Accepted Manuscript

Reactivity of $[Mo(CO)_3(NCMe)_3]$ towards pyrimidine-2-thiol (pymSH) and thiophenol (PhSH) in the presence of phosphine auxiliaries: Synthesis of monoand dinuclear complexes bearing κ^2 and μ,κ^2 -pymS coordination motifs

Roknuzzaman, S.M. Tareque Abedin, Mohd. Rezaul Haque, Shishir Ghosh, Derek A. Tocher, Michael G. Richmond, Shariff E. Kabir

PII:	S0277-5387(19)30124-X
DOI:	https://doi.org/10.1016/j.poly.2019.02.023
Reference:	POLY 13767
To appear in:	Polyhedron
Received Date:	8 January 2019
Revised Date:	4 February 2019
Accepted Date:	5 February 2019



Please cite this article as: Roknuzzaman, S.M.T. Abedin, d.R. Haque, S. Ghosh, D.A. Tocher, M.G. Richmond, S.E. Kabir, Reactivity of $[Mo(CO)_3(NCMe)_3]$ towards pyrimidine-2-thiol (pymSH) and thiophenol (PhSH) in the presence of phosphine auxiliaries: Synthesis of mono- and dinuclear complexes bearing κ^2 and μ,κ^2 -pymS coordination motifs, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.02.023

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Reactivity of $[Mo(CO)_3(NCMe)_3]$ towards pyrimidine-2-thiol (pymSH) and thiophenol (PhSH) in the presence of phosphine auxiliaries: Synthesis of mono- and dinuclear complexes bearing κ^2 and μ,κ^2 -pymS coordination motifs

Roknuzzaman ^a, S.M. Tareque Abedin ^a, Mohd. Rezaul Haque ^a, Shishir Ghosh ^{a,*}, Derek A. Tocher ^b, Michael G. Richmond ^c, Shariff E. Kabir ^{a,*}

^a Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

^c Department of Chemistry, University of North Texas, 1155 Union Circle, Box 305070, Denton, TX 76203, USA

*Corresponding authors.

E-mail addresses: sghosh_006@yahoo.com (S. Ghosh); skabir_ju@yahoo.com (S.E. Kabir)

Abstract

The reaction of $[Mo(CO)_3(NCMe)_3]$ with added thiol in the presence of a phosphine auxiliary has been investigated. Treatment of $[Mo(CO)_3(NCMe)_3]$ with pyrimidine-2-thiol (pymSH) and PPh₃ at 60 °C in MeCN afforded the known mononuclear compounds *cis*- $[Mo(CO)_4(PPh_3)_2]$ (1) and $[Mo(\kappa^2-pymS)_4]$ (2), and the new binuclear compound $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(PPh_3)_2]$ (3), which possesses an idealized C₂ symmetry. A different product distribution was found when dppm was employed as the phosphine ligand. Of the five reaction products isolated, three consisted of mononuclear compounds, $[Mo(CO)_4(\kappa^2-dppm)]$ (4), $[Mo(CO)_3(\kappa^2-dppm)(\kappa^1-dppm)]$ (5) and $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6), with the remaining two products corresponding to dinuclear compounds, $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7) and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8). Products 6-8 are new and have been fully characterized in solution by IR and NMR spectroscopy, and by X-ray crystallography in the case of 6 and 7. The reaction of $[Mo(CO)_3(NCMe)_3]$ with PhSH and dppm at 60 °C in MeCN was

also examined to assess the effect of thiol on the product distribution. The two principal products isolated were identified as the mononuclear compound $[Mo(CO)_2(\kappa^1-PhS)_2(\kappa^2-dppm)]$ (9) and the dinuclear compound $[Mo_2(CO)_6(\mu,\kappa^1-PhS)_2(\mu,\kappa^2-dppm)]$ (10). The bonding in compounds 3, 6 and 7 was also examined by DFT, and highlights between the computational and experimental structures are discussed.

Keywords: Mono- and di-molybdenum complexes; Thiol activation; Phosphine mediators; X-ray structures; DFT.

1. Introduction

Reactions of heterocyclic thiols with transition metal complexes have been widely investigated over the past four decades since the resultant complexes often show exotic structural motifs due to the ability of these ligands to display a diverse range of coordination modes at mono- and polynuclear metal centers [1-6]. Consequently, our group and others have also been studying the reactivity of these heterocyclic thiols with low-valent metal carbonyls over the years which reveal that the output of these reactions depends on both the structure of these thiols and the intrinsic reactivity of the metal carbonyls [4-14]. However, in comparison to the number of Group 7 and 8 metal carbonyl complexes bearing these ligands [5-12], only a few examples of Group 6 metal carbonyl complexes containing these ligands have been reported [13-18]. In 1990, Deeming *et al.* reported the synthesis of the seven-coordinate complexes $[M(CO)_3(\kappa^2-pyS)_2]$ (M = Mo, W) from the direct reactions of $[M(CO)_3(NCMe)_3]$ with pySH, along with the phosphine derivative Mo(CO)₂(PMe₂Ph)(κ^2 -pyS)₂ [15]. More recently, Shi and co-workers reported that the reaction of [Mo(CO)₃(NCMe)₃] with pySH and PPh₃ that gave predominantly the dimolybdenum complexes $[Mo_2(CO)_5(\mu,\kappa^2-pymS)_2(PPh_3)]$ and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(PPh_3)_2]$, in addition to a trace amount of the mixed-valence trimolybdenum complex $[Mo_3(CO)_6(\mu,\kappa^2-pymS)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\kappa^2-\mu_3)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^2)_2(\mu_3,\mu^$ pymS)₂] [19]. On the contrary, the reaction of [Mo(CO)₃(NCMe)₃] with pySH and dppm afforded predominantly the binuclear compound $[Mo_2(CO)_4(\mu-\kappa^2-pyS)_2(\kappa^2-dppm)]$ and two mononuclear complexes [Mo(CO)(κ^2 -PhS)₂(κ^2 -dppm)] and [Mo(CO)₄(κ^2 -dppm)] (Scheme 1).



