

Bent vs. linear imido ligation at the octahedral molybdenum(VI) dithiocarbamate stabilised centre

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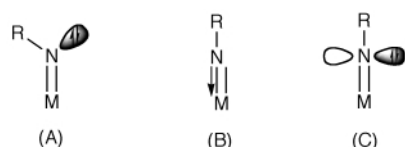
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Molybdenum(VI) bis(imido) complexes $[\text{Mo}(\text{NR})_2(\text{S}_2\text{CNET}_2)_2]$ **3a–3p** have been prepared *via* two synthetic routes and their structures investigated. Thermolysis of $[\text{MoO}_2(\text{S}_2\text{CNET}_2)_2]$ **1** with 2,6-disubstituted aryl isocyanates affords air-stable bis(imido) complexes **3i–3m** in high yields after column chromatography, a route which fails for sterically less demanding isocyanates. A more general preparation involves room temperature addition of two equivalents of $[\text{S}_2\text{CNET}_2]^-$ to the labile bis(imido) complexes $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2a–2p** ($\text{dme} = 1,2$ -dimethoxyethane) to afford **3a–3p** in high yields. In this manner related complexes $[\text{Mo}(\text{NR})_2(\text{S}_2\text{CNMe}_2)_2]$ **4** ($\text{R} = \text{Ph}$ or Bu^t) and $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{PPh}_2)_2]$ **5a** have also been prepared. Structural and spectroscopic studies have been carried out in order to determine the degree of bending of the imido ligands. Six complexes have been characterised by X-ray crystallography. In all cases one of the imido ligands is linear ($\text{Mo–N–C} \geq 160^\circ$), while the angle at the second is dependent upon the nature of R and ranges from 180 to 139° . Solid-state ^{13}C CPMAS spectroscopy reveals that the difference in bond angles at the two nitrogen centres (Δ°) correlates closely with the difference in chemical shifts of the *ipso*-carbon atoms ($\Delta\delta$). This then has been used to probe the relative bond angles at nitrogen for non-crystallographically characterised complexes. In solution even at low temperatures both imido ligands are equivalent indicating a rapid interconversion between linear and bent bonding modes.

Introduction

Considerable current interest surrounds transition metal imido complexes, primarily since they are anticipated to be potential aziridination and amination reagents,¹ but also as a result of their application as catalysts for ring opening metathesis polymerisation (ROMP).² The imido moiety is a strong π -donor ligand, and as such is generally found bound to metals in high oxidation states, that is with d^0 – d^2 electronic configurations.³ When binding to a single metal centre, two extreme coordination geometries can be identified, being classified as linear when the M–N–C angle is between 180 and 160° and bent when between 150 and 130° .³ These can easily be conceptualised in terms of valence bond theory, such that in the bent case a lone pair of electrons is localised on nitrogen (A), while for



linear co-ordination the two electrons are delocalised between nitrogen and the metal centre (B). A further linear form (C) results when symmetry restrictions do not allow for lone-pair donation, giving a linear imido ligand with a formal metal–nitrogen double bond.^{3,4} If we consider the electron donor capacity of the imido moiety in terms of a radical formulation, then we would consider the linear (B) and bent (A) forms to be 4- and 2-electron donor ligands respectively. For M–N–C angles of between 160 and 150° the term “semi-bent” has appeared in the literature,^{4–12} although it is now generally considered that this falls at the low end of linear co-ordination.^{3,12}

During the thirty years since the report of the first imido containing complex, $[\text{OsO}_3(\text{N}^t\text{Bu})]$,¹³ a large number of such complexes have been prepared and structurally characterised and in by far the vast majority the imido adopts a linear geom-

etry.³ Indeed, simple well characterised examples of bent imido ligands remain rare,^{14–17} although complexes are also known in which the imido ligand is forced to bend by virtue of being part of a chelate ring,^{18–24} and transient bent imido complexes have also been proposed.^{25–27} In 1979, Haymore *et al.*¹⁴ gave details of the first bent imido complex, reporting the synthesis and crystal structure of $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNET}_2)_2]$. This molybdenum(VI) bis(imido) complex was shown to contain inequivalent imido ligands in the solid state, being characterised by bent and linear Mo–N–C angles of $139.4(4)$ and $169.9(2)^\circ$ respectively at -80°C . Such a geometry is easily understood in terms of the valence bond descriptions of linear and bent imido ligation previously alluded to. Thus, the molybdenum bis-(dithiocarbamate) moiety is a 12-electron fragment and the further 6 electrons required for an 18-electron configuration at the metal centre are provided by 2- and 4-electron bent and linear imido ligands respectively.

During attempts to develop applications of imido complexes as nitrene transfer reagents, high-valent imido complexes containing only linear imido ligands have generally shown poor reactivity towards a range of unsaturated organics and thus are unsuitable in this capacity.³ We reasoned that complexes containing the bent ligand were likely to be far more reactive, since sterically the nitrogen centre was more accessible, the localisation of charge should induce higher reactivity, while the formal metal–nitrogen double bond should be less thermodynamically stable than linear triply bonded counterparts and thus more easily be cleaved. In light of the success of the analogous bis(oxo) complexes towards a range of oxo transfer reactions,²⁸ molybdenum(VI) bis(imido) complexes appeared to be particularly attractive as nitrene transfer reagents. During the transfer of the multiply bonded ligand, the metal centre formally undergoes a 2-electron reduction and thus ancillary ligands should be capable of stabilising the metal centre in a range of oxidation states. Dithiocarbamate ligands have this ability, for example they are known to stabilise molybdenum in oxidation states from $+6$ to -1 ,²⁹ and thus bis(imido) com-

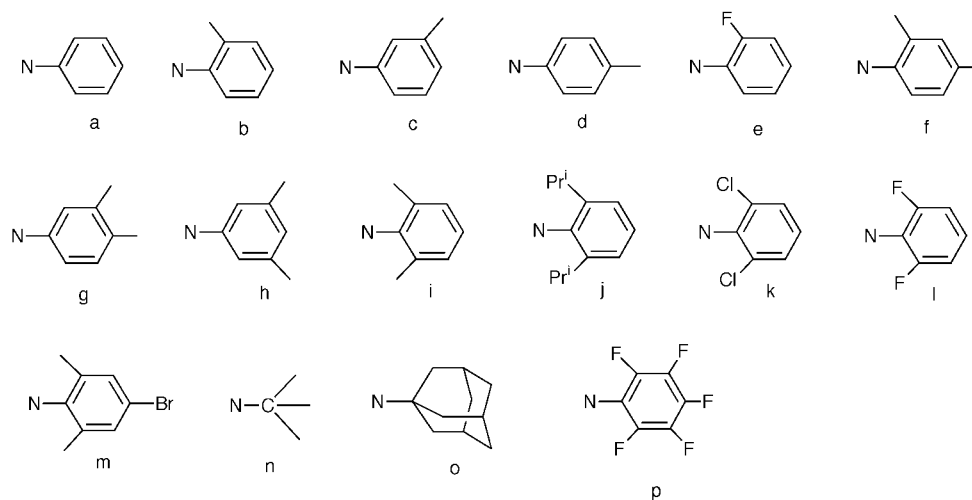


Chart 1

plexes of the type $[\text{Mo}(\text{NR})_2(\text{S}_2\text{CNEt}_2)_2]$ appear to be potentially attractive nitrene transfer reagents.

Two examples of this class of complex have previously been prepared, namely the phenyl and *para*-tolyl derivatives and on the basis of the crystallographic structure of the former they were assumed to adopt a similar structure, that is with one linear and one bent imido ligand.¹⁴ The synthetic route employed by Maatta and Wentworth involves oxidative addition of two equivalents of an aryl azide to the molybdenum(II) dicarbonyl complex $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2]$. Reasoning that if such complexes were to act as nitrene transfer reagents, then a range of aryl- and alkyl-substituted analogues would be required, but wanting to avoid use of organic azides we sought alternative synthetic routes to such complexes. Herein we describe the development of two of these, the first being quite general, while the second is only applicable for aryl complexes with *ortho*-substituents. Investigation of their solid-state structural properties by both room temperature X-ray crystallographic and ¹³C CPMAS NMR spectroscopy reveals that the difference in bond angles at the two imido ligands depends critically upon the nature of the organic substituent, which in turn affects the reactivity of the complexes with respect to their stability in air and their ability to act as nitrene transfer reagents. An aspect of this work has been previously communicated.³⁰

