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The crystal structure of [Mo(NCS)(CO)$_2$(η^3-C$_3$H$_5$)(NCMe)$_2$]·MeCN and the reactions of {Mo(CO)$_2$(η^3-C$_3$H$_5$)$^+$} containing species with symmetric alkynes

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Abstract

In the solid-state [Mo(NCS)(CO)$_2$(η^3-C$_3$H$_5$)(NCMe)$_2$] · MeCN (**1**) contains a pseudo-octahedral arrangement of ligands about molybdenum, with carbonyls and nitriles in the equatorial plane and an N-bonded thiocyanate group *trans* to the allyl ligand. In refluxing methanol or acetonitrile both **1**, and the analogous chloro-complex [MoCl(CO)$_2$(η^3-C$_3$H$_5$)(NCMe)$_2$] (**2**) catalytically convert PhC≡CPh to a mixture of hexaphenylbenzene and *E*,*E*-1,2,3,4-tetraphenylbutadiene. By contrast MeO$_2$CC≡CCO$_2$Me is not oligomerised. In methanol, complex **2** dimerises 1,4-diphenylbutadiyne to *Z*,*E*-1,4,5,8-tetraphenyl-1,7-octa-3,5-diene-1,7-diyne, whereas in the presence of base both the complex and the diyne, react preferentially with the solvent to generate the [Mo$_2$(CO)$_4$(η^3-C$_3$H$_5$)$_2$(OMe)$_3$]$^-$ anion and *Z*-1,4-diphenyl-3-methoxy-but-3-ene-1-yne, respectively.

Keywords: Molybdenum(II)allyl; Solid-state structure; Alkyne and diyne oligomerisation

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1. Introduction

Molybdenum(II) complexes of the type [MoX(CO)$_2$(η^3-allyl)(NCMe)$_2$] (X = halide or pseudohalide) have been used extensively over several decades as synthetic precursors for a wide variety of Mo(II)-allyl derivatives containing the 12e$^-$ {Mo(CO)$_2$(η^3-allyl)$^+$} fragment, which are formed by substitution of the labile nitrile ligands and/or the anion X [1]. This group of compounds includes the historically significant complex [Mo(CO)$_2$(η^3-allyl)(Bpyr$_2$Et$_2$)] {Bpyr$_2$Et$_2$ = (3,5-diethylpyrazolyl)borato anion}, which provided the first structurally characterised example of a molecular species with a C–H···M agostic interaction [2], some pyridylphosphane derivatives which exhibit three independent fluxional processes in solution [3], and novel heteronuclear molybdenum/bismuth alkoxides of interest as models of propene oxidation catalysts [4].

The η^3-allyl group in several {Mo(CO)$_2$(η^3-allyl)$^+$} containing species has also been shown to be susceptible to highly regioselective as well as entioselective reactions [5], and subsequently routes to stoichiometric and catalytic allylic alkylations which involve Mo(0)/Mo(II)-allyl intermediates, have been reported [6]. More recently stoichiometric alkyne-allyl coupling reactions have been demonstrated for two dithiophosphinate derivatives, [Mo(CO)$_2$(η^3-allyl)(S$_2$PX$_2$)(MeCN)] (X = OEt, Ph), resulting in the formation of intramolecularly stabilised σ-alkenyl complexes [7]. Reductive elimination of allyl halides from [MoX(CO)$_2$(η^3-allyl)(NCMe)$_2$] also provides a facile entry into electron-rich Mo(0)-dicarbonyl species, [Mo(CO)$_2$L$_4$] and [Mo(CO)$_2$L$_2$L$'_2$], which are not available by direct substitution in Mo(CO)$_6$ [8].

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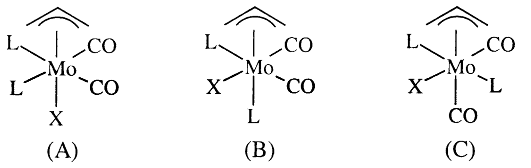


Scheme 1. The structural isomers of $[MoX(CO)_2(\eta^3\text{-allyl})L_2]$ compounds.

The structures of many complexes in which the nitrile ligands in $[MoX(CO)_2(\eta^3\text{-allyl})(NCMe)_2]$ have been replaced by stronger σ-donors have been reported in the literature [9]. They all adopt one of the three basic structures (A)–(C), illustrated in Scheme 1. Structural types (A) and (B) are most frequently found, and these are conveniently described as pseudooctahedral with the allyl ligand occupying a single coordination site. However, if the η^3-allyl ligand is regarded as occupying two coordination sites, then all three structural types can be related either to the capped trigonal-prismatic or the pentagonal-bipyramidal structures commonly found for other seven-coordinate species.