Scheme 1. Reactions of $[Mo(CO)_3(NCMe)_3]$ with pySH in the presence of the phosphine auxiliaries PPh₃ and dppm.

In the above scheme, the pyS ligand displays a μ,κ^2 coordination mode in each of the polynuclear pyS-substituted derivatives. The observed products are also influenced by the nature of the phosphine ligand, and we suspect that the phosphine auxiliary ligand plays a crucial role in helping to determine the ratio of dinuclear to mononuclear products. The monodentate PPh₃ ligand permits higher order coordination of the pySH ligand relative to dppm, which in turn favors the formation of di- or even trinuclear complexes. This structural diversity has inspired us to investigate further the reactivity of [Mo(CO)₃(NCMe)₃] with the thiols pymSH and PhSH in the presence of phosphine auxiliary ligands, the results of which are discussed in this contribution.

2. Experimental section

2.1. General procedures

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Reagent grade solvents were freshly distilled using an appropriate drying agent prior to use. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer, while the NMR spectra were recorded on a Bruker DPX 400 spectrometer. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvent (¹H) and external 85% H₃PO₄ (³¹P), as appropriate. Elemental analyses were performed by the Microanalytical Laboratories of Wazed Miah Science Research Center at Jahangirnagar University. The reactions products were separated in the air by TLC plates coated with 0.25 mm of silica gel (HF254-type 60, E. Merck, Germany). Me₃NO·2H₂O was purchased from Lancaster Chemical. The waters of hydration were removed using a Dean-Stark apparatus by azeotropic distillation from benzene. The anhydrous Me₃NO was stored under N₂. The chemicals dppm, PPh₃, pyrimidine-2-thiol and thiophenol were purchased from Sigma-Aldrich Chemical Co. and used as received. [Mo(CO)₃(NCMe)₃] was prepared from [Mo(CO)₆] according to a literature method [20]. The calculated yields of the isolated products are based on [Mo(CO)₃(NCMe)₃].

2.2. Reaction of $[Mo(CO)_3(NCMe)_3]$ with pymSH and PPh₃

PPh₃ (210 mg, 0.801 mmol) and pymSH (90 mg, 0.802 mmol) were added to an MeCN solution (15 mL) of [Mo(CO)₃(NCMe)₃] (120 mg, 0.396 mmol) at 60 °C and the reaction was then stirred for 2 h, during which time the color of the solution changed from yellow to red. The solvent was removed under reduced pressure, the residue was dissolved in a minimum volume of CH₂Cl₂ and separated by TLC on silica gel. Elution with hexane/acetone (7:3, v/v) developed several bands, of which the first three bands were identified as [Mo(CO)₆], pymSH and PPh₃, in order of elution. The fourth and fifth bands yielded the known compounds *cis*-[Mo(CO)₄(PPh₃)₂] (1) (94 mg, 32%) and [Mo(κ^2 -pymS)₄] (2) (64 mg, 30%), whilst the sixth band afforded the new compound [Mo₂(CO)₄(μ , κ^2 -pymS)₂(PPh₃)₂] (3) (54 mg, 26%) as black crystals after crystallization from hexane/CH₂Cl₂ at 4 °C.

Analytical and spectral data for **3**: Anal. Calc. for $C_{48}H_{36}Mo_2N_4O_4P_2S_2$: C, 54.86; H, 3.45; N, 5.33. Found: C, 55.22; H, 3.49; N, 5.39%. IR (ν (CO), CH₂Cl₂, cm⁻¹): 1920vs, 1845s. ¹H NMR (CDCl₃, δ , ppm): 7.65 (m, 12H), 7.34 (m, 20H), 6.42 (m, 2H), 5.67 (m, 2H). ³¹P{¹H} NMR (CDCl₃, δ , ppm): 54.8 (s).

2.3. Reaction of $[Mo(CO)_3(NCMe)_3]$ with pymSH and dppm

The reactants pymSH (180 mg, 1.605 mmol) and dppm (294 mg, 0.765 mmol) were added to an acetonitrile solution (15 mL) of $[Mo(CO)_3(NCMe)_3]$ (230 mg, 0.759 mmol) at 60 °C, and the solution was stirred for an additional 2 h. Upon cooling, the solvent was removed under reduced pressure, the resulting residue was dissolved in a minimum volume of CH₂Cl₂ and purified by chromatography over silica gel. Elution with hexane/acetone (7:3, v/v) developed several bands which afforded, in order of elution, the known compounds $[Mo(CO)_4(\kappa^2-dppm)]$ (4) (41 mg, 9%) and $[Mo(CO)_3(\kappa^2-dppm)(\kappa^1-dppm)]$ (5) (26 mg, 4%), and the new compounds $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6)] (52 mg, 9%) as red crystals, $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7) (80 mg, 22%) as dark red crystals and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8) (20 mg, 6%) as orange crystals after recrystallization from hexane/CH₂Cl₂.

Analytical and spectral data for **6**: Anal. Calc. for $C_{34}H_{28}MoN_4OP_2S_2$: C, 55.89; H, 3.86; N, 7.67. Found: C, 56.05; H, 3.92; N, 7.72%. IR (v(CO), CH_2Cl_2 , cm^{-1}): 1805vs. ¹H NMR ($CDCl_3$, δ , ppm): 8.93 (m, 1H), 8.31 (m. 1H), 8.19 (m, 2H), 7.80 (m, 8H), 7.55 (m, 7H), 7.20 (m, 1H), 6.98 (m, 4H), 6.80 (m, 1H), 6.50 (m, 1H), 4.24 (m, 2H). ³¹P{¹H} NMR ($CDCl_3$, δ , ppm): 28.6 (s).

