); Anal: Calc. for Mo₁C₁₆H₂₄N₃S₄Cl₂I₁, %C 28.24, %H 3.53, %N 6.11; Found, %C 28.38, %H 3.51, %N 6.11.

An orange solution of *para*-nitroaniline (0.012 g, 0.084 mmol) in methanol (20 cm³) was added to a suspension of $[MoO(S_2CNEt_2)_2Cl_2]$ (0.040 g, 0.084 mmol) and the mixture was stirred for 6 h. The solvent was removed under reduced pressure to give an oily orange–red solid which was washed with light-petroleum (10 cm³). Dissolution in dichloromethane (7 cm³) and addition of light-petroleum (10 cm³) afforded $[Mo(p-NC_6H_4NO_2)(S_2-M_2)]$

 $CNEt_2_2Cl_2$] **1b** as a beige powder (0.027g, 54%). Orange **1c** (46%) was prepared in a similar fashion after stirring overnight.

1b: IR (KBr) 1626 m, 1587 m, 1528 s, 1458 m, 1345 m, 1279 m, 1205 m, 1151 w, 1096 w, 1075 m, 852 m cm⁻¹; ¹H NMR (CDCl₃) δ 8.18 (d, J 9.3, 2H, Ar), 7.59 (d, J 9.3, 2H, Ar), 4.02–3.72 (m, 8H, CH₂), 1.43 (t, J 7.3, 6H, CH₃), 1.42 (d, J 7.3, 6H, CH₃); ¹³C NMR (CDCl₃) 198.4 (CN), 131.1, 127.3, 113.8, 43.7, 42.8, 12.5, 12.6 ppm; mass spectrum (FAB⁺) m/z 565 (M⁺–Cl), 528 (M⁺–2Cl); Anal: Calc. for Mo₁C₁₆H₂₄N₄S₄Cl₂O₂, %C 32.05, %H 4.01, %N 9.34; Found, %C 31.05, %H 3.85, %N 8.56.

1c: IR (KBr) 1627 m, 1566 vs, 1443 m, 1400 s, 1312 s, 1245 m, 1156 m, 1054 w, 1016 m, 967 m, 937 m, 907 m, 798 vw, 708 vw, 632 m, 581 m cm⁻¹; ¹H NMR (CDCl₃) δ 7.49 (d, J 9.0, 2H, Ar), 6.46 (d, J 9.0, 2H, Ar), 3.84 (m, 4H, CH₂), 3.74 (m, 4H, CH₂), 3.11 (s, 6H, NMe₂), 1.33 (t, J 7.0, 12H, CH₃); mass spectrum (FAB⁺) m/z 562 (M⁺ – Cl), 526 (M⁺ – 2Cl).

4.2. Synthesis of para-substituted phenylene amine complexes 2a-g

A solution of para-phenylenediamine (0.045 g, 0.42 mmol) in methanol (15 cm³) was added to a stirred suspension of [MoO(S₂CNEt₂)₂Cl₂] (0.20 g, 0.42 mmol) in methanol (20 cm^3). The solution turned orange within seconds and darkened to red over 10 mins. After stirring for 4h there was no remaining yellow solid. The solvent was removed under reduced pressure at 40°C and a small amount of unreacted diamine sublimed onto the walls of the schlenk tube. The oily red solid remaining was dissolved in dichloromethane (5 cm³) and filtered. Removal of the solvent afforded a dry red solid which was washed with light-petroleum (10 cm³). Three recrystallisations from cooled dichloromethane:light-petroleum solutions afforded red-orange crystalline [Mo(*p*- $NC_6H_4NH_2$)(S₂CNEt₂)₂Cl₂] **2a** (0.15 g, 63%). Other complexes were prepared in a similar manner giving; red **2b** (47%), red **2c** (61%), red **2d** (61%), red **2e** (56%), orange 2f (50%), red 2g (59%).

2a: IR (KBr) 1623 m, 1589 vs, 1521 vs, 1442 s, 1380 sh, 1345 s, 1278 s, 1207 m, 1158 s, 1076 m, 1006 w, 840 m, 600 w, 553 w, 476 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.38 (d, J 8.8, 2H, Ar), 6.45 (d, J 8.8, 2H, Ar), 4.27 (br, 2H, NH₂), 3.83 (m, 4H, CH₂), 3.74 (m, 4H, CH₂), 1.35 (t, J 7.1, 6H, CH₃), 1.33 (t, J 7.3, 6H, CH₃); ¹³C NMR (CDCl₃) 198.2 (CN), 151.7, 144.7, 132.1, 130.7, 113.8, 43.7 (CH₂), 42.8 (CH₂), 12.5 (CH₃) ppm; mass spectrum (FAB⁺) m/z 534 (M⁺ – Cl), 498 (M⁺ – 2Cl); Anal: Calc. for Mo₁C₁₆H₂₆N₄S₄Cl₂, %C 33.74, %H 4.56, %N 9.90, %Cl 12.48, %S 22.50; Found, %C 33.72, %H 4.28, %N 9.57, %Cl 12.86, %S 22.53.