Of the parent nitrile species, $[MoX(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]$, whose reactions lead to products with this extremely wide variety of different structural motifs, dynamic behaviour, and synthetic applications, only the structure of the bromo derivative has been reported [10]. In this investigation a single crystal X-ray study of the thiocyanate derivative, **1**, has been undertaken, and the reactions between **1**, and its chloro-analogue, **2**, with diphenylacetylene, dimethyl acetylenedicarboxylate and 1,4-diphenylbutadiyne have also been elucidated.

2. Results and discussion

2.1. Structural studies on $[Mo(NCS)(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]\cdot MeCN$ (1)

Complex **1** was prepared in good yield by the reaction of $Mo(CO)_6$ with allyl thiocyanate in refluxing acetonitrile. Crystals of **1** suitable for an X-ray structure determination were obtained directly from the cooled reaction solution. The structure of **1**, showing the atom-labelling scheme used, is shown in Fig. 1. The molecular unit possesses a mirror plane, and the geometry about molybdenum can be described as pseudooctahedral with carbonyl and nitrile ligands in the equatorial plane, and an N-bonded thiocyanate *trans* to the allyl group.

Significant bond lengths and angles are given in Table 1. Compared with other known complexes of the type $[Mo(\text{halide})(CO)_2(\eta^3\text{-}C_3H_5)(\text{N-donor})_2]$ which adopt structural type (A) [9,10], the bond lengths and angles

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **1**

Bond lengths			
Mo(1)–N(1)	2.157(4)	Mo(1)–N(2)	2.243(3)
Mo(1)–C(4)	1.950(4)	Mo(1)–C(5)	2.333(3)
Mo(1)–C(6)	2.212(5)	C(5)–C(6)	1.397(5)
C(1)–N(1)	1.154(7)	C(2)–N(2)	1.134(5)
C(1)–S(1)	1.617(5)	C(2)–C(3)	1.444(5)
Bond angles			
N(1)–Mo(1)–N(2)	83.37(12)	N(1)–Mo(1)–C(4)	89.88(14)
N(2)–Mo(1)–N(2)′	81.6(2)	C(4)–Mo(1)–C(4)′	81.5(2)
N(2)–Mo(1)–C(4)	97.92(14)	Mo(1)–N(1)–C(1)	173.8(4)
C(5)–C(6)–C(5)′	116.5(5)		

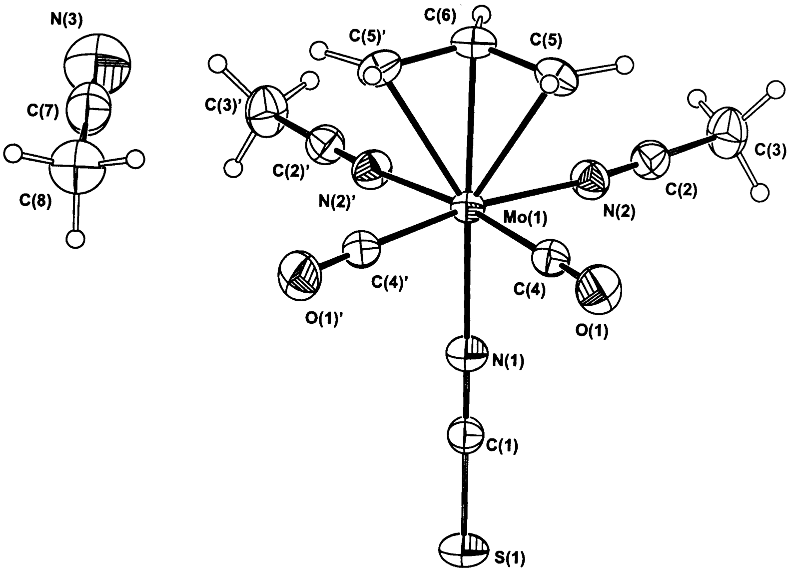


Fig. 1. The structure of $[Mo(NCS)(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]\cdot MeCN$ (**1**).

in the primary coordination sphere of the metal and in the η^3-bonded propenyl group are unexceptional, although the Mo–N(1) separation at 2.157(4) Å is slightly greater than that of 2.119(7) Å found in the only other structurally characterised thiocyanate analogue containing an unsubstituted allyl ligand, $[Mo(NCS)(CO)_2(\eta^3\text{-}C_3H_5)(2,2'\text{-bipyridine})]$ [11]. Both compounds contain an almost linear Mo–N–C–S arrangement. There are no abnormally short contacts involving the lattice solvent molecule, which has a shortened C–N and a lengthened C–C bond [C(7)–N(3) = 1.101(11) and C(7)–C(8) = 1.423(14) Å, respectively], compared to those in the coordinated MeCN in **1** (Table 1).