Analytical and spectral data for 7: Anal. Calc. for $C_{39}H_{28}Mo_2N_4O_6P_2S_2$: C, 48.46; H, 2.92; N, 5.80. Found: C, 48.79; H, 2.95; N, 5.86%. IR (v(CO), CH₂Cl₂, cm⁻¹): 2022m, 1980vs, 1943m, 1921m, 1869w. ¹H NMR (CD₂Cl₂, δ , ppm): 8.55 (m, 5H), 7.35 (m, 7H), 7.20 (m, 9H), 7.00 (m, 3H), 5.33 (m, 2H), 2.38 (m, 2H). ³¹P{¹H} NMR (CD₂Cl₂, δ , ppm): 19.6 (s).

Analytical and spectral data for **8**: Anal. Calc. for $C_{37}H_{28}Mo_2N_4O_4P_2S_2$: C, 48.80; H, 3.10; N, 6.15. Found: C, 49.06; H, 3.16; N, 6.22%. IR (v(CO), CH_2Cl_2 , cm^{-1}): 1958vs, 1886w, 1850s. ¹H NMR ($CDCl_3$, δ , ppm): 8.82 (d, J 4.8 Hz, 1H), 8.46 (d, J 4.8 Hz, 1H), 8.04 (m, 4H), 7.78 (m, 3H), 7.67 (m, 2H), 7.54 (m, 4H), 7.40 (m, 2H), 7.37 (m, 3H), 6.92 (m, 4H), 5.51 (m,

2H), 5.20 (m, 1H), 4.59 (m, 1H). ${}^{31}P{}^{1}H$ NMR (CDCl₃, δ , ppm): 18.7 (d, J 20 Hz 1P), δ 16.8 (d, J 20 Hz 1P).

2.4. Reaction of $Mo(CO)_3(NCMe)_3$ with PhSH and dppm

To an acetonitrile solution (15 mL) of $[Mo(CO)_3(NCMe)_3]$ (230 mg, 0.759 mmol) at 60 °C was added sequentially thiophenol (178 mg, 1.62 mmol) and dppm (294 mg, 0.765 mmol). The reaction was stirred for 2 h, after which time the solution was allowed to cool to room temperature before the solvent was removed under reduced pressure. Compounds **9** and **10** were subsequently isolated by TLC using hexane/acetone (7:3, v/v) as the eluent. $[Mo(CO)_2(\kappa^1 - PhS)_2(\kappa^2 - dppm)]$ (**9**) (72 mg, 13%) was isolated as yellow crystals and $[Mo_2(CO)_6(\mu, \kappa^1 - PhS)_2(\mu, \kappa^2 - dppm)]$ (**10**) (40 mg, 11%) was isolated as red crystals.

Analytical and spectral data for **9**: Anal. Calc. for $C_{39}H_{32}MoO_2P_2S_2$: C, 62.07; H, 4.27. Found: C, 62.42; H, 4.34%. IR (υ (CO), CH₂Cl₂, cm⁻¹): 1896vs. ¹H NMR (CD₂Cl₂, δ , ppm): 7.50 (m, 6H) 7.40 (m, 16H), 7.28 (m, 1H), 7.15 (m, 7H), 3.96 (m, 1H), 3.81 (m, 1H). ³¹P{¹H} NMR (CD₂Cl₂, δ , ppm): 12.2 (s).

Analytical and spectral data for **10**: Anal. Calc. for $C_{43}H_{32}Mo_2O_6P_2S_2$: C, 53.65; H, 3.35. Found: C, 53.89; H, 3.41%. IR (v(CO), CH₂Cl₂, cm⁻¹): 2021s, 1973vs, 1913s cm⁻¹. ¹H NMR (CD₂Cl₂, δ , ppm): 7.84 (d, J 7.6 Hz, 4H), 7.30 (m, 10H), 7.20 (m, 16H), 2.42 (t, J 9.4 Hz, 2H). ³¹P{¹H} NMR (CDCl₃, δ , ppm): 17.7 (s).

2.5. X-ray crystallography

Single crystals of **3**, **6**, **7** and **9** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a CH₂Cl₂ solution. Suitable crystals were mounted on an Agilent Super Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) using a Nylon loop with an inert oil and the diffraction data were collected at 150(1) K using Mo-K α radiation ($\lambda = 0.71073$ Å). Unit cell determination, data reduction and absorption corrections were carried out using CrysAlisPro [21]. The structures were solved with the ShelXS [22] structure solution program by direct methods and refined by full-matrix least-squares on the basis of F^2 using

ShelXL [22,23] within the OLEX2 [24] graphical user interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Pertinent crystallographic parameters are given in Table 1.

2.5. Computational methodology

All calculations were performed with the hybrid meta exchange-correlation functional M06 [25], as implemented by the Gaussian 09 program package [26]. The molybdenum atoms were described by Stuttgart–Dresden effective core potentials (ecp) and an SDD basis set [27], while the 6-31G(d') basis set was employed for the remaining atoms. The reported geometries were fully optimized and the analytical second derivatives were evaluated and found to possess only positive eigenvalues. A scaling factor of 0.94 was employed in the vibrational analysis of the v(CO) band in **B**. The natural charges and Wiberg indices were computed using Weinhold's natural bond orbital (NBO) program (version 3.1) [28,29]. The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program [30].

3. Results and discussion

3.1. Synthesis of dinuclear $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(PPh_3)_2]$ (3)

The one pot reaction between $[Mo(CO)_3(NCMe)_3]$, pyrimidine-2-thiol (pymSH) and PPh₃ in acetonitrile at 60 °C furnished a ternary mixture of compounds with the known mononuclear compounds *cis*- $[Mo(CO)_4(PPh_3)_2]$ (1) and $[Mo(\kappa^2-pymS)_4]$ (2), isolated in 32 and 30% yield, respectively [31,32]. The dinuclear complex $[Mo_2(CO)_4(\mu,\kappa^2pymS)_2(PPh_3)_2]$ (3) is new and was isolated as a black crystalline solid in 26% yield. This reaction is illustrated in Scheme 2.