Results and discussion

Synthesis

Imido ligands used in this work are shown in Chart 1 together with the two synthetic pathways utilised. As previously alluded to, Maatta and Wentworth¹⁴ prepared the bis(imido) complexes **3a** and **3d** via addition of two equivalents of the respective aryl azide to $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2]$.¹⁴ We have now developed two new synthetic routes to **3**. The substitution of oxo for imido ligands upon addition of isocyanates to metal oxides has widely been utilised in order to prepare a range of new imido complexes.^{31–33} This strategy benefits from the ready availability of a wide range of metal oxides and organic isocyanates, but a major disadvantage is the high temperatures generally required. Since the required molybdenum(VI) bis(oxo) complex $[\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2]$ **1** is easily prepared on a large scale,³⁴ this appeared to be a potentially excellent route to **3**. Indeed, thermolysis of toluene solutions of **1** with a slight excess of 2,6-disubstituted aryl isocyanates afforded the required bis(imido) complexes **3i–3m** in yields of 14–27% after chromatography on

deactivated alumina. In all cases, however, the major reaction product was the molybdenum(VI) imidodisulfur complex $[\text{Mo}(\text{NR})(\text{S}_2)(\text{S}_2\text{CNEt}_2)_2]$ formed as a result of a double sulfur–carbon bond cleavage of a dithiocarbamate ligand,³² while small amounts of dimeric molybdenum(V) complexes were also isolated.³³ With less sterically demanding aryl isocyanates significant amounts of the bis(imido) complexes were not isolated, but rather yields of the co-products detailed above increased. The only exception to this was the reaction with *ortho*-tolyl isocyanate in which **3b** was prepared in moderate amounts, however since it did not survive chromatography separation from co-products proved impossible. Reaction with the bulky tertiary butyl isocyanate did not afford **3n**. We attribute the latter to the reduced reactivity of alkyl *versus* aryl isocyanates in oxo substitution reactions, a result of the electron-releasing alkyl substituent reducing the dipole moment at carbon. The reason for the lack of formation of the relevant bis(imido) complexes from reactions with sterically undemanding aryl isocyanates was initially thought to be the thermal instability of the products. However, prolonged thermolysis of *d*⁸-toluene solutions of **3a** and **3b** in sealed NMR tubes revealed no evidence of degradation products. In contrast, however, heating the mixed oxo–imido complex $[\text{MoO}(\text{NPh})(\text{S}_2\text{CNEt}_2)_2]$ ³⁵ under the same conditions resulted in slow formation of the imidodisulfur complex, $[\text{Mo}(\text{NPh})(\text{S}_2)(\text{S}_2\text{CNEt}_2)_2]$.³² Thus, we conclude that, while in all cases the first oxo substitution readily occurs at 110 °C, for sterically undemanding isocyanates the product formed is unstable at these elevated temperatures and dithiocarbamate degradation must be more rapid than the second substitution. In the case of the 2,6-disubstituted aryl isocyanates, the second substitution process must be in competition with the ancillary ligand degradation and thus significant amounts of the bis(imido) complexes are produced. We have not been able to ascertain whether this is attributable to an increase in the rate of the second substitution process or a decrease in the rate of the dithiocarbamate degradation. On steric grounds the former seems improbable, and since both electron-releasing and -withdrawing substituents favour bis(imido) formation it is difficult to see how electronic factors influence the rate of the second substitution. We thus favour a decrease in the rate of dithiocarbamate degradation upon introduction of 2,6-substituents on the aryl ring. Since this process involves addition of the sulfur–carbon bonds to the metal centre, then an increase in the co-ordination number is anticipated in the transition state, the energy of which will be increased upon

introduction of sterically demanding ligands within the coordination sphere.

Since the isocyanate route is limited to arylimido complexes containing 2,6-substituents, we sought a more general synthetic strategy towards **3**. Schrock and co-workers³⁶ have developed a very simple and generally applicable route to molybdenum(vi) bis(imido) complexes of the type $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2** ($\text{dme} = 1,2\text{-dimethoxyethane}$), which has been extended and elaborated on by Gibson and his group.^{5,11} This method is particularly beneficial since the source of the imido ligands is widely available primary amines, while sodium molybdate is cheap and plentiful. Addition of two equivalents of $[\text{NH}_4][\text{S}_2\text{CNET}_2]$ or dehydrated $\text{Na}[\text{S}_2\text{CNET}_2]$ to diethyl ether solutions of $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2a–2p** at room temperature resulted over approximately 12 h in the slow formation of $[\text{Mo}(\text{NR})_2(\text{S}_2\text{CNET}_2)_2]$ **3a–3p** in yields of 20–96% after removal of volatiles and extraction into benzene. In all cases the reaction was clean and appreciable amounts of other metal-containing products were not formed. The extraction procedure proved necessary to remove salts and the isolated yields of the bis(imido) complexes were to some extent a function of their solubility; examination of the reaction mixtures by ^1H NMR spectroscopy showed that all reactions were essentially quantitative.

All aryl complexes were brown or red-brown solids, while alkyl complexes were orange. The stability of the complexes in air was found to be highly dependent upon the nature of the organic substituent. Thus, solutions of the 2,6-disubstituted complexes **3i–3m** proved to be indefinitely stable in air and could easily be recrystallised upon slow diffusion of methanol into dichloromethane solutions. The tertiary butyl complex **3n** and aryl complexes containing a single *ortho*-substituent **3b** and **3e** were air-stable in the solid state, but decomposed over a period of hours when solutions were exposed to air. The phenylimido complex **3a** and other complexes which did not have substituents in the *ortho* positions were found to be highly air-sensitive in solution, decomposing over a period of minutes, while even in the solid state reaction with moisture resulted in the slow formation of the bis(oxo) complex and primary amines. Recrystallisation of the more air-sensitive complexes was best effected upon cooling concentrated diethyl ether solutions to -40°C .

Characterisation and solution fluxionality

Characterisation of bis(imido) complexes **3** proved straightforward. The IR spectra were relatively uninformative showing the anticipated absorptions associated with the dithiocarbamate ligands, the absence of metal–oxo stretches and the appearance of absorptions between 1300 and 1200 cm^{-1} tentatively assigned to the molybdenum–nitrogen moieties.^{3,37} EI Mass spectra showed molecular ions for all complexes, however it is noteworthy that FAB spectra consistently showed ions that were too heavy for the mononuclear formulation. At room temperature, ^1H NMR spectra confirmed that the ratio of imido to dithiocarbamate ligands was 1:1, the latter appearing as a quartet and triplet respectively at room temperature. The simplicity of these signals suggests that the two imido ligands are equivalent under these conditions, and indeed for all complexes a single imido environment was observed. While this is to be expected if both of the imido ligands are linear, if as is the case with **3a**, one is bent and the other linear, then two separate environments are expected. For the latter, Maatta and Wentworth¹⁴ previously reported the observation of a complex multiplet (no further details were given) in the aromatic region of the spectrum. In contrast to this, we find that at *all* temperatures this region of the spectrum appears simply as a doublet and two triplets as would be expected for two equivalent phenyl groups. We also find analogous behaviour for all other complexes down to temperatures of -100°C . We attribute these

observations, and specifically the behaviour of **3a**, to the rapid interconversion of bent and linear imido functionalities in solution on the NMR timescale (Scheme 1).



Scheme 1

While the aromatic region of the ^1H NMR spectra does not change significantly upon varying the temperature from -80 to $+100^\circ\text{C}$, substantial changes were seen in other regions. At elevated temperatures the methyl and ethyl resonances of the dithiocarbamate ligands appeared as a sharp triplet and quartet respectively; upon lowering the temperature these broadened and then reappeared as pairs of triplets and quartets. We attribute these changes to the well established restricted rotation about the carbon–nitrogen bond of dithiocarbamates,²⁹ a result of the resonance hybrid in which positive charge is localised on nitrogen. For the 2,6-diisopropyl-substituted complex, **3j**, other features of the ^1H NMR spectrum were also found to be temperature dependent. At 100°C the methyls of the isopropyl group appear as a single triplet, which collapses upon cooling into two equal intensity triplets at -20°C , and we associate these changes with the geared rotation of the aryl groups about the carbon–nitrogen bond and in support of this supposition have previously noted the restricted rotation of other sterically demanding arylimido ligands.³³

Solid-state structures

In order to probe the changes in bond angles at nitrogen upon varying the nature of the organoimido ligands, room temperature X-ray crystallographic studies were carried out on five of the new bis(imido) complexes, namely **3b**, **3i–3k** and **3n**. Since the original solid-state studies of **3a** were carried out at -130°C , for the sake of direct comparison, the structure of the latter was redetermined at room temperature and only slight differences were noted. The results of these studies are summarised in Fig. 1 and Table 1, which shows a comparison of the essential structural features of the six bis(imido) complexes at room temperature and **3a** at -130°C .