2b: IR (KBr) 1624 w, 1592 w, 1536 vs, 1458 m, 1440 m, 1380 m, 1354 m, 1277 s, 1204 m, 1150 m, 1092 m, 1073 m, 946 s, 849 w, 777 w, 576 w, 411 w cm⁻¹; ¹H

NMR (CDCl₃) δ 7.60 (d, J 7.6, 1H, Ar), 7.17 (s, 1H, Ar), 6.47 (d, J 7.6, 1H, Ar), 3.84 (m, 10H, CH₂+NH₂), 1.75 (s, 3H, CH₃), 1.30 (t, J 7.0, 12H, CH₃); mass spectrum (FAB⁺) m/z 545 (M⁺-Cl), 510 (M⁺-2Cl).

2c: IR (KBr) 1623 m, 1590 vs, 1521 vs, 1400 m, 1343 m, 1158 s, 841 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.57 (d, J 8.4, 1H, Ar), 6.38 (d, J 8.4, 1H, Ar), 4.14 (br, 2H, NH₂), 3.84 (m, 4H, CH₂), 3.74 (m, 4H, CH₂), 2.54 (s, 3H, CH₃), 1.97 (s, 3H, CH₃), 1.33 (t, J 6.9, 12H, CH₃); mass spectrum (FAB⁺) m/z 562 (M⁺-Cl), 526 (M⁺-2Cl); Anal: Calc. for Mo₁C₁₈H₃₀N₄S₄Cl₂.0.5CH₂Cl₂, %C 34.71, %H 4.84, %N 8.76; Found, %C 34.41, %H 4.89, %N 9.38.

2d: IR (KBr) 1620 m, 1591 vs, 1551 s, 1342 m, 1160 s, 841 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.36 (s, 1H, Ar), 6.29 (s, 1H, Ar), 4.70 (br, 2H, NH₂), 3.91 (m, 4H, CH₂), 3.69 (m, 4H, CH₂), 2.43 (s, 3H, CH₃), 1.99 (s, 3H, CH₃), 1.40 (t, J 7.0, 6H, CH₃), 1.29 (t, J 7.0, 6H, CH₃); mass spectrum (FAB⁺) m/z 562 (M⁺-Cl), 526 (M⁺-2Cl).

2e: IR (KBr) 1635 m, 1573 s, 1519 vs, 1456 s, 1438 s, 1380 w, 1355 w, 1312 s, 1296 m, 1277 s, 1204 m, 1149 m, 1092 w, 1075 m, 942 w, 910 s, 847 w, 800 m, 731 w, 713 w, 663 w, 571 w, 557 w cm⁻¹; ¹H NMR (CDCl₃) δ 3.90 (m, 10H, CH₂ + NH₂), 2.66 (s, 6H, CH₃), 1.96 (s, 6H, CH₃), 1.39 (t, J 7.0, 6H, CH₃), 1.29 (t, J 7.0, 6H, CH₃); mass spectrum (FAB⁺) m/z 590 (M⁺-Cl), 554 (M⁺ - 2Cl).

2f: IR (KBr) 1530 vs, 1404 m, 1345 m, 1280 m, 1202 m, 1148 m, 1096 m, 853 m cm⁻¹; ¹H NMR (CDCl₃) δ 8.19 (s, 1H, Ar), 7.52 (d, J 9.0, 1H, Ar), 6.88 (d, J 9.0, 1H, Ar), 3.79 (m, 8H, 3CH₂ + NH₂), 3.47 (q, J 6.4, 2H, CH₂), 1.37 (t, J 7.0, 6H, CH₃), 1.34 (t, J 7.0, 6H, CH₃); mass spectrum (FAB⁺) m/z 579 (M⁺-Cl), 541 (M⁺-2Cl).