Scheme 2. Reaction of [Mo(CO)₃(MeCN)₃] with pymSH and PPh₃

An ORTEP plot depicting the molecular structure of **3** is shown in Fig. 1, together with selected bond distances and bond angles. The asymmetric unit also contains a half dimer, which is completed through space group symmetry. The molecule consists of two [Mo(CO)₂(PPh₃)] fragments linked by a Mo-Mo bond and by two doubly-bridging pymS ligands. The Mo(1)-Mo(2) bond distance of 2.9552(4) Å in 3 is consistent with its single bond designation and is comparable to the Mo-Mo distance in the related dinuclear compounds $[Mo_2(CO)_4(\mu,\kappa^2$ $pyS_{2}(PPh_{3})_{2}$ [2.974(1) Å] [19] and $[Mo_{2}(CO)_{4}(\mu,\kappa^{2}-pyS)_{2}(\kappa^{2}-dppm)]$ [2.9775(5) Å] [14]. There is a crystallographically imposed two-fold rotational axis through the middle of the Mo-Mo bond and perpendicular to the Mo_2S_2 ring, which is non-planar with a dihedral angle of 17.73° between the Mo(1)Mo(2)S(1) and Mo(1)Mo(2)S(2) planes. Each pymS ligand functions as a chelating ligand with sulfur and nitrogen coordination to one metal center in addition to bridging the adjacent molybdenum center via the sulfur group. The metric parameters for the bridging of both metals by the sulfur moieties are similar to those distances and angles reported for the related derivative $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(PPh_3)_2]$ [19]. The two pyrimidine rings are on the same side of the Mo₂S₂ skeleton, and each molybdenum center is six-coordinate and exhibits a slightly distorted octahedral geometry due to the constraints imposed on the metals by the two pymS ligands. The Mo(1)–S(1) bond distance [2.5587(10) Å] is 0.0638 Å longer than the Mo(1)–S(2) [2.4949(10) Å] bond distance. The average Mo-N [2.258(3) Å] and Mo-S [2.4817(8) Å] bond

distances in **3** are comparable to the corresponding Mo–N and Mo–S bond distances in $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(PPh_3)_2]$ [2.261(5) and 2.479(2) Å] [19].

Place Figure 1 Here

The bonding in **3** was examined by electronic structure calculations and the DFToptimized structure **A** is depicted alongside the experimental structure in Fig. 1. Good agreement between the two structures is noted and the computed Mo–Mo bond distance of 2.9960 Å closely matches the experimental Mo–Mo bond distance [2.9552(4) Å]. The computed Wiberg bond index (WBI) for the Mo-Mo bond is 0.57, a value consistent with the existence of a metal-metal single bond in **A**. The WBI for the Mo-Mo bond in **A** is similar in magnitude to the WBIs computed by us for the dinuclear molybdenum compounds *trans*-[Cp₂Mo₂(O)(CO)(PPh₃)₂] and [Mo₂(O)(CO)₂(μ,κ^2 -edt)₂(κ^2 -dppm)] (*cis* and *trans* isomers) that exhibit a Mo–Mo bond order of one [33]. The Mo–S bonds display a mean WBI of 0.71, confirming the symmetrical bonding of each bridging thiolate group to the dimolybdenum core. The molybdenum and nitrogen atoms in **A** are electron rich based on *Q* values of -1.43 (Mo), -0.45 (coordinated N) and -0.48 (free N), while the bridging thiolate and phosphine atoms are electron poor based on *Q* values of 0.42 and 1.32, respectively. The computed charges for the latter groups are similar to the values reported for the isomeric [Mo₂(O)(CO)₂(μ,κ^2 -edt)₂(κ^2 -dppm)] [33].

The spectroscopic data recorded for **3** are fully consistent with the solid-state structure. The IR spectrum shows two strong CO absorptions at 1920 and 1845 cm⁻¹ that closely align with the computed values of 1900 and 1848 cm⁻¹ found for species **A** which correspond to the vibrationally coupled symmetric and antisymmetric v(CO) bands. The ¹H NMR spectrum exhibits multiplets at δ 7.65, 7.34, 6.42, and 5.67 ppm, corresponding to the aryl hydrogen atoms of the pyrimidine and phosphine moieties. The ³¹P{¹H} NMR spectrum exhibits a singlet at δ 54.8 ppm, confirming the presence of equivalent PPh₃ groups.

3.2. Synthesis of the mononuclear complex $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6) and the dinuclear complexes $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7), and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8)

Use of the diphosphine dppm in place of PPh₃ in the reaction of $[Mo(CO)_3(MeCN)_3]$ with pymSH led to a different series of products. Heating the three reactants in acetonitrile at 60 °C furnished the known compounds $[Mo(CO)_4(\kappa^2-dppm)]$ (4) [34] and $[Mo(CO)_3(\kappa^2-dppm)(\kappa^1-dppm)]$ (5) [35] in 9 and 4% yields, respectively, along with the new compounds $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6), $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7) and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8) in 9, 22 and 6% yields, respectively (Scheme 3). Since the formation of 8 could arise from the loss of CO ligands and rearrangement of the dppm ligand in 7, we performed a control experiment using isolated 7. Heating 7 at 60 °C in MeCN revealed no evidence for the formation of 8, monitoring the reaction by TLC and IR spectroscopy; these data support independent pathways for the formation of these two products.



Scheme 3. Synthesis of $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6), $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7), and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8).