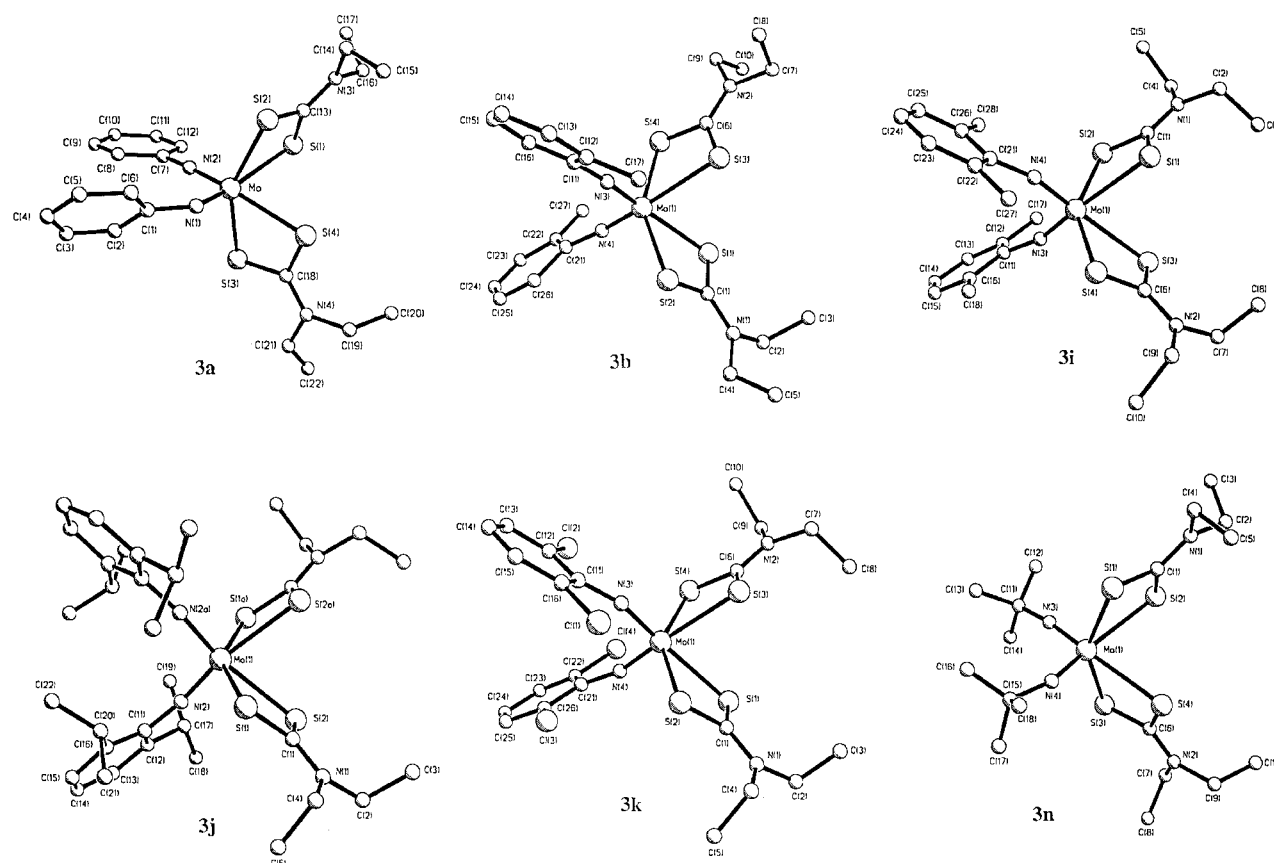
All show the same gross structural features and consist of discrete molecular units which contain a central, approximately octahedral, molybdenum centre. The imido ligands adopt a relative *cis* conformation with the N–Mo–N angle varying between $101.4(3)$ and $107.3(3)^\circ$. This variation appears not to be a function of steric effects since it is the bulky 2,6- Cl_2 aryl complex **3k** for which the closest approach is found. The structure of **3a** is widely quoted in the literature as a rare example of the coexistence of both linear and bent imido moieties at the same metal centre,¹⁴ the difference in bond angles at nitrogen being $29.5(8)^\circ$. Inspection of the other five structures reveals that the angles at nitrogen are highly sensitive to the nature of the organic substituent. In the case of the bulky 2,6-disubstituted aryl complexes **3i–3k**, the two bond angles are the same within experimental error (in **3j** the imido ligands are symmetry related) while differences of $8.3(7)$ and $10.7(1.1)^\circ$ are found for **3b** and **3n** respectively. In all the five new structures, however, the most acute angle is 162° and both imido ligands can only be considered as being linear. Thus, while the bond angle at nitrogen is quite soft in these complexes, varying between $162.0(6)$ and $175.1(4)^\circ$, they differ with respect to **3a** in best being classified as linear–linear rather than linear–bent species.

It is well established that the metal–nitrogen bonds in a wide range of imido complexes show only a small variation in length.³ The linear–bent complex **3a** is characterised by short $[1.745(5)\text{ \AA}]$ and long $[1.774(5)\text{ \AA}]$ molybdenum–nitrogen

Table 1 Selected bond lengths (Å) and angles (°)

Complex	Mo–N ^a	Mo–S ^b	Mo–S ^c	N–C ^a	Mo–N–C ^a	N–Mo–N	S–Mo–S ^d
3a	1.774(5)	2.762(2)	2.464(2)	1.402(9)	141.4(5)	103.2(2)	67.3(1)
	1.745(5)	2.605(2)	2.454(2)	1.383(9)	170.9(6)		69.2(1)
3b	1.776(5)	2.682(2)	2.462(2)	1.352(9)	166.8(6)	105.7(3)	68.6(1)
	1.757(6)	2.652(2)	2.458(2)	1.373(8)	175.1(4)		68.3(1)
3i	1.770(6)	2.685(2)	2.462(2)	1.374(9)	162.0(6)	102.5(3)	68.2(1)
	1.756(6)	2.684(2)	2.462(2)	1.398(9)	162.8(6)		68.0(1)
3j^e	1.776(2)	2.672(1)	2.464(1)	1.376(3)	169.9(2)	104.7(1)	68.6(1)
	1.760(7)	2.648(3)	2.452(3)	1.368(11)	162.2(7)	101.4(3)	68.6(1)
3k	1.769(7)	2.651(3)	2.449(3)	1.346(11)	162.9(7)		68.8(1)
	1.753(7)	2.719(2)	2.469(3)	1.418(10)	162.5(7)	107.3(3)	67.4(1)
3n	1.721(8)	2.694(3)	2.468(3)	1.429(15)	173.2(8)		67.6(1)
	1.789(4)	2.755(2)	2.461(2)	1.392(6)	139.4(4)	103.5(2)	69.51(4)
3a (143 K)^f	1.754(4)	2.602(2)	2.453(2)	1.386(6)	169.4(4)		67.60(5)

^a First entry corresponds to the *most* bent and the second the *least* bent imido ligand. ^b First entry is that *trans* to the *most* bent and the second is *trans* to the *least* bent imido ligand. ^c *cis* to the imido ligands: first entry is associated with the same dithiocarbamate ligand as that *trans* to the most bent imido ligand, etc. ^d Associated with the dithiocarbamate ligands represented by the distances in the rows. ^e The molecule has a crystallographic plane of symmetry. ^f Ref. 14.

**Fig. 1** Molecular structures of bis(imido) complexes **3**.

vectors respectively. For the four new arylimido complexes, the molybdenum–nitrogen bond lengths vary between 1.776(5) and 1.756(6) Å, with the largest difference of 0.019(7) Å being found in the *ortho*-tolyl complex **3b**, which also exhibits the largest bond angle difference of 8.3(7)°. For the alkyl-substituted complex **3n** a difference in bond lengths of 0.032(10) Å is found, which is close to that of 0.029(7) Å seen in linear-bent **3a**. The former is, however, only associated with a 10.7° difference in bond angles at nitrogen. In the three complexes where there is a significant difference in bond angles at nitrogen, namely **3a–3b** and **3n**, it is noteworthy that the shorter molybdenum–nitrogen bond is associated with the more linear imido ligand and *vice versa*. Thus, while in general metal–nitrogen bond lengths may be somewhat insensitive to the degree of bending at nitrogen, the small differences observed may be significant.

As has previously been noted for dithiocarbamate-stabilised molybdenum imido complexes,¹⁴ the nature of molybdenum–sulfur interactions are highly dependent upon the relative orientation of the chalcogen with respect to the strong π -donor ligand. Thus, for all complexes, the molybdenum–sulfur vectors *cis* to the imido ligands are short and essentially invariant [2.449(3)–2.469(3) Å], while those *trans* to imido ligands are elongated significantly [2.762(2)–2.605(2) Å], the precise value being highly dependent upon the nature of the imido ligand it lies *trans* to, long distances being associated with bending at nitrogen and *vice versa*. Thus, the *trans* molybdenum–sulfur bond length of 2.762(2) Å in **3a** is the only one associated with a truly bent, 2-electron donor imido ligand, the next longest distance being 2.719(2) Å found in the tertiary-butyl complex **3n** and associated with a bond angle at nitrogen of 162.5(7)°. For the linear imido ligand in **3a**, formally a 4-electron donor,

the *trans* molybdenum–sulfur bond length of 2.605(2) Å is significantly shorter than for the other bis(imido) complexes. In the latter, the range of *trans* molybdenum–sulfur bond lengths is far more limited varying only between 2.651(3) and 2.694(3) Å, while the biggest difference within any one complex is 0.030(3) Å seen in **3b**, which is considerably smaller than the 0.157(3) Å difference found in **3a**. We believe that this is further evidence that in the five new complexes the essentially linear imido ligands are best considered as acting as net 3-electron donors to the molybdenum centre.

Other structural features are generally unremarkable. The small bite-angle dithiocarbamate ligands subtend angles of approximately 68° at molybdenum, while no obvious trends are apparent in the N–C_{*ipso*} distances. One further significant point of note, however, is that in all structures the most bent imido ligand bends in towards the second and not away from it. At first sight this appears counter intuitive, especially for the relatively bulky 2,6-disubstituted complexes **3i–3k**, since the organoimido ligands would generally be considered as more sterically demanding than dithiocarbamates. The bending of imido ligands towards each other has previously been observed in [OsO₂(NR)₂].⁵ Given the lack of steric hindrance here it suggests that the origin of the bending is electronic in nature.

For both complexes **3i** and **3j**, the origin of the different alkyl signals in the low-temperature limiting ¹H NMR spectra is easily explained in light of the solid-state structures, being attributed to the restricted rotation about the N–C_{*ipso*} vector. Thus, for each imido ligand one of the substituents lies over the aryl ring of the second imido ligand, while the other lies towards the ethyl substituents of the dithiocarbamate ligand. With respect to this, a comparison of the structure of the *ortho*-tolyl complex **3b** with that of the dimethyl substituted **3i** reveals that the preferred orientation is that in which the methyl group lies over the aryl ring of the second since the second rotamer was not observed either in solution or the solid state.