2g: IR (KBr) 1611 vs, 1565 w, 1524 vs, 1458 m, 1441 m, 1358 s, 1281 s, 1208 m, 1150 m, 1078 m, 1036 m, 871 m, 794 w, 475 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.39 (s, 2H, Ar), 4.98 (br, 2H, NH₂), 3.84 (m, 4H, CH₂), 3.76 (m, 4H, CH₂), 1.35 (t, J 7.2, 6H, CH₃), 1.34 (t, J 7.2, 12H, CH₃); mass spectrum (FAB⁺) m/z 603 (M⁺ – Cl), 568 (M⁺ – 2Cl); Anal: Calc. for Mo₁C₁₆H₂₄N₄S₄Cl₄, %C 30.09, %H 3.76, %N 8.78; Found, %C 30.26, %H 3.91, %N 8.41.

4.3. Synthesis of biaryl and alkynyl diamine complexes *3a-c*

Methanol (40 cm³) was added to a mixture of 3,3',5,5'tetramethylbiphenylene diamine (0.02 g, 0.084 mmol) and [MoO(S₂CNEt₂)₂Cl₂] (0.04 g, 0.084 mmol) and the suspension was stirred at room temperature for 10h. Filtration afforded an orange solution from which volatiles were removed under reduced pressure. The oily red solid was washed with light-petroleum (10 cm³) and diethyl ether (10 cm³) and pumped dry to give oily red **3a** (0.06g, 56%). Attempts at crystallisation from a range of common organic solvents was unsuccessful. Oily red **3b** (47%) was prepared in an analogous fashion. **3a**: IR (KBr) 1624 m, 1590 s, 1518 s, 1507 s, 1457 m, 1438 m, 1380 w, 1336 m, 1276 m, 1205 m, 1160 s, 1074 m, 1003 w, 955 m, 914 w, 836 m, 798 m, 598 vw, 574 vw, 554 vw cm⁻¹; ¹H NMR (CDCl₃) δ 7.13 (s, 2H, Ar), 7.04 (s, 2H, Ar), 3.78 (m, 10H, CH₂+NH₂), 2.77 (s, 6H, CH₃), 2.20 (s, 6H, CH₃), 1.32 (t, J 7.0, 6H, CH₃), 1.30 (t, J 7.1, 6H, CH₃); mass spectrum (FAB⁺) m/z 667 (M⁺ – Cl).

3b: IR (KBr) 1580 s, 1521 vs, 1440 s, 1270 s, 1205 m, 1150 m, 809 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.65 (d, J 8.2, 1H, Ar), 7.00–6.89 (m, 4H, Ar), 6.73 (d, J 8.2, 1H, Ar), 3.89 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.69 (m, 8H, CH₂), 3.01 (br, 2H, NH₂), 1.33 (t, J 7.0, 12H, CH₃); mass spectrum (FAB⁺) m/z 670 (M⁺-Cl), 634 (M⁺-2Cl).

4.4. Synthesis of naphthalene-1,5-diamine complexes **4***a*-**b**

Addition of methanol (30 cm³) to a mixture of 1,5naphthalene diamine (0.04 g, 0.25 mmol) and $[MoO(S_2CNEt_2)_2Cl_2]$ (0.12 g, 0.25 mmol) resulted in the slow formation of a purple solution over 10h. Filtration and removal of solvent under reduced pressure afforded a purple solid which was washed with light-petroleum (10 cm³). Cooling an acetonitrile–diethyl ether solution afforded a microcrystalline purple solid (0.084g, 54%) which consisted predominantly of **4a** but was contaminated with **4b**. All attempts to separate the two were unsuccessful. When the same reaction was carried out over 20h with a 0.5 equivalents of the diamine, a similar work-up afforded pure **4b** (0.11 g, 78%).

4a: IR (KBr) 1624 m, 1577 w, 1522 vs, 1457 s, 1439 s, 1393 w, 1379 w, 1354 m, 1275 s, 1263 s, 1204 m, 1149 m, 1094 m, 1075 m, 1045 m, 955 m, 916 m, 848 w, 800 s, 721 w, 705 w, 609 vw, 572 vw cm⁻¹; ¹H NMR (CDCl₃) δ 8.06 (d, J 8.4, 1H, Ar), 7.84 (d, J 8.0, 1H, Ar), 7.75 (d, J 8.4, 1H, Ar), 7.29–7.15 (m, 3H, Ar), 6.69 (d, J 8.0, 1H, Ar), 3.77 (m, 10H, CH₂ + NH₂), 1.32 (t, J 7.0, 12H, CH₃); mass spectrum (FAB⁺) m/z 585 (M⁺-Cl), 549 (M⁺-2Cl).