The ORTEP diagram of the molecular structure of $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6), shown in Fig. 2, confirms the mononuclear nature of the product and the seven-coordinate geometry at the molybdenum center. Selected bond distances and bond angles for 6 are given in the figure caption. The molecule is coordinatively saturated based on a count of 18-valence

electrons where the CO and the chelating dppm and pymS ligands contribute a total of 12e to the overall electron count. The structure of **6** is best viewed as a pentagonal bipyramid whose ligand arrangement about the metal center is not unlike that found in $[Mo(CO)(\kappa^2-pyS)_2(\kappa^2-dppm)]$ [14] and $[Mo(CO)(\kappa^2-pyS)_2(\kappa^2-dppe)]$ [14]. The Mo–S, Mo–N and Mo–P bond distances in **6** are consistent with the values reported for $[Mo(CO)(\kappa^2-pyS)_2(\kappa^2-dppm)]$ [14] and $[Mo(CO)(\kappa^2-pyS)_2(\kappa^2-dppe)]$ [14]. The CO ligand is roughly *trans* to one of the coordinating nitrogen atoms of the κ^2 -pymS ligand [C(1)-Mo(1)-N(3) 166.67(15)°], and the remaining five donor atoms form a nearly planar pentagon arrangement of atoms. The deviation from planarity of the pentagonal base can be best described in terms of the location of the S(2) atom, which lies 1.094 Å below the mean plane constituted by the remaining four atoms S(1), N(1), P(1) and P(2). The Mo(1)–N(1) bond distance [2.223(3) Å] that is "*trans*" to the phosphorus atom P(2) atom is 0.044 Å shorter than the corresponding Mo(1)–N(3) bond distance. The mean bite angle [N(1)-Mo(1)-S(1) and N(2)-Mo(1)-S(2)] for the chelating pymS ligand of 64.40° is unremarkable relative to related compounds containing a κ^2 -pymS ligand [14,15,19].

Place Figure 2 Here

Compound **6** was also examined by DFT, and the M06-optimized structure **B** is depicted in Fig. 2 (right). The distribution of the ligands about **B** is similar to that found in the experimental structure and this confirms the pentagonal bipyramid as a stable ground-state minimum. The computed v(CO) stretch for the lone CO group of 1814 cm⁻¹ is in good agreement with the experimental value of 1805 cm⁻¹, whose low frequency underscores the high degree of electron donation of the other ligands to the molybdenum center. The molybdenum and nitrogen atoms are electron rich with an atomic charge of -1.32 for the metal and a mean *Q* value of -0.48 for the four nitrogen atoms. The sulfur and phosphine ligands display a positive charge with an average charge of 0.10 and 1.38 for the sulfur and phosphorus centers, respectively.

An ORTEP plot depicting the molecular structure of **7** is shown in Fig. 3, whose caption contains selected bond distances and bond angles. The molecule consists of a dinuclear core of two molybdenum atoms that are bridged by the dppm and a pair of pymS ligands. The heterocyclic thiolates coordinate the two molybdenum centers via the thiolate moieties. The

dppm ligand lies orthogonal to the plane defined by the bridging thiolate ligands and the two metal centers. There is a crystallographically imposed two-fold axis of rotation through the middle of the Mo-Mo bond, perpendicular to the Mo₂S₂ ring. The Mo₂S₂ square is essentially planar, based on a dihedral angle of 5.79° that is formed between the Mo₁Mo₂S₁ and Mo₁Mo₂S₂ planes. The pymS ligands function as 3e donors that promote the union of both metals via a common edge in the edge-bridged bioctahedron. Here each metal is best viewed as a Mo(I) center, and the observed diamagnetism supports the presence of a Mo-Mo single bond, which is slightly longer [2.9959(2) Å] than that in **3** [2.9552(4) Å]. The Mo–P bond distances in **7** [Mo(1)–P(1) 2.5543(5) and Mo(2)–P(2) 2.5659(5) Å] are somewhat longer than that observed in the dinuclear complex **3** [av. 2.4859(8) Å], while the Mo–S bond distances in **7** [av. 2.4670(5) Å] are quite similar to those found in **3** [2.4817(8) Å].

Place Figure 3 Here

The DFT-optimized structure C (Fig. 3) reproduces the important structural features found in the experimental structure. The atomic charges for the Mo, S, N and P atoms parallel the data in A, with the electron-rich Mo and N centers revealing mean Q values of -1.85 and - 0.51, respectively. The S and P centers are electron poor and exhibit an average charge of 0.43 and 1.30, respectively. The WBI of 0.46 is comparable to the value reported for compound A and is in concert with a Mo-Mo single bond in C.

The spectroscopic data recorded for **7** are consistent with the solid-state structure, and the IR spectrum verifies the presence of only terminal CO ligands. The ¹H NMR spectrum reveals several multiplets centered at δ 8.55, 7.35, 7.20, 7.00 and 5.33 ppm, corresponding to the aryl hydrogen atoms of the pyrimidine and dppm aromatic groups. The high-field ¹H multiplet at δ 2.38 ppm is ascribed to the diastereotopic methylene hydrogen atoms of the dppm ligand. The ³¹P{¹H} NMR spectrum exhibits a singlet at δ 19.6 ppm that supports the symmetrical coordination of the Mo₂ frame by the diphosphine ligand.

Attempts to grow single crystals of complex 8 were unsuccessful and the identity of this product was established by spectroscopic and analytical methods. The spectroscopic data are

consistent with the formulated structure for complex **8** (Scheme 3) that is isostructural with the dinuclear compound $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(\kappa^2-dppm)]$, where one of the molybdenum centers supports a chelating dppm ligand [14]. The combustion data agree with $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(\kappa^2-dppm)]$ composition for **8** and the IR spectrum (1958, 1886 and 1850 cm⁻¹) reveals nearly identical stretching frequencies for the v(CO) bands compared to the IR spectrum reported for $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(\kappa^2-dppm)]$ (1954, 1882 and 1846 cm⁻¹) [14]. The ³¹P{¹H} NMR spectrum exhibits two closely spaced doublets at δ 18.7 and 16.8 ppm that display a geminal coupling (²J_{PP}) of 20 Hz, supporting the existence of inequivalent phosphorus centers. The recorded ³¹P chemical shifts and the magnitude of the P-P coupling are virtually identical to the ³¹P NMR data reported for the dppm-chelated relative $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(\kappa^2-dppm)]$ [14]. Complex **8** contains 34 valence electrons and one of the metal centers comprising the $[Mo_2(CO)_4(\mu,\kappa^2-pyS)_2(\kappa^2-dppm)]$ [14].