¹³C CPMAS NMR Spectroscopy

From the crystallographic analyses described above, it is apparent that the metal–nitrogen–carbon angle in the bis(imido) complexes **3** is relatively soft, varying over approximately 40°. As the study developed it became obvious that, short of carrying out a single crystal X-ray diffraction study on each new complex, another method of characterising the degree of bending of the M–N–C angle was needed. Since even in **3a**, which has very different imido environments in the solid state, imido ligands interconvert in solution *via* a process which we have not been able to freeze out even at low temperatures, then a solid-state technique was required. To the best of our knowledge, solid-state NMR data have not previously been reported for imido complexes. This is, however, potentially an excellent way of characterising differences in bond angles at nitrogen with bis- and poly-imido complexes, since the chemical shift of the carbon directly bound to nitrogen is likely to be highly dependent upon the degree of bending at the latter.

In order to test this hypothesis, the ¹³C CPMAS spectra of complexes **3** were recorded at room temperature. The results are given in Table 2 while key spectra are shown in Fig. 2. While the general features of the spectrum are as expected, the main feature is the appearance of inequivalent *ipso*-carbon resonances at δ 161.5 and 156.5, that is a Δδ of 5.0 ppm. This confirms the results of the crystallographic studies, that is the two imido environments are quite different. In contrast, but again in accord with the structural study, the spectrum of **3j** shows only a single *ipso*-carbon resonance (Δδ 0 ppm) as expected for equivalent imido environments. Similar spectra for the other crystallographically characterised complexes revealed Δδ to be a function of the difference in bond angles (Δ°) at nitrogens, **3b** (1.3 ppm, 8.3°); **3i/3k** (0 ppm, 0°); **3n** (2.0 ppm, 10.7°), the latter representing the difference in chemical shift of the α-carbons of

Table 2 ¹³C CPMAS data for the *ipso*-carbons (δ) and Mo–N–C bond angle differences (°) for crystallographically characterised complexes (first block) and extrapolated values from the NMR data (second block)

Complex	<i>ipso</i> -C	Δδ	Δ°
3a	161.5 156.6	5.0	29.5
3b	158.6 157.3	1.3	8.3
3i	157.4	0	0.8
3j	153.9	0	0
3k	152.1	0	0.7
3n^a	71.7 69.7	2.0	10.7
3d	155.5 151.7	3.8	23
3e	146.2	0	0
3f	155.5	0	0
3g	158.2 155.4	2.8	17
3h	160.4 156.8	3.6	22
3l	153.2	0	0
3o^a	71.1	0	0
4a	160.3	0	0
4n	72.8 69.9	2.9	15
5a	156.7 155.1	1.6	9

^a Values refer to the α-carbons of the ¹Bu groups.

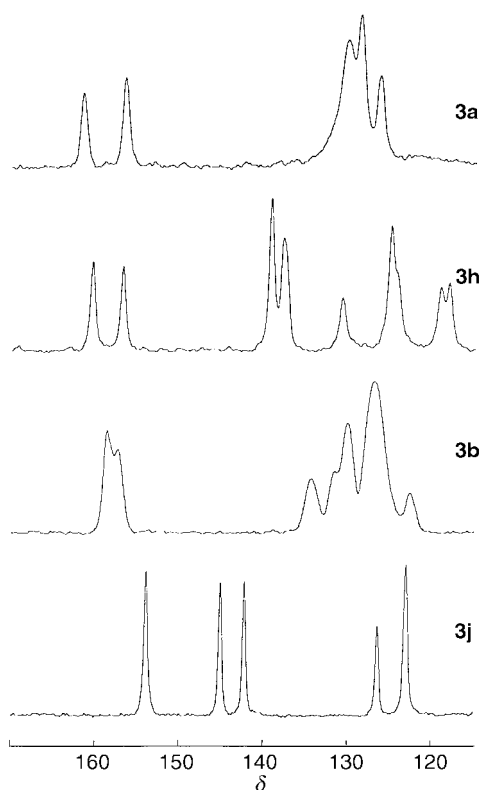


Fig. 2 ¹³C CPMAS spectra of the aryl region of bis(imido) complexes **3**.

the *t*-butyl groups. These data are presented graphically in Fig. 3, the main feature of which is the relatively linear nature of the relationship, although it is acknowledged that the plot comprises only four points. Regardless of the physical basis of this relationship, it provides a quick and easy method of screening new complexes. Hence from the measurement of the chemical shift difference (Δδ), the difference in bond angles at nitrogen (Δ°) can easily be determined. The results of this analysis for a number of complexes **3** are displayed in Table 2. It is clear from these data that complexes which are substituted in one or both *ortho* positions always adopt the linear–linear conformation. The *meta*- and *para*-substituted complexes, however, adopt a more distorted co-ordination geometry. Thus, Δ° for the tolyl derivatives vary in the order *para* (23.1°) **3d**, *para*–*meta* (17.0°)

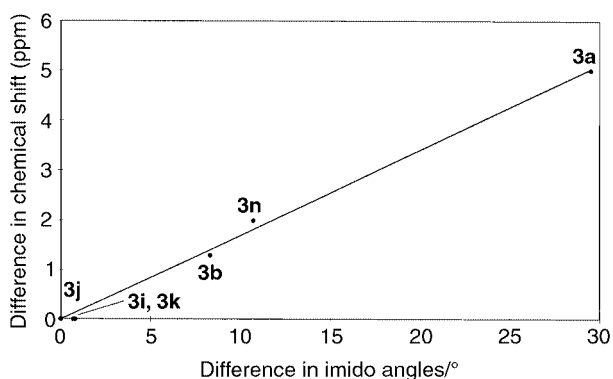


Fig. 3 Relationship between $\Delta\delta$ and Δ° for bis(imido) complexes **3**.

3g (a sufficiently pure sample of **3c** was not obtained), *ortho* (8.3°) **3b**. Since the electronic properties of these substituents is anticipated to be essentially invariant, we surmise that it is steric factors which are primarily responsible for these differences. A further series of dimethyl-substituted complexes **3f–3i** also supports this hypothesis, since it is only those that are not *ortho* substituted which show any significant difference in bond angles. That this is not a result of the electron-donating nature of the methyl group is confirmed by the observation that 2,6-dichloro **3k** and 2,6-difluoro **3l** derivatives both adopt equivalent imido environments.

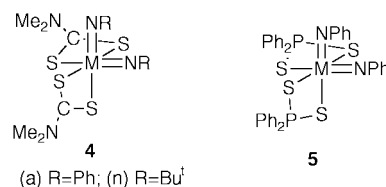
This analysis only provides information as to the *relative* bending of ligands and cannot give absolute bond angles at nitrogen. We have tried to correlate the chemical shifts (corrected for substituent effects) with bond angles, however no meaningful relationship could be discerned. If we assume that, as is the case with all structurally characterised complexes, one of the imido ligands is linear ($160\text{--}180^\circ$), then for complexes with a measurable $\Delta\delta$ we can place upper and lower limits on the degree of bending at the second ligand. For example, the *para*-tolyl complex **3d** has a $\Delta\delta$ of 3.8 ppm, that is a Δ° of 23.1° placing limits on the more bent imido ligand of $157\text{--}137^\circ$. Perhaps the most noteworthy feature of the solid-state ^{13}C NMR spectra is the realisation that the parent complex **3a**, originally prepared by Maatta and Wentworth,¹⁴ is significantly different to all other complexes of this type reported here. Hence, it is the only complex that can unambiguously be described as containing both linear and bent imido moieties and appears to represent an extreme case.

In light of the sensitivity of the chemical shift of the *ipso*-carbon to variations in bond angle, solid-state ^{15}N NMR spectroscopy should be a useful tool in determining the degree of bending of imido ligands. Bradley *et al.*³⁸ have previously recorded natural abundance ^{15}N NMR spectra for a range of imido complexes in solution. Notably in this study the spectrum of **3a** was shown to contain only a single resonance, further evidence for the interconversion of imido environments. As far as we are aware, ^{15}N CPMAS spectra have not previously been reported for imido complexes, although dithiocarbamate complexes have been studied.³⁹ For **3a** a major drawback is the low amounts of natural abundance ^{15}N , which makes accumulation times very long. In order to test the viability of this technique, the ^{15}N CPMAS spectrum of **3j** (in which imido sites are crystallographically equivalent) was recorded over 24 h. Two nitrogen environments are seen, the high-field signal at $\delta -210.82$ being assigned to the dithiocarbamate ligands, while that to lower field at $\delta 77.37$ is due to the equivalent imido ligands. For **3n** at room temperature, two dithiocarbamate resonances are seen at $\delta -214.5$ and -209.0 . This is as expected from the crystal structure in which the two imido ligands are inequivalent ($\Delta^\circ 10.7^\circ$) and suggests that ^{15}N CPMAS may be a sensitive probe to bending. However, no resonances could be observed for the imido nitrogens at room temperature or 100°C , an observation which we are at a loss to explain. Fur-

ther, a ^{15}N CPMAS TOSS (total sideband suppression) experiment on **3b** run over 5 d showed a single strong dithiocarbamate resonance at $\delta -206.0$ and two very weak broad resonances at $\delta 67$ and 55 tentatively assigned to the inequivalent imido environments ($\Delta^\circ 8.3^\circ$). The observation of only a single dithiocarbamate resonance, however, suggests that interpretation of ^{15}N CPMAS data in terms of imido bending requires further consideration.