On dissolution in deuterated methanol only a single set of signals was apparent in the proton NMR spectrum of **1**, whereas in deuterated acetonitrile a second, weaker set of allyl signals with chemical shifts and coupling constants appropriate for the known $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3]^+$ cation [12,13] were also present. Addition of $AgBF_4$ resulted in precipitation of AgNCS and an increase in the intensity of the weaker set of signals due to the cationic species. Thus partial solvolysis of **1** occurs in acetonitrile as indicated in the equation below.

$$[MoNCS(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3] + MeCN \rightarrow [Mo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3]^+ + NCS^-$$

The extreme solvent dependency of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]$ (**2**) has been described previously [12,13]. Auto-ionisation as described by the equation below occurs at room temperature in non-protonic solvents, including acetonitrile, and the ionic compound $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_3][Mo_2Cl_3(CO)_4(\eta^3\text{-}C_3H_5)_2]$, which has been structurally characterised [14], was obtained by recrystallisation of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]$ from dry benzene.

$$3[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2] \rightarrow 3MeCN + [Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_3]^+ + [Mo_2Cl_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$$

In protic solvents, including methanol and water, NMR studies have shown that only a single allyl-containing species is formed [15]. The spectra of **1** and **2** do not change in methanolic solutions on heating in the absence of air, and consequently this solvent was preferred for our initial studies of the alkyne reactions.

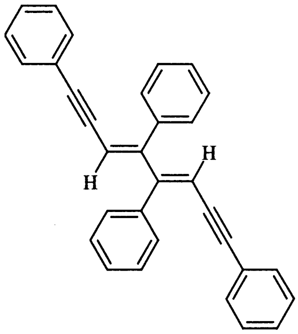
2.2. Alkyne and diyne reactions

Reactions in refluxing methanol between complex **1** or **2** and excess diphenylacetylene were complete in 24 hours, by which time the metal complex had lost its catalytic activity, and solution infrared measurements showed that no metal carbonyl species remained. Column separation of the organic products afforded 1,2,3,4-tetraphenylbutadiene, **3**, and hexaphenylbenzene, **4**. Both the melting point and the NMR spectra of the diene showed it to be the *E*,*E*-isomer. Although the yields of the two products **3** and **4** were slightly dependent upon the metal complex, Ph_6C_6 was consistently the major product. Reactions carried out in methanol for a shorter period of time, or at room temperature, failed to produce any new, isolable organic products or metal complexes. Therefore, the reaction between **2** and diphenylacetylene was repeated using acetonitrile as solvent. Reaction at reflux temperatures again produced a mixture of hexaphenylbenzene and 1,2,3,4-tetraphenylbutadiene. Under less forcing conditions only starting materials were isolated from the reaction mixtures.

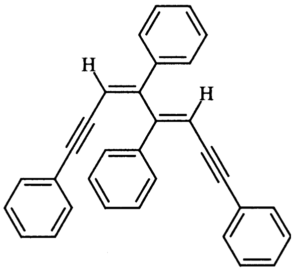
Even at ambient temperature there was a slow colour change from yellow to brown on reacting $C_2(CO_2Me)_2$ with a solution of **1** or **2** in methanol. The alkene $MeCO_2C(OMe){=}CH(CO_2Me)$ (**5**) was isolated in good yield from heated solutions, and small quantities of a second product, **6**, were also isolated from some reactions. This was shown to be $MeCO_2C(C_3H_5){=}CH(CO_2Me)$ and it was the only organic product incorporating the allyl group found in this study. It has been reported previously [7] that the allyl ligand in $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)(S_2PX_2)]$, X = OEt or Ph, couples with dimethyl acetylenedicarboxylate to form a metal complex which decomposes on exposure to moist air yielding dimethyl 2-allylfumurate. It appears that a similar allyl-alkyne coupling reaction may occur above, and that the excess alkyne present in the reaction mixture reacts with the solvent. On using acetonitrile instead of methanol as solvent, unreacted $C_2(CO_2Me)_2$ was recovered, but we were unsuccessful in isolating any intermediate metal complex.