4b: IR (KBr) 1533 vs, 1438 m, 1354 m, 1277 s, 1025 m, 933 m, 786 s cm⁻¹; ¹H NMR (CDCl₃) δ 8.69 (d, J 8.6, 2H, Ar), 7.91 (d, J 8.6, 2H, Ar), 7.48 (t, J 8.6, 2H, Ar), 3.78 (m, 16H, 7CH₂ + NH₂), 3.45 (q, J 7.0, 2H, CH₂), 1.32 (t, J 7.0, 12H, CH₃), 1.30 (t, J 7.0, 12H, CH₃); mass spectrum (FAB⁺) m/z 1046 (M⁺ - Cl), 1010 (M⁺ - 2Cl); Anal: Calc. for Mo₂C₃₀H₄₆N₆S₈Cl₄, %C 33.33, %H 4.26, %N 7.78; Found, %C 33.83, %H 4.60, %N 7.48.

4.5. Synthesis of $[\{Mo(S_2)(S_2CNEt_2)_2\}_2(\mu-p-NC_6H_4N)]$ 5

Heating a toluene solution (200 cm^3) of $[MoO_2(S_2CNEt_2)_2]$ (5.30 g, 12.5 mmol) and *para*phenylenediisocyanate (1.0 g, 6.25 mmol) for 3d resulted in the formation of a green solution after filtering off a brown precipitate. Volatiles were removed under reduced pressure and the resulting oily green solid was absorbed onto deactivated alumina via dissolution in dichloromethane and subsequent removal of solvent. Column chromatography afforded a number of bands. Eluting with dichloromethane:light-petroleum (3:1) gave a yellow band which afforded $[MoO(\mu-S)(S_2CNEt_2)]_2$ (0.83 g, 13%) [23]. Eluting with dichloromethane:light-petroleum (4:1) gave green band which afforded а $[{Mo(S_2)(S_2CNEt_2)_2}_2(\mu-p-NC_6H_4N)]$ 5 (1.62 g, 26%). Further purple, orange and red bands were eluted from the column but were not successfully characterised. Dark green crystals of 5 were grown upon mixing of methanol into a saturated dichloromethane solution. When this solution was left to stand for long periods (over 2d) substantial decomposition was noted. Complex 5 was also isolated in 18% yield from a similar reaction of $[MoO(S_2)(S_2CNEt_2)_2]$ with *para*-phenylenediisocyanate in refluxing toluene for 1d.

5: IR (KBr) 1508 s, 1467 m, 1458 m, 1450 m, 1436 s, 1418 w, 1378 w, 1356 w, 1310 m, 1271 m, 1206 m, 1151 m, 1095 m, 1074 m, 1002 w, 978 w, 842 m, 551 w cm⁻¹; ¹H NMR (CDCl₃) δ 7.06 (s, 4H, C₆H₄), 3.97–3.47 (m, 16H, CH₂), 1.45–1.1 (m, 24H, CH₃); Anal: calc. for Mo₂C₂₆H₄₄N₆S₁₂.0.5CH₂Cl₂; %C 30.03, %H 4.28, %N 7.93, %S 36.30; Found, %C 30.05, %H 4.58, %N 7.73, %S 36.75; E_{pc} (irrev) -0.91 V, E_{pa} (irrev) +0.61 V.

4.6. Attempted imido coupling reactions

Activated copper (0.05 g, 0.74 mmol) was added to a yellow solution of 1a (0.10 g, 0.15 mmol) in dmf (20 cm³). Upon heating to 110°C, the solution became red and a fine grey precipitate of copper iodide was deposited. The solution was cooled and filtered and volatiles were removed under reduced pressure to give an oily red solid. A number of attempts were made to wash and triturate the oily solid but with little success. IR (KBr) 1644 s, 1513 m, 1436 m, 1264 s, 1203 w, 1147 w, 1094 s, 1075 sh, 1051 sh, 1025 s, 1001 s, 804 s, 684 m cm⁻¹; mass spectrum $(FAB^+) m/z$ 759, 727, 698, 658, 646, 611, 510. When the reaction was carried out in the presence of half an equivalent of para-diiodobenzene a similar red solution was formed. IR (KBr) 1646 s, 1559 m, 1520 vs, 1439 m, 1381 w, 1355 m, 1277 s, 1204 m, 1001 m, 823 w cm⁻¹ mass spectrum (FAB⁺) m/z 1116, 727, 657, 625, 510, 478, 426, 394.

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