3.3. Synthesis of $[Mo(CO)_2(\kappa^1 - PhS)_2(\kappa^2 - dppm)]$ (10) and $[Mo_2(CO)_6(\mu, \kappa^1 - PhS)_2(\mu, \kappa^2 - dppm)]$ (9)

The role played, if any, by the pymSH reactant in controlling the product distribution was examined by repeating the reaction using PhSH in place of PymSH. Treatment of $[Mo(CO)_3(MeCN)_3]$ with PhSH and dppm at 60 °C furnished the thiolate-substituted compounds $[Mo(CO)_2(\kappa^1-PhS)_2(\kappa^2-dppm)]$ (9) and $[Mo_2(CO)_6(\mu,\kappa^1-PhS)_2(\mu,\kappa^2-dppm)]$ (10) in 13 and 11% yields, respectively (Scheme 4) as the major isolable products of the reaction. The identity of both products was assigned through a combination of spectroscopic, combustion and crystallographic methods. We note that the TLC plate exhibited much streaking and there was an extensive amount of a red-brown colored material that remained at the origin and whose nature was not established.



Scheme 4. Synthesis of $[Mo(CO)_2(\kappa^1-PhS)_2(\kappa^2-dppm)]$ (9) and $[Mo_2(CO)_6(\mu,\kappa^1-PhS)_2(\mu,\kappa^2-dppm)]$ (10).

The unequivocal identity of 9 was established by X-ray crystallography. The ORTEP plot depicting the molecular structure of 9 is shown in Fig. 4, together with selected bond distances and bond angles. Complex 9 contains a single, six-coordinate molybdenum center whose geometry is best viewed as an octahedron, as opposed to a trigonal prismatic geometry exhibited by numerous Group 6 $M(CO)_2P_2S_2$ (where P and S = monodentate phosphine and thiolate ligands) and $M(CO)_2(PP)(SS)$ derivatives (where PP and SS = chelating diphosphine and dithiolate ligands) [14,15,18,36]. The geometry displayed by this genre of d⁴ complexes is sensitive to the steric properties and coordination mode adopted by the ancillary phosphine and thiolate ligands. Hoffmann and co-workers have investigated the theoretical underpinnings for the octahedral \rightleftharpoons trigonal prism transformation where the energetic preference for d⁴ isomers is small and the thermodynamically favored species is controlled by secondary ligand effects [37]. Relative the chelating dppm ligand, the two PhS moieties adopt sites in the equatorial plane *trans* to the diphosphine ligand. Each CO group occupies an axial site within the octahedron and they are consequently oriented *trans* to each other. Both sulfur atoms lie *trans* to one phosphorus atom $[S(1)-Mo(1)-P(1) 155.20(4)^{\circ}; S(2)-Mo(1)-P(2) 156.16(4)^{\circ}]$ and *cis* to the pnictogen donor $[S(1)-Mo(1)-P(2) 89.31(4); S(2)-Mo(1)-P(1) 90.14(4)^{\circ}]$. The angular arrangement of the S and

P ligands in the equatorial plane, along with the C(1)–Mo(1)–C(2) bond angle of $178.68(18)^{\circ}$, strongly support an octahedral environment at the molybdenum center in **9**. The mean Mo–P [2.5244(10) Å] and Mo–S [2.3668(12) Å] bond distances in **9** are very similar to those reported for related molybdenum complexes of the general formula [Mo(CO)₂(PR₃)₂(κ^2 -SR'S)₂] [38].

Place Figure 4 Here

The recorded IR and NMR spectroscopic data for **9** are consistent with the solid-state structure. The IR spectrum exhibits a single carbonyl stretching band at 1896 cm⁻¹, and the aryl hydrogen atoms of the dppm and PhS ligands appear in the ¹H NMR spectrum as four multiplets at δ 7.50, 7.40, 7.28 and 7.15 ppm, with a relative intensity of 6:16:1:7. The two multiplets centered at δ 3.96 and 3.81 ppm, each integrating for one hydrogen atom, are assigned to the diastereotopic methylene protons of the dppm ligand. The observation of two distinct multiplets for the methylene moiety indicates that any potential ring flipping with the dppm chelate is slow and that the "puckered" four-membered ring defined by the C(27)–P(1)–Mo(1)–P(2) atoms maintains its orientation in solution. Finally, the phosphorus atoms of the dppm ligand are equivalent based on the appearance of a single ³¹P resonance at δ 12.2 ppm in the ³¹P{¹H} NMR spectrum.

Despite repeated attempts to grow single crystals of **10** for analysis by X-ray crystallography, we could not grow publication-acceptable crystals. However, we were able to establish the gross structural composition of **10** using a set of poor quality crystals [39]. The crude diffraction data revealed a Mo₂ core with bridging thiolate and dppm groups, in a fashion similar to that exhibited by compound **7**. The pattern and frequencies of the v(CO) bands in the IR spectrum of **10** match the spectral data for **7** and support the formulated structure of **10** that is depicted in Scheme 3. The recorded ¹H and ³¹P NMR data, which are summarized in the experimental section, are in concert with the asserted composition of **10**.

4. Conclusions

We have synthesized new mono- and dinuclear thiolate-substituted compounds through a series of one-pot syntheses. The new compounds have the potential to serve as novel substrates in redox and photophysical studies involving non-innocent thiolates utilized in light harvesting and proton-reduction chemistry. The new compound $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^1-PPh_3)_2]$ (3), bearing C_2 symmetry, was obtained as one of the three products from the reaction of [Mo(CO)₃(NCMe)₃] with pymSH and PPh₃ at 60 °C. On the other hand, the analogous reaction involving [Mo(CO)₃(NCMe)₃] and pyrimidine-2-thiol in the presence of the the diphosphine dppm gave a total of six products, from which the new compounds $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2-rymS)_2(\kappa^2$ dppm)] (6), $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7) and $[Mo_2(CO)_4(\mu,\kappa^2-pymS)_2(\kappa^2-dppm)]$ (8) have been isolated. The striking difference between 7 and 8 is the different coordination mode adopted by the dppm ligand. The dppm ligand functions as a bridging ligand in 7 and as a chelating ligand in 8. Repeating the last reaction with PhSH in place of pymSH affords a binary product mixture consisting of $[Mo(CO)_2(\kappa^2-dppm)]$ (9) and $[Mo_2(CO)_6(\mu,\kappa^2-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS)_2(\mu-PhS$ κ^2 -dppm)] (10). Future studies using different thiols and phosphines are planned in the hope of determining the precise role played by the ancillary ligands in controlling the product distribution in these reactions.