Other ancillary ligands

A further approach adopted was to explore briefly the effect of changing the ancillary ligand on the structure adopted. For this $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNMe}_2)_2]$ **4a** and $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{PPh}_2)_2]$ **5** were prepared in 40 and 52% yield respectively in a manner analogous to the synthesis of **3a**. At room temperature both showed a single imido-phenyl environment in the ^1H NMR spectrum and as we were unable to grow suitable single crystals of either, ^{13}C CPMAS spectra were recorded. Somewhat surprisingly in view of the bent-linear structure of **3a** only a single *ipso*-carbon resonance was observed for **4a** ($\delta 160.3$) suggesting that both imido ligands are equivalent. For **5** two *ipso* resonances were seen at $\delta 156.7$ and 155.1 , the difference ($\Delta\delta 1.6$ ppm) being comparable to a 9° difference in bond angles. In order further to probe **5**, a ^{31}P CPMAS spectrum was run and showed two distinct resonances at $\delta 68.6$ and 65.5 , while in solution a single peak was observed ($\delta 64.5$). The $\Delta\delta$ here of 3.1 ppm has no direct comparison but does suggest that ^{31}P NMR may be a sensitive tool for probing imido environments in appropriate systems. While these results should be treated with caution as they are not supported by crystallographic data, they do suggest that the difference in bond angles at the imido ligands (*i.e.* the conformation adopted) may be very sensitive to the nature of the ancillary ligands. Indeed we have also run the $^{13}\text{CPMAS}$ of $[\text{Mo}(\text{NPh})_2\text{Cl}_2(\text{dme})]$ **2a** and this shows a single *ipso*-carbon resonance as do almost all the other dme complexes **2**.



In a further experiment $[\text{Mo}(\text{NBu}^t)_2(\text{S}_2\text{CNMe}_2)_2]$ **4n** was prepared in 41% yield. In solution a single tertiary butyl resonance was indicative of a single imido environment, however, two C_α resonances were seen in the ^{13}C CPMAS spectrum at $\delta 72.8$ and 69.9 ($\Delta\delta 2.9$) suggesting a bond angle difference (Δ°) of around 15° . We do not have crystallographic verification of this but again it suggests that ancillary ligand choice can play a significant role in the adopted bis(imido) configuration.

Conclusions

This work has shown that the bond angle at nitrogen in molybdenum(vi) bis(imido) complexes depends strongly upon the nature of the substituents on nitrogen and also on the ancillary ligand. The precise reason for the former dependence is not totally clear. Extended Hückel calculations carried out by Nik Kaltsayannis and Woo-Sung Kim of our department⁴⁰ have revealed that the total energy change upon deformation of one M–N–C angle in $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2]$ **3a** between 180 and 140° is essentially zero suggesting that there is no electronic preference for the adoption of a bent-linear over a linear-linear conformation. This in turn suggests that the bent-linear structure found for **3a** may be a result of crystal packing effects or other undetected intermolecular interactions (although no such

interactions are seen in the crystal structure). This is further supported by our solid-state NMR data for $[\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNMe}_2)_2]$ **4a** which suggest that the two imido ligands are equivalent and as such are both linear. Clearly further work is needed to determine the precise role of the ancillary ligand, and we note that in $[\text{Mo}(\text{NPh})_2\text{Cl}_2(\text{dme})]$ **2a** again only a single *ipso* resonance is seen in the ^{13}C solid-state NMR spectrum. Further calculations on $[\text{Mo}(\text{NBu}^t)_2(\text{S}_2\text{CNET}_2)_2]$ **3n** and $[\text{Mo}(\text{N-C}_6\text{H}_3\text{Cl}_2-2,6)_2(\text{S}_2\text{CNET}_2)_2]$ **3k**⁴⁰ show that while the total energy varies little upon deformation from 180 to 160°, at around 155° it rises steeply. This indicates that a major factor favouring the adoption of linear-linear co-ordination for *ortho*-substituted aryl and *t*-butyl complexes is the adverse steric interactions between these substituents upon bending.

Experimental

General

All reactions were carried out under an atmosphere of dinitrogen using standard vacuum line and glove-box techniques. Liquids were transferred *via* stainless-steel cannulae using a dinitrogen pressure and filtrations by using cannulae modified to accept a glass micro-fibre filter at one end. Solvents were dried over suitable drying agents under a dinitrogen atmosphere, stored in ampoules over 4 Å molecular sieves or sodium-potassium alloy and degassed thoroughly before use. Chromatography was performed on columns of deactivated alumina (6% w/w water) wet packed with light petroleum (bp 40–60 °C). Solutions were absorbed onto approximately 5 g of alumina before chromatography. Chemicals were purchased from Aldrich, Fluka, Lancaster Synthesis, Avocado and Janssen and used as supplied. All amines were distilled prior to use as was Me_3SiCl . Dithiocarbamate salts were dried under vacuum prior to use, while sodium salts were dehydrated *in vacuo* whilst heating at 80 °C. Both $[\text{MoO}_2(\text{S}_2\text{CNET}_2)_2]$ **1**³⁴ and $\text{Na}[\text{S}_2\text{PPh}_2]$ were prepared by standard literature methods. 1,2-Dimethoxyethane (dme) complexes $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2** were prepared *via* the method of Schrock and co-workers.³⁶ Many have previously been described, but some here for the first time. Since these were merely precursors to dithiocarbamate complexes full characterisation was not attempted. Microanalyses were performed in-house and IR spectra were recorded on a Nicolet 205-FT-IR spectrometer as KBr discs. Solution NMR spectra were recorded on a Varian VXR400 spectrometer at 20 °C in C_6D_6 unless otherwise stated and referenced internally to residual solvent. Air-sensitive samples were prepared in a glove-box in tubes fitted with a Young's valve or sealed under vacuum. Solid-state ^{13}C and ^{15}N NMR spectra were recorded on a Bruker MSL300 spectrometer as part of the University of London Intercollegiate Research Service (ULIRS) and mass spectra were obtained in-house.

Syntheses

$[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2.** White anhydrous sodium molybdate (2.00 g, 9.72 mmol) was thoroughly degassed and 1,2-dimethoxyethane (40 cm³) added to give a suspension. Triethylamine (5.4 cm³, 38.98 mmol), trimethylsilyl chloride (10.0 cm³, 78 mmol) and two equivalents of the amine (19.44 mmol) were added *via* a degassed syringe to the stirred suspension. This solution was left to stir at 65 °C for 18 h during which time it became highly coloured (red, brown or yellow). After cooling to room temperature, filtration and removal of volatiles under reduced pressure gave solid **2** which was washed with light petroleum (2 × 20 cm³) and dried under vacuum. The solid was redissolved in the minimum volume of diethyl ether and filtered. Cooling to −20 °C gave crystalline samples which were dried and transferred into the glove-box for storage. Red **2a** (72%); red **2b** (65%); brown **2c** (58%); brown **2d** (60%); red **2e** (73%); red **2f** (80%); red **2g** (82%); red **2h** (85%); red **2i** (94%);

red **2j** (90%); brown **2k** (92%); red **2l** (65%); brown **2m** (88%); yellow **2n** (85%); yellow **2o** (90%); red **2p** (62%); red **2a-d**⁶ (70%).

$[\text{Mo}(\text{NR})_2(\text{S}_2\text{CNET}_2)_2]$ **3.** Solid $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ **2** (4.56 mmol) and $[\text{NH}_4][\text{S}_2\text{CNET}_2]$ (9.20 mmol) were loaded into a Schlenk tube. To this was added diethyl ether (40 cm³) and the mixture stirred for 16 h at room temperature. This solution was filtered into another Schlenk tube, the remaining residues were washed with diethyl ether (2 × 25 cm³) and added to the original solution. The solution was concentrated to *ca.* 20 cm³ under reduced pressure, cooled to −20 °C to give crystalline **3**, which was isolated after filtration, washed with light petroleum (10 cm³) and dried under vacuum. Red **3a** (53%); brown **3b** (45%); brown **3c** (23%); brown **3d** (20%); red **3e** (42%); brown **3f** (55%); brown **3g** (58%); purple **3h** (48%); brown **3i** (80%); brown **3j** (85%); brown **3k** (75%); red **3l** (38%); brown **3m** (96%); orange **3n** (60%); orange **3o** (70%); red **3p** (28%); red **3a-d**¹⁰ (46%).

The 2,6-disubstituted aryl complexes **3i–3k** were also prepared upon thermolysis of toluene solutions of $[\text{MoO}_2(\text{S}_2\text{CNET}_2)_2]$ **1** and the appropriate isocyanate. For **3i**, $[\text{MoO}_2(\text{S}_2\text{CNET}_2)_2]$ **1** (1.34 g, 3.16 mmol) was dissolved in toluene (100 cm³) and 2,6-dimethylphenyl isocyanate (0.50 ml, 3.42 mmol) added *via* a degassed syringe. The resulting solution was refluxed for 1 d, after which time the volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band $[\text{Mo}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2(\text{S}_2\text{CNET}_2)_2]$ **3i** (0.60 g, 26%) was obtained upon elution with 20% dichloromethane in light petroleum. Complexes **3j** (27%) and **3k** (14%) were prepared in an analogous fashion. Crystals of **3i–3k** were obtained by slow diffusion of methanol into dichloromethane solutions.