Column separation of the products of the reaction in boiling methanol between 1 or 2 and 1,4-diphenylbutadiyne yielded small quantities of unreacted diyne and yellow crystals of a single ene-yne product formed by diyne dimerisation. Of the two possible isomers, NMR measurements confirmed that the *E*,*Z*-isomer of $PhC{\equiv}CC(H){=}CPhCPh{=}C(H)C{\equiv}CPh$ (**7b**) had been formed, albeit in quite low yield.

Addition of base to the above reaction completely altered the nature of the reaction. Here, no new C–C bond formation occurred, and instead MeOH added across one of the acetylenic bonds of the diyne. Of the four possible isomers, chemical shifts of nOe measurements indicated that the *Z*-isomer of 1,4-diphenyl-3-methoxy-but-3-ene-1-yne (**8a**), was formed. The same product was formed in 90% yield in the absence of the metal complex, confirming that nucleophilic addition across a single triple bond in 1,4-diphenylbutadiyne is not affected by the presence of the metal species, which in this case is the known [15] $[Mo_2(OMe)_3(CO)_4(\eta^3\text{-}$

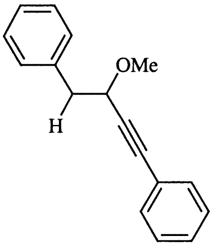


(7a)



(7b)

$C_3H_5)_2]^-$ ion, formed by the reaction of methoxide with **2**. This metal-containing cation could be isolated as a tetraalkylammonium salt from basic methanolic solutions of either **1** or **2** in the presence or absence of the diyne.



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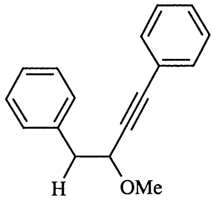

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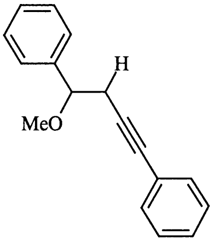
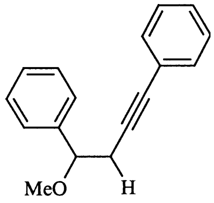


(8c)



(8d)

3. Conclusions

There has been considerable interest in the reactivity of seven-coordinate Mo(II) and W(II) complexes towards alkenes and alkynes in the last two decades, and several have been shown to act as homogeneous catalysts for alkyne dimerisation and [2+2+2] cycloaddition reactions [16]. Surprisingly, considering that complexes of the type $[MoX(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]$, where X = halide or pseudohalide, have been known for thirty years, this is the first report of their reactivity towards alkynes. Studies of the reactivity of **1** and **2** are complicated by their unusual solution behaviour as described above, but in hot methanol both complexes oligomerise $Ph(C{\equiv}C)_nPh$, where $n = 1$ or 2, but not $C_2(CO_2Me)_2$. Under similar reaction conditions $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(2,2'\text{-dipyridyl})]$ is inactive.

4. Experimental

4.1. General

Acetonitrile was distilled over calcium hydride under a dry nitrogen atmosphere immediately prior to use. Other solvents were dried over molecular sieves (type 4A). Allyl isothiocyanate and allyl chloride purchased from commercial sources were distilled and dried over molecular sieves. Column chromatography was carried out using silica gel or fluorosil. The starting material $[MoCl(CO)_2(\eta^3\text{-allyl})(NCMe)_2]$ (**2**) was prepared in 80% yield either by Hayter's method [17], or a modification thereof [13]. Infra-red analyses were carried out using a Nicolet 510P or Perkin–Elmer 1600 FT-IR spectrometer on solid samples mulled with Nujol between sodium chloride discs; liquid samples were suspended between NaCl discs. Elemental microanalyses were determined by the Departmental Microanalytical Services Unit using a Carlo–Erba 1106 analyser. Proton and ^{13}C-NMR spectra were recorded on JEOL 270 and EX400 instruments using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Shift values are given in ppm. Mass spectral data were obtained using a VG 7070E instrument.