Acknowledgments

This research has been sponsored by the Ministry of Science and Technology, Government of the People's Republic of Bangladesh. MGR thanks the Robert A. Welch Foundation (grant B-1093) for financial support and acknowledges UNT computational resources provided through CASCaM, which is an NSF-supported facility (CHE-1531468). We also thank the Wazed Miah Science Research Center, Jahangirnagar University, Bangladesh for providing us with some technical facilities required for this work.

Appendix A. Supplementary material

CCDC 1888840, 1888841, 1888842 and 1888844 contain the supplementary crystallographic data for **3**, **6**, **7** and **9**, respectively. These data may be obtained free of charge from the

Cambridge Crystallographic Data Center via <u>www.ccdc.cam.ac.uk/data_request/cif</u>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk, while the atomic coordinates of all the optimized structures are available from MGR upon request.

References

[1] (a) N. Choi, G. Conole, M. Kessler, J.D. King, M.J. Mays, M. McPartlin, G.E. Pateman, G.A. Solan, J. Chem. Soc., Dalton Trans. (1999) 3941; (b) S.G. Rosenfield, S.A. Swedberg, S.K. Arora, P.K. Mascharak, Inorg. Chem. 25 (1986) 2109; (c) D.J. Rose, Y.-D. Chang, Q. Chen, J. Zubieta, Inorg. Chem., 33 (1994) 5167; (d) S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, S. Masuda, J. Chem. Soc., Dalton Trans. (1990) 2105.

[2] (a) I.P. Evans, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1974) 946; (b) B.P. Kennedy,
A.B.P. Lever, Can. J. Chem. 50 (1972) 3488; (c) K. Umakoshi, A. Ichimura, I. Kinoshita, S. Ooi,
Inorg. Chem. 29 (1990) 4005; (d) P. Mura, B.J. Olby, S. D. Robinson, J. Chem. Soc., Dalton
Trans. (1985) 2101; (e) B.K. Santra, M. Menon, C.K. Pal, G.K. Lahiri, J. Chem. Soc., Dalton
Trans., 1997, 1387.

[3] (a) N. Lugan, J.J. Bonnet, J.A. Ibers, J. Am. Chem. Soc. 107 (1985) 4484; (b) B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Chem. Soc., Dalton Trans. (1981) 407; (c) D.J. Rose, Y.D. Chang, Q. Chen, J. Zubieta, Inorg. Chem. 23 (1994) 5167; (d) S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, S. Masuda, J. Chem. Soc., Dalton Trans. (1990) 2105.

[4] (a) S. Jeannin, Y. Jeannin, G. Lavigne, Inorg. Chem. 17 (1978) 2103; (b) A.M. Brodie, H.D.
Holden, J. Lewis, M.J. Taylor, J. Chem. Soc., Dalton Trans. (1986) 633; (c) A.M. Brodie, H.D.
Holden, J. Lewis, M.J. Taylor, J. Organomet. Chem. 253 (1983) C1; (d) S.G. Rosenfield, H.P.
Berends, L. Gelmini, D.W. Stephan, P.K. Mascharak, Inorg. Chem. 26 (1987) 2792.

[5] (a) B. Cockerton, A.J. Deeming, M. Karim, K.I. Hardcastle, J. Chem. Soc., Dalton Trans.(1991) 431; (b) A.J. Deeming, M. Karim, N.I. Powell, K.I. Hardcastle, Polyhedron 9 (1990) 623;

(c) A.J. Deeming, K.I. Hardcastle, M.N. Meah, P.A. Bates, H.M. Dawes, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1988) 227; (d) A.J. Deeming, M. Karim, P.A. Bates, M.B. Hursthouse, Polyhedron 7 (1988) 1401.

[6] (a) K.A. Azam, K.M. Hanif, A.C. Ghosh, S.E. Kabir, S.R. Karmakar, K.M.A. Malik, S. Parvin, E. Rosenberg, Polyhedron 21 (2002) 885; (b) S.E. Kabir, M.M. Karim, K. Kundu, S.M. B. Ullah, K.I. Hardcastle, J. Organomet. Chem. 517 (1996) 155; (c) S. Ghosh, S.E. Kabir, M. Khatun, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, J. Chem. Crystallogr. 39 (2009) 632; (d) M. Islam, C.A. Johns S. E. Kabir, K. Kundu, K.M.A. Malik, S. M. B. Ullah, J. Chem. Crystallogr. 29 (1999) 1001.

[7] (a) M. Islam, S.E. Kabir, K. Kundu, K.M.A. Malik, S.M.B. Ullah, J. Chem. Crystallogr. 30 (2000) 379; (b) G. Ara, S.E. Kabir, K. Kundu, K.M.A. Malik, J. Chem. Crystallogr. 33 (2003) 851; (c) S.E. Kabir, K.M.A. Malik, E. Molla, M.A. Mottalib, J. Organomet. Chem. 616 (2000) 157; (d) S.E. Kabir, G. Hogarth, Coord. Chem. Rev. 253 (2009) 1285.