3a.¹⁴ IR: 1501m, 1468m, 1431m, 1383m, 1357w, 1266s, 1207w, 1146m, 1095m, 1068m, 1020m, 803w, 755w, 686m and 670w cm^{−1}. Mass spectrum (EI): *m/z* 575 (*M*⁺), 486 (*M* − NPh), 429 (*M* − dtc), 397 (*M* − 2NPh) and 369 (*M* − NPh − dtc). ¹H NMR: δ 7.47 (d, 4 H, *J* 7.3, H^{2,6}), 6.97 (t, 4 H, *J* 7.5, H^{3,5}), 6.70 (t, 2 H, *J* 7.4, H⁴), 3.25 (q, 8 H, *J* 7.0, CH₂) and 0.74 (t, 12 H, *J* 7.0 Hz, Me). ¹³C-¹H NMR: δ 202.8 (C=N), 158.7 (*C*_{ipso}), 128.6, 125.3, 123.4, 46.1 (CH₂) and 12.1 (Me). ¹³C CPMAS TOSS: δ 200.7, 161.5 (*C*_{ipso}), 156.5 (*C*_{ipso}), 130.1, 128.6, 126.7, 47.5, 44.5, 13.8 and 12.6. Found (calc.) for C₂₂H₃₀MoN₄S₄: C, 45.56 (45.98); H, 5.28 (5.26); N, 9.63 (9.75); S, 21.66 (22.30)%.

3b. IR: 1633w, 1497s, 1432s, 1295m, 1273s, 1206m, 1146m, 1076m and 759m cm^{−1}. Mass spectrum (EI): *m/z* 604 (*M*⁺), 499 (*M* − NR), 457 (*M* − dtc) and 352 (*M* − NR − dtc). ¹H NMR (*C*₆D₅CD₃): δ (333 K) 7.36 (d, 2 H, *J* 7.9, H⁶), 6.83 (dd, 4 H, *J* 7.9, 7.4, H^{3,5}), 6.62 (t, 2 H, *J* 7.4, H⁴), 3.33 (q, 8 H, *J* 7.1, CH₂), 2.44 (s, 6 H, Me) and 0.84 (t, 12 H, *J* 7.1 Hz, Me); (213 K): 7.55 (d, 2 H, *J* 7.6, H⁶), 6.80 (t, 2 H, *J* 7.6, H⁵), 6.72 (d, 2 H, *J* 7.5, H₃), 6.61 (t, 2 H, *J* 7.3, H⁴), 3.15 (br, 8 H, CH₂), 2.53 (s, 6 H, Me) and 0.57 (d, 12 H, *J* 6.2 Hz, Me). ¹³C-¹H NMR (*C*₆D₅CD₃): δ (333 K) 203.2 (C=N), 158.2 (*C*_{ipso}), 130.2, 129.9, 126.2, 45.8 (CH₂), 18.9 (Me) and 12.3 (Me); (193 K) 200.9 (C=N), 157.8 (*C*_{ipso}), 130.5, 129.2, 126.3, 45.2 (CH₂), 45.0 (CH₂), 19.8 (Me), 12.3 (Me) and 11.6 (Me). ¹³C CPMAS TOSS: δ 202.4, 199.0, 158.6 (*C*_{ipso}), 157.3 (*C*_{ipso}), 134.3, 131.6, 130.1, 127.0 (br), 122.6, 49.1, 45.9, 23.1, 21.2, 19.8, 14.1 and 12.8. ¹⁵N CPMAS TOSS: δ 67, 55 and −206. Found (calc.) for C₂₄H₃₄MoN₄S₄: C, 47.77 (47.82); H, 5.70 (5.69); N, 9.18 (9.29); S, 21.33 (21.28)%.

3c. IR: 1527s, 1458s, 1438s, 1402s, 1356m, 1278m, 1205w, 1153m, 1094m, 1075m and 793w cm^{−1}. Mass spectrum (EI): *m/z* 604 (*M*⁺), 499 (*M* − NR), 457 (*M* − dtc) and 352 (*M* − NR − dtc). ¹H NMR: δ 7.01 (t, *J* 7.6, 2 H, H⁵), 6.56 (t, 2 H, *J* 7.6, H^{4,6}), 6.49 (s, 2 H, H²), 6.47 (d, *J* 7.9, 2 H, H^{4,6}), 3.92–3.79 (m, 8 H, CH₂), 2.24 (s, 6 H, Me) and 1.46 (t, 12 H, *J* 7.0 Hz, Me). Satisfactory elemental analysis could not be obtained.

3d. ^1H NMR: δ 7.50 (d, 4 H, J 7.9, $\text{H}^{2,6}$), 6.79 (d, 4 H, J 7.9, $\text{H}^{3,5}$), 3.27 (q, 8 H, J 7.0, CH_2), 1.90 (s, 6 H, Me) and 0.75 (t, 12 H, J 7.0 Hz, Me). ^{13}C CPDAS: δ 203.0 (C=N), 155.5 (C_{ipso}), 151.7 (C_{ipso}), 46.8 (CH_2), 22.0 (Me) and 13.4 (Me).

3e. Mass spectrum (EI): m/z 612 (M^+), 503 ($\text{M} - \text{NR}$) and 465 ($\text{M} - \text{dtc}$). ^1H NMR: δ 7.54 (t, 2 H, J 7.9, H^6), 6.68 (t, 2 H, J 8.0, $\text{H}^{4,5}$), 6.64 (t, 2 H, J 7.7, $\text{H}^{4,5}$), 6.43 (q, J 6.1, 2 H, H^3), 3.21 (m, 8 H, CH_2) and 0.73 (t, 12 H, J 6.9 Hz, Me). ^{13}C CPDAS TOSS: δ 201.2, 199.4, 151.0 (C-F), 146.2 (C_{ipso}), 132–116 (br), 46.1 and 12.8. ^{13}C CPDAS NQS (non-quaternary suppression): δ 201.2, 199.4, 150.9, 146.1, 13.4 and 12.8. Found (calc.) for $\text{C}_{22}\text{H}_{28}\text{F}_2\text{MoN}_4\text{S}_4$: C, 42.16 (43.26); H, 4.68 (4.62); N, 8.75 (9.17); S, 20.07 (21.00)%.

3f. IR: 1497s, 1474m, 1456m, 1429m, 1357m, 1300m, 1274s, 1208w, 1148m, 1092w, 1073w and 814m cm^{-1} . Mass spectrum (EI): m/z 633 (M^+), 513 ($\text{M} - \text{NR}$), 483 ($\text{M} - \text{dtc}$) and 361 ($\text{M} - 2\text{NR}$). ^1H NMR: δ 7.60 (d, 4 H, J 7.9, H^6), 6.74 (d, 2 H, J 8.1, H^5), 6.71 (s, 2 H, H^3), 3.30 (q, 8 H, J 6.1, CH_2), 2.65 (s, 6 H, Me), 2.03 (s, 6 H, Me) and 0.79 (t, 12 H, J 7.0 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 203.1 (C=N), 156.0 (C_{ipso}), 134.9, 130.7, 130.6, 127.0, 125.6, 45.7 (CH_2), 21.1 (Me), 19.0 (Me) and 12.3 (Me). ^{13}C CPDAS TOSS: δ 202.0, 155.5, 138.5, 135.6, 133.9, 132.4, 130.4, 127.6, 126.8, 50.7, 45.7, 23.9, 23.3, 21.6, 19.6, 16.8, 13.3 and 11.5. ^{13}C CPDAS NQSTOSS: δ 202.0, 155.5, 138.6, 135.6, 134.0, 132.4, 23.3, 19.6, 16.8, 13.3 and 11.4. Found (calc.) for $\text{C}_{26}\text{H}_{38}\text{MoN}_4\text{S}_4$: C, 48.62 (49.50); H, 5.93 (6.07); N, 8.57 (8.88); S, 19.57 (20.33)%.

3g. IR: 1497s, 1456m, 1429m, 1384s, 1336m, 1306m, 1275s, 1208m, 1147m, 1022m, 845m and 813m cm^{-1} . Mass spectrum (EI): m/z 632 (M^+), 513 ($\text{M} - \text{NR}$), 485 ($\text{M} - \text{dtc}$), 397 ($\text{M} - 2\text{NR}$) and 366 ($\text{M} - \text{dtc} - \text{NR}$). ^1H NMR: δ 7.42 (d, 2 H, J 6.1, H^6), 7.41 (s, 2 H, H^2), 6.81 (d, 2 H, J 6.1, H^5), 3.29 (q, 8 H, J 7.0, CH_2), 1.91 (s, 6 H, Me), 1.84 (s, 6 H, Me) and 0.77 (t, 12 H, J 7.2 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 203.2 (C=N), 157.8 (C_{ipso}), 136.3, 134.1, 129.7, 125.2, 121.8, 40.5 (CH_2), 19.6 (Me), 19.4 (Me) and 12.3 (Me). ^{13}C CPDAS TOSS: δ 202.1, 158.2 (C_{ipso}), 155.4 (C_{ipso}), 136.1, 130.4, 124.6, 122.9, 48.0, 21.2 and 14.8. Found: C, 48.71; H, 6.20; N, 8.69; S, 20.01%.