4.2. Synthesis

4.2.1. Preparation of $[Mo(NCS)(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]\cdot MeCN$ (1)

$Mo(CO)_6$ [2.64 g (10.0 mmol)] was added to a stirred acetonitrile (25 cm^3) solution of allyl thiocyanate (3.0 cm^3, 28.0 mmol). The clear solution was heated under reflux for 3.5 h in an atmosphere of nitrogen gas. At the end of the reaction the solvent volume was reduced by half, and the deep orange solution cooled and held at 0 °C for 12 h. Bright yellow X-ray quality crystals of **1** were isolated by filtration, washed with ice-cold acetonitrile and stored under an inert atmosphere. Yield 2.34 g (78%). Anal. Found: C, 38.5; H, 3.72; N, 14.75. Calc. for $C_{12}H_{14}MoN_4O_2S$: C, 38.5; H, 3.77; N, 14.95%. IR (Nujol, cm^{-1}) ν_{max} 2307 s (CN str, MeCN), 2280 s (CN str, MeCN), 2094 vs (CN str, NCS), 1929 (CO str), 1848 (CO str). ^{1}H-NMR (CD_3CN), δ_{ppm} 1.28 (d, 2 H, allylH$_{anti}$, $J = 9.8$ Hz); 2.15 (s, 6H, MeCN$_{coordinated}$); 3.39 (d, 2H allylH$_{syn}$, $J = 4.9$ Hz); 3.84 (m, 1H). Low intensity signals at 1.47 (d, $J = 9.6$ Hz), 3.56 (d, $J = 6.0$ Hz) and 4.02 (tt, $J = 9.6$ and 6.0 Hz) with relative intensities 2:2:1 are assigned to allyl resonances of the known [13] cationic species $[Mo(CO)_2(\eta^3\text{-}$

$C_3H_5)(MeCN)_3]^+$. In CD_3OD the proton NMR spectrum of **1** in the allyl region was similar to that of **2** [13].

4.3. Alkyne and diyne reactions

A solution of the alkyne or diyne (5.0 mmol) in methanol (50 cm^3) was treated with finely divided **1** or **2** (0.75 mmol), and then heated under reflux under a N_2 atmosphere for 24 h. The cooled reaction mixture was then treated as follows.

PhC≡CPh — A light brown solid was removed by filtration and shown by TLC to consist of two major products. These were separated on a fluorosil column eluted first with petrol/diethyl ether (3:1 v/v), and then dichloromethane to remove the second product. Compound **3**, yield 0.30 g (34%); m.p. 182 °C (lit. [18] 184 °C). Anal. Found: C, 93.3; H, 6.14. Calc. for $C_{28}H_{22}$: C, 93.9; H 6.18%. MS (70 eV) *m/e* 358. Compound **4**, yield 0.52 g (58%); m.p. 453 °C (lit. [19] 454 °C). Anal. Found: C, 94.2; H, 5.66. Calc. for $C_{42}H_{30}$: C, 94.3; H, 5.65%. MS (70 eV) *m/e* 534.

$MeO_2CC{\equiv}CCO_2Me$ — The oily residue remaining after removal of the solvent was eluted from a silica column using first cyclohexane/ethyl acetate (9:1 v/v), and then dichloromethane, to afford **5** and **6** as oils. Yield of **5**, 0.56 g (64%). Anal. Found: C, 48.2; H, 5.74. Calc. for $C_7H_{10}O_5$: C, 48.2; H, 5.75%. MS (70 eV) *m/e* 174. ^{1}H-NMR: ($CDCl_3$), δ_{ppm} 3.76 (s, 3 H Me), 3.85 (s 3 H Me), 3.95 (s 3 H, Me), 6.19 (s 1 H, CH). ^{13}C-NMR: ($CDCl_3$), δ_{ppm} 164.7 (CO_2), 163.3 (CO_2), 154.7 (*C*=CH), 107.7 (C=*C*H), 61.1 (Me), 52.9 (Me), 51.8 (Me). Yield of **6**, 0.10 g (72%). Anal. Found: C, 39.0; H, 5.50. Calc. for $C_9H_{12}O_4$: C, 39.5; H, 5.69%. MS (70 eV) *m/e* 184. ^{1}H-NMR: ($CDCl_3$), δ_{ppm} 6.76 (s, 1H C*H*CH_2), 5.80 (m, 1CH) 5.10–5.00 (m, 2H, C=CH_2) 3.80 (s 6H Me), 3.50 (d 2H, CH_2, $J = 16$ Hz).