3h. IR: 1629m, 1613m, 1596m, 1529s, 1501m, 1456m, 1438m, 1382m, 1354m, 1323w, 1274s, 1263s, 1206m, 1146m, 1095s, 1078s, 1021s, 845w and 803m cm^{-1} . Mass spectrum (EI): m/z 633 (M^+), 514 ($\text{M} - \text{NR}$), 485 ($\text{M} - \text{dtc}$), 397 ($\text{M} - 2\text{NR}$) and 366 ($\text{M} - \text{dtc} - \text{NR}$). ^1H NMR: δ 7.21 (s, 4 H, $\text{H}^{2,6}$), 6.44 (s, 2 H, H^4), 3.29 (q, 8 H, J 7.0, CH_2), 1.96 (s, 12 H, Me) and 0.77 (t, 12 H, J 7.1 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 203.1 (C=N), 158.1 (C_{ipso}), 137.8, 127.3, 121.4, 45.8 (CH_2), 21.1 (Me) and 12.3 (Me). ^{13}C CPDAS TOSS: δ 201.4, 160.4 (C_{ipso}), 156.8 (C_{ipso}), 139.1, 137.7, 130.7, 124.9, 118.1, 47.9, 43.9, 25.2, 23.7, 22.5, 15.5, 14.7 and 12.1. Found: C, 48.51; H, 6.11; N, 8.40%.

3i. IR: 1504s, 1457w, 1440w, 1426m, 1352m, 1274s, 1245w, 1149w, 1092w, 957w, 846w, 778w and 572w cm^{-1} . ^1H NMR (CDCl_3): δ (313 K) 6.90 (d, 4 H, J 7.2, $\text{H}^{3,5}$), 6.73 (t, 2 H, J 7.2 Hz, H^4), 3.83 (br, 8 H, CH_2), 2.35 (s, 12 H, $\text{CH}_3\text{C}_6\text{H}_3$) and 1.28 (s, 12 H, CH_2CH_3); (213 K) 6.90 (d, 4 H, J 7.2, $\text{H}^{3,5}$), 6.73 (t, 2 H, J 7.2, H^4), 3.96–4.05 (m, 2 H, CH_2), 3.78–3.82 (m, 4 H, CH_2), 3.60–3.69 (m, 2 H, CH_2), 1.34 (s, 12 H, $\text{CH}_3\text{C}_6\text{H}_3$), 1.26 (t, 6 H, J 7.2, CH_2CH_3) and 1.23 (t, 6 H, J 7.2 Hz, CH_2CH_3). ^{13}C CPDAS TOSS: 199.9, 157.4 (C_{ipso}), 133.3, 128.2, 125.7, 47.5, 46.3, 20.3, 18.9 and 11.4. Found: C, 49.37; H, 5.63; N, 8.68; S, 20.14%.

3j. IR: 1267s, 1210m, 1149m, 1095w, 1075m, 962m, 847w and 755s cm^{-1} . ^1H NMR ($\text{C}_6\text{D}_6\text{CD}_3$): δ (373 K) 6.95 (d, 4 H, J 7.6, $\text{H}^{3,5}$), 6.80 (t, 2 H, J 7.6, H^4), 4.08 (septet, 4 H, J 6.8, CHMe_2), 3.46 (q, 8 H, J 7.0, CHMe_2), 1.19 (d, 24 H, J 6.8, CHMe_2) and 0.96 (t, 12 H, J 7.0 Hz, CH_2Me); (253 K) 6.96 (d, 4 H, J 7.6, $\text{H}^{3,5}$), 6.84 (t, 2 H, J 7.6, H^4), 4.17 (septet, 4 H, J 6.8, CHMe_2), 3.47 (septet, 2 H, J 6.8, CH_2Me), 3.14 (m, 4 H, CH_2Me), 2.93 (septet, 2 H, CH_2Me), 1.28 (d, 12 H, J 6.8, CHMe_2), 1.16 (d, 12 H, J 6.8, CHMe_2), 0.81 (t, 6 H, J 6.8, CH_2Me) and 0.74 (t, 6 H, J 7.0 Hz, CH_2Me). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3 , 253 K): δ 201.4

(S_2CN), 153.8 (ipso-C), 141.6 ($o\text{-C}$ of C_6H_3), 124.0 ($p\text{-C}$ of C_6H_3), 122.1 ($m\text{-C}$ of C_6H_3), 46.0, 45.4 (CH_2), 28.1 (CH), 24.5, 23.6 ($(\text{CH}_3)_2\text{CH}$), 12.8 and 12.1 (CH_3CH_2). ^{13}C CPDAS TOSS: δ 200.4, 182.0, 153.9 (C_{ipso}), 145.0, 142.2, 126.4, 123.0, 45.8, 27.6, 27.2, 25.1, 21.0, 14.7 and 13.9. ^{13}C CPDAS NQSTOSS: δ 200.4, 153.9, 145.0, 142.2, 27.6, 27.2, 25.1, 21.0, 14.7 and 13.9. ^{15}N CPDAS: δ 77.4 and -210.8 . Found (calc.) for $\text{C}_{34}\text{H}_{54}\text{MoN}_4\text{S}_4$: C, 54.54 (54.96); H, 7.32 (7.32); N, 7.31 (7.54); S, 17.50 (17.26)%.

3k. IR: 1508s, 1432s, 1311m, 1275m, 1205w, 1070w, 960m and 790m cm^{-1} . ^1H NMR (CDCl_3): δ 7.12 (d, 4 H, J 7.5, $\text{H}^{3,5}$), 6.68 (t, 2 H, J 7.2 Hz, H^4), 3.82 (br, 8 H, CH_2) and 1.46 (br, 12 H, CH_3). ^{13}C CPDAS TOSS: δ 199.9, 152.1 (C_{ipso}), 134.0, 128.9, 125.8, 122.6, 47.6, 46.3 and 11.4. ^{13}C CPDAS NQSTOSS: δ 199.8, 152.0, 137.4, 130.0, 126.9, 123.2 and 11.4. Found (calc.) for $\text{C}_{22}\text{H}_{26}\text{Cl}_4\text{MoN}_4\text{S}_4$: C, 37.48 (37.08); H, 3.94 (3.68); Cl, 19.90 (19.72); N, 7.63 (7.87); S, 18.07 (17.96)%.

3l. IR: 1508s, 1468s, 1436m, 1384s, 1275m, 1265m, 1236w, 1208w, 1019w, 1001m, 965w and 649w cm^{-1} . Mass spectrum (EI): m/z 647 (M^+), 520 ($\text{M} - \text{NR}$) and 500 ($\text{M} - \text{dtc}$). ^1H NMR: δ 6.37 (dd, 4 H, J 7.6, $\text{H}^{3,5}$), 6.12 (m, 2 H, H^4), 3.19 (q, 8 H, J 6.7, CH_2) and 0.72 (t, 12 H, J 6.7 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 202.6 (C=N), 157.3 (C_{ipso}), 154.8, 128.6, 127.4, 127.2, 124.0, 111.1, 110.9, 45.6 (CH_2), 21.1 (Me) and 12.2 (Me). ^{13}C CPDAS: δ 199.2, 195.5, 153.2 (C_{ipso}), 136.1, 127.8, 121.7, 111.6, 46.8 and 13.2. ^{13}C CPDAS NQS: δ 201.5, 199.5, 136.2 and 13.0. Found (calc.) for $\text{C}_{22}\text{H}_{26}\text{F}_4\text{MoN}_4\text{S}_4$: C, 39.99 (40.87); H, 4.10 (4.02); N, 8.45 (8.67); S, 20.21 (19.81)%.

3m. IR: 1494s, 1457s, 1420s, 1390m, 1356m, 1319s, 1273s, 1247s, 1208m, 1147m, 1089w, 953m, 868w, 858w and 817s cm^{-1} . Mass spectrum (EI): m/z 788 (M^+) and 591 ($\text{M} - \text{NR}$); ^1H NMR: δ 7.04 (s, 4 H, $\text{H}^{3,5}$), 3.84 (br, 8 H, CH_2), 2.30 (s, 12 H, Me) and 1.30 (t, 12 H, J 7.1 Hz, Me). Found (calc.) for $\text{C}_{26}\text{H}_{36}\text{Br}_2\text{MoN}_4\text{S}_4$: C, 40.11 (39.59); H, 4.68 (4.57); N, 7.12 (7.11)%.

3n. IR: 1497s, 1429m, 1263s, 1209m, 1097s, 1022s and 802s cm^{-1} . Mass spectrum (EI): m/z 536 (M^+), 465 ($\text{M} - \text{NBU}^t$) and 316 ($\text{M} - \text{NBU}^t - \text{dtc}$). ^1H NMR: δ 3.36 (q, 8 H, J 7.0, CH_2), 1.57 (s, 18 H, Me) and 0.82 (t, 12 H, J 7.1 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 203.9 (C=N), 71.2 (C_q), 45.8 (CH_2), 31.3 (CMe_3) and 12.4 (Me). ^{13}C CPDAS: δ 203.3, 201.4, 71.7 (C_q), 69.7 (C_q), 47.2, 44.4, 32.1, 14.3 and 13.0. ^{15}N CPDAS: δ (373 K) -214.1 and -209.1 ; (293 K) -214.5 and -209.0 . Found (calc.) for $\text{C}_{18}\text{H}_{38}\text{MoN}_4\text{S}_4$: C, 39.85 (40.43); H, 6.82 (7.16); N, 10.22 (10.48); S, 24.06 (23.99)%.

3o. IR: 1490s, 1449m, 1426s, 1301m, 1270s, 1211m, 1144m and 1095m cm^{-1} . Mass spectrum (EI): m/z 692 (M^+) and 543 ($\text{M} - \text{NRm}$). ^1H NMR: δ 3.40 (q, 8 H, J 7.0, CH_2), 2.35 (s, 12 H, H_β), 2.01 (s, 6 H, H_γ), 1.59 (d, 6 H, J 11.8, H_δ), 1.49 (d, 6 H, J 11.8, H_δ) and 0.86 (t, 12 H, J 7.0 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 204.2 (C=N), 71.1 (C_q), 45.8 (C_β), 45.0 (CH_2), 36.7 (CH_3), 30.2 (C_γ) and 12.5 (Me). ^{13}C CPDAS: δ 202.6, 71.7 (C_q), 45.8, 45.6, 37.4, 30.7, 30.4, 15.4 and 13.1. Found (calc.) for $\text{C}_{30}\text{H}_{50}\text{MoN}_4\text{S}_4$: C, 51.97 (52.15); H, 7.31 (7.29); N, 8.03 (8.11); S, 18.72 (18.56)%.

3p. Mass spectrum (EI): m/z 756 (M^+), 608 ($\text{M} - \text{dtc}$), 575 ($\text{M} - \text{NR}$), 460 ($\text{M} - 2\text{dtc}$) and 427 ($\text{M} - \text{NR} - \text{dtc}$). ^1H NMR: δ 3.26 (q, 8 H, J 7.0 Hz, CH_2) and 2.32 (s, 12 H, CH_2). ^{13}C - $\{^1\text{H}\}$ NMR: δ 201.3 (C=N), 142–114 (m, Ph), 45.7 (CH_2) and 12.1 (Me). ^{13}C CPDAS: δ 200.9, 137.3, 133.8, 49.9, 46.5, 14.9 and 11.8. ^{13}C CPDAS TOSS: δ 200.9, 150–130 (br), 133.7, 49.8, 14.9 and 11.7. ^{13}C CPDAS NQSTOSS: δ 200.9, 133.8, 14.9 and 11.7. Satisfactory elemental analysis could not be obtained.

3a-d¹⁰. Mass spectrum (EI): m/z 584 (M^+), 490 ($\text{M} - \text{NPh}$) and 439 ($\text{M} - \text{dtc}$). ^1H NMR: δ 3.28 (q, 8 H, J 7.1, CH_2) and 0.77 (t, 12 H, J 7.1 Hz, Me). ^{13}C - $\{^1\text{H}\}$ NMR: δ 202.8 (C=N), 158.5 (C_{ipso}), 124.9, 124.7, 124.5, 123.2, 122.9, 122.6, 45.8 (CH_2) and 12.3 (Me). ^{13}C CPDAS TOSS: δ 200.7, 161.2, 156.3, 129.6, 125.9, 120.2, 47.5, 44.6, 13.7 and 12.6. Found (calc.) for

Table 3 Crystallographic data for complexes **3a**, **3b**, **3i–3k** and **3n** at 293 K

	3a	3b	3i	3j	3k	3n
Formula	C ₂₂ H ₃₀ MoN ₄ S ₄	C ₂₄ H ₃₄ MoN ₄ S ₄	C ₂₆ H ₃₈ MoN ₄ S ₄	C ₃₄ H ₅₄ MoN ₄ S ₄	C ₂₂ H ₂₆ Cl ₄ MoN ₄ S ₄	C ₁₈ H ₃₈ MoN ₄ S ₄
Formula weight	574.74	602.80	630.86	742.99	712.50	534.78
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	16.973(4)	8.467(2)	10.753(2)	16.336(2)	10.690(4)	17.014(7)
<i>b</i> /Å	10.293(1)	10.486(3)	10.761(1)	12.977(2)	10.701(3)	9.193(4)
<i>c</i> /Å	17.369(3)	16.388(4)	26.972(5)	19.230(2)	26.728(5)	19.064(7)
<i>a</i> /°		73.32(2)				
<i>β</i> /°	116.01(2)	86.18(2)		111.70(2)		115.09(3)
<i>γ</i> /°		89.13(2)				
<i>V</i> /Å ³	2727.1	1390.6	3120.9	3788.7	3057.3	2700.4
<i>Z</i>	4	2	4	4	4	4
<i>μ</i> (Mo–K α)/cm ^{−1}	7.79	7.68	6.87	5.76	10.54	7.82
Data measured	5402	5442	3677	4593	3078	5463
Unique data used	5231	5140	3622	4556	3029	5061
No. parameters	280	298	316	195	316	244
<i>R</i>	0.048	0.050	0.040	0.031	0.040	0.049
<i>R</i> '	0.042	0.054	0.049	0.035	0.043	0.050

C₂₂H₂₀D₁₀MoN₄S₄·0.5CH₂Cl₂: C, 43.44 (43.09); H, 3.17 (3.35); N, 9.14 (8.94)%.

[Mo(NPh)₂(S₂CNMe₂)₂] 4a. A diethyl ether solution (50 cm³) of [Mo(NPh)₂Cl₂(dme)] **2a** (2.00 g, 4.56 mmol) and Na[S₂CNMe₂] (1.32 g, 9.20 mmol) was stirred for 16 h at room temperature. Filtration gave a brown solution and residue. The latter was extracted with dichloromethane (3 × 30 cm³) and added to the dme solution. Removal of volatiles under reduced pressure gave a black solid which was washed with light petroleum. This was then redissolved in the minimum amount of dichloromethane and light petroleum added. Cooling to −20 °C gave complex **4a** (0.94 g, 40%) as a dark brown solid. Orange **4n** (41%) was prepared in a similar fashion.

4a. Mass spectrum (EI): *m/z* 521 (M⁺), 430 (M – NPh) and 398 (M – dtc). ¹H NMR: δ 7.50 (d, 4 H, *J* 8.1, H^{2,6}), 6.98 (t, 4 H, *J* 7.5, H^{3,5}), 6.71 (t, 2 H, *J* 7.5 Hz, H⁴) and 2.48 (s, 12 H, Me). ¹³C CPMAS TOSS: δ 199.8, 190.6, 189.4, 184.0, 177.6, 160.3 (C_{ipso}), 129.5, 128.2, 124.4, 123.8, 116.6 and 39.7. ¹³C CPMAS NQSTOSS: δ 199.9, 160.3, 128.8 and 39.7. Found (calc.) for C₁₈H₂₂MoN₄S₄·0.5CH₂Cl₂: C, 39.00 (39.47); H, 4.22 (4.09); N, 10.41 (9.96)%.

4n. Mass spectrum (EI): *m/z* 480 (M⁺) and 409 (M – NBU⁺). ¹H NMR: δ 2.61 (s, 12 H, Me) and 1.58 (s, 18 H, BU⁺). ¹³C-¹H NMR: δ 204.9 (C=N), 71.1 (C_o), 40.3 (Me) and 31.4 (BU⁺). ¹³C CPMAS TOSS: δ 204.1, 203.3, 72.8 (C_o), 69.9 (C_o), 44.0, 42.4, 41.9, 32.4 and 31.8. Found (calc.) for C₁₄H₃₀MoN₄S₄·CH₂Cl₂: C, 31.78 (31.86); H, 6.26 (5.66); N, 10.65 (9.91)%.

[Mo(NPh)₂(S₂PPh₂)₂] 5a. A diethyl ether solution (50 cm³) of [Mo(NPh)₂Cl₂(dme)] **2a** (2.00 g, 4.56 mmol) and Na[S₂PPh₂] (2.50 g, 9.20 mmol) was stirred for 16 h at room temperature. Filtration gave a red solution which after removal of volatiles under reduced pressure gave a bright red solid. This was washed with light petroleum then redissolved in the minimum volume of diethyl ether. Cooling to −20 °C gave complex **5a** (1.84 g, 52%) as a dark red microcrystalline solid. ¹H NMR: δ 8.05–7.69 (m, 6 H, PPh₂ + H^{2,6}), 6.92 (m, 6 H, PPh₂), 6.84 (t, 4 H, *J* 7.6, H^{3,5}) and 6.68 (t, 2 H, *J* 7.3 Hz, H⁴). ¹³C-¹H NMR: δ 158.2 (C_{ipso}) and 137.9–131.3 (m, Ph). ¹³C CPMAS: δ 156.7 (C_{ipso}), 155.1 (C_{ipso}), 139.0, 132.3, 128.1 and 124.5. ³¹P NMR: δ 64.5 (s). ³¹P CPMAS: δ 68.6 and 65.5. Found (calc.) for C₃₆H₃₀MoN₄P₂S₄: C, 54.86 (55.66); H, 3.82 (3.89); N, 3.18 (3.61); P, 8.17 (7.97); S, 16.41 (16.51)%.

X-Ray crystallography

Suitable single crystals were mounted on a glass fibre and all geometric and intensity data were taken from these samples

using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo–K α radiation (λ = 0.71073 Å). Important crystallographic parameters are summarised in Table 3. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω – 2θ technique was used to measure reflections in the range $5 \leq 2\theta \leq 50^\circ$ and three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz-polarisation effects, and empirically for absorption. The unique data with $I \geq 3.0\sigma(I)$ were used to solve and refine the structures, being solved by direct methods and developed using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å²). Structure solution used either the SHELXTL⁴¹ or SHELXTL PLUS⁴² program packages on a microVax or IBM PC respectively.

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