PhC≡C–C≡CPh — The solid remaining after evaporation of the solvent was extracted with 2 × 5 cm^3 of petrol and the combined extract columned on fluorosil using petrol/diethyl ether (1:1 v/v) to elute unchanged diyne, followed by petrol/dichloromethane (1:1 v/v) to elute the yellow product **7**. Yield 0.12 g (24)%, m.p. 232 °C. Anal. Found: C, 93.7; H, 5.46. Calc. for $C_{32}H_{22}$: C, 94.5, H, 5.46%. MS (70 eV) *m/e* 406. ^{1}H-NMR: ($CDCl_3$), δ_{ppm} 6.65 (s, 1H, CH), 6.80 (s, 1H, CH), 7.1–8.0 (m, 20H, aromatics). ^{13}C-NMR: ($CDCl_3$), δ_{ppm} 152.3, 138.6, 137.8, 136.3, 131.6, 131.4, 130.2, 129.6, 128.7, 128.5, 128.2, 123.7, 123.1, 122.8, 110.8, 89.3 (≡*C*Ph), 86.8 (≡*C*–C).

PhC≡C–C≡CPh — The reaction was repeated as above using a solution of NaOH (0.40 g, 10 mmol) in MeOH (50 cm^3) as solvent. The reaction mixture was evaporated to dryness; the residue treated with cyclohexane (10 cm^3) and the extract columned on fluorosil to afford starting material followed by a yellow solution from which crystal of product **8** were obtained on evaporation. Yield 0.27 g (24%). Anal. Found: C, 86.8; H, 6.06. Calc. for $C_{17}H_{14}O$: C, 87.2; H, 6.02%. MS *m/e* 234. ^{1}H-NMR: ($CDCl_3$), δ_{ppm} 4.20 (s, 3H, OMe), 5.55 (s, 1H, CH), 7.40 (m, 10H, aromatics). ^{13}C-NMR: ($CDCl_3$), δ_{ppm} 163.7 (*C*OMe), 133.8, 131.0, 129.2, 128.4, 128.3, 127.8, 125.9, 124.0 (aromatics), 93.6 (*C*HPh), 86.5 (*C*Ph), 86.4 (*C*Ph), 59.7 (OMe) The same product was prepared in 90% yield in the absence of a metal complex.

4.4. X-ray crystallography

A crystal of **1** (0.3 × 0.3 × 0.2 mm^3) was selected for data collection. X-ray data was collected on an Enraf–Nonius CAD4 automatic four-circle diffractometer and the structure solved using XCAD [20] and SHELX [21] software. The asymmetric unit consists of half of one organometallic molecule and half of one acetonitrile molecule, with atoms Mo1, C5, H6, N1, C1, S1, C8, C7, N3 and H8A seated on the mirror plane at $y = 1/4$ in the space group.

Table 2
Crystallographic data and structure refinement for **1**

Empirical formula	$C_{12}H_{14}MoN_4O_2S$
Formula weight	374.27
Temperature (K)	293(2)
Wavelength (Å)	0.70930
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	
a (Å)	6.3530(10)
b (Å)	10.2580(10)
c (Å)	12.502(2)
β (°)	90.97
V (Å^3)	814.6(2)
Z	2
D_{calc} (Mg m^{-3})	1.526
Absorption coefficient (mm^{-1})	0.938
F(000)	376
Crystal size $(mm)^3$	0.3 × 0.3 × 0.2
θ Range for data collection (°)	2.56–26.91
Index ranges	$-8 \le h \le 0$; $-12 \le k \le 0$; $-15 \le l \le 15$
Reflections collected	3522
Independent reflections	1870 [$R_{int} - 0.0055$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1870/8/123
Goodness-of-fit on F^2	1.090
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0468$, $wR_2 = 0.1225$
Largest difference peak and hole (e Å^{-3})	1.362 and −0.815
Weighting scheme	Calc $w = 1/[\sigma^2(F_o^2)+(0.1000P)^2+0.000P]$, where $P = (F_o^2+2F_c^2)/3$
Extinction coefficient	0.0050(29)
Extinction expression	$F_c^* = kF_c[1+0.001 \times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Full-matrix least-squares anisotropic refinement for all non-H atoms yielded $R_1 = 0.0468$ and $wR_2 = 0.1110$ at convergence. Hydrogen atoms were included at calculated positions where relevant, except in the case of the allyl and solvent moieties. These positions were located in the penultimate difference fourier map and positionally refined at a distance of 0.98 Å from the relevant parent atoms. Crystal data and refinement details are given in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 158092 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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