[8] (a) A. Hoque, S. Islam, M. Karim, S. Ghosh, G. Hogarth, Inorg. Chem. Commun. 54 (2015)
69; (b) M.S. Rahman, J.C. Sarker, S. Ghosh, S.E. Kabir, Aus. J. Chem. 65 (2012) 796.; (c) S.E. Kabir, F. Ahmed, S. Ghosh, R.A. Mamun, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, J. Chem. Crystallogr. 39 (2009) 595; (d) M.A. Khaleque, K.A. Azam, M.M. Karim, S. Ghosh, G. Hogarth, S.E. Kabir, Aus. J. Chem. 65 (2012) 773; (e) M.R. Moni, S. Ghosh, S.M. Mobin, D.A. Tocher, G. Hogarth, M.G. Richmond, S.E. Kabir, J. Organomet. Chem. 871 (2018) 167.

[9] (a) S.E. Kabir, J. Alam, S. Ghosh, K. Kundu, G. Hogarth, D.A. Tocher, G.M.G. Hossain, H.W. Roesky, Dalton Trans. (2009) 4458; (b) S. Ghosh, S.E. Kabir, M. Khatun, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, J. Chem. Crystallogr. 39 (2009) 632; (c) S. Ghosh, K.N. Khanam, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, G. Hogarth, S.E. Kabir, New J. Chem. 34 (2010) 1875.

[10] (a) S. Ghosh, S.E. Kabir, S. Pervin, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman,

T.A. Siddiquee, D.W. Bennett, H.W. Roesky, Z. Anorg, Allg. Chem. 635 (2009) 76; (b) M.F. Ahmad, J.C. Sarker, K.A. Azam, S.E. Kabir, S. Ghosh, G. Hogarth, T.A. Siddiquee, M.G. Richmond, J. Organomet. Chem. 728 (2013) 30; (c) S. Ghosh, S.E. Kabir, S. Pervin, A.K. Raha,

G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, D.W. Bennett, T.A. Siddiquee, L. Salassa, H.W. Roesky, Dalton Trans. (2009) 3510.

[11] (a) S. Ghosh, K.N. Khanam, M.K. Hossain, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, G. Hogarth, S.E. Kabir, J. Organomet. Chem. 695 (2010) 1146; (b) S. Ghosh, F.K. Camellia, K. Fatema, M.I. Hossain, M.R. Al-Mamum, G.M.G. Hossain, G. Hogarth, S.E. Kabir, J. Organomet. Chem. 696 (2011) 2935; (c) A.K. Raha, S. Ghosh, I. Hossain, S.E. Kabir, B.K. Nicholson, G. Hogarth, L. Salassa, J. Organomet. Chem. 696 (2011) 2153.

[12] (a) M.R. Moni, M.J. Mia, S. Ghosh, D.A. Tocher, S.M. Mobin, T.A. Siddiquee, S.E. Kabir, Polyhedron 146 (2018) 154; (b) T.S.M. Abedin, M.R. Moni, S. Ghosh, D.A. Tocher, G.M.G. Hossain, S.M. Mobin, S.E. Kabir, Polyhedron 152 (2018) 164; (c) S. Ghosh, M.S.A. Mia, E. Begum, G.M.G. Hossain, S.E. Kabir, Inorg. Chim. Acta 384 (2012) 76.

[13] (a) M.A.H. Chowdhury, S. Rajbangshi, M. Karim, S. Ghosh, S.E. Kabir, T.A. Siddiquee,
V.N. Nesterov, M.G. Richmond, Inorg. Chim. Acta 434 (2015) 97; (b) M.R. Al-Mamun, S.
Ghosh, S.E. Kabir, J.C. Sarker, G. Hogarth, B.K. Nicholson, J. Coord. Chem. 68 (2015) 1903.

[14] M.R. Haque, S. Ghosh, G. Hogarth, M.G. Richmond, S.E. Kabir, Inorg. Chim. Acta 434 (2015) 150.

- [15] A.J. Deeming, M. Karim, N.I. Powell, J. Chem. Soc., Dalton Trans. (1990) 2321;
- [16] J.A. Broomhead, R. Greenwood, W. Pienkowski, M. Sterns, Aust. J. Chem. 39 (1986) 1895.
- [17] K. Sukcharoenphon, K.B. Capps, K.A. Abboud, C.D. Hoff, Inorg. Chem. 40 (2001) 2402.
- [18] K.-H. Yih, G.-H. Lee, Y. Wang, Inorg. Chem. 42 (2003) 1092.
- [19] Y. Shi, S. Lu, H. Guo, Q. Wu, N. Hu, J. Organomet. Chem. 514 (1996) 183.
- [20] D.P. Tate, W.R. Knipple, H. Kaesz, Inorg. Chem. 2 (1962) 433.
- [21] CrysAlisPro; Oxford Diffraction: Yarnton, England, 2015.
- [22] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [23] G.M. Sheldrick, Acta Cryst. C71 (2015) 3.
- [24] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl.
- Crystallogr. 42 (2009) 339.
- [25] Y. Zhao, D.G. Truhlar, Theor. Chem. Acc. 120 (2008) 215.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P.

Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.
Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N.
Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar,
J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C.
Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C.
Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador,
J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski,
D.J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford, CT, USA, 2009.
[27] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990)

123.

[28] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[29] K.B. Wiberg, Tetrahedron 24 (1968) 1083.

[30] (a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall, R.F. Fenske, Inorg. Chem. 11 (1972) 768; (b) J. Manson, C.E. Webster, M.B. Hall, Texas A&M University, College Station, TX, 2006, http://www.chem.tamu.edu/jimp2/index.html

[31] G. Hogarth, T. Norman, Inorg. Chim. Acta 254 (1997) 167.

[32] I.A. Latham, G.J. Leigh, C.J. Pickett, G. Huttner, I. Jibrill, J. Zubieta, Dalton Trans. (1986) 1181.

[33] M.R. Haque, S. Ghosh, M.M. Rahman, T.A. Siddiquee, V.N. Nesterov, M.G. Richmond, G. Hogarth, S.E. Kabir, Dalton Trans. 47 (2018) 10102.

[34] (a) J. Chatt, H.R. Watson, J. Chem. Soc. (1961) 4980; (b) K.K. Cheung, T.F. Lai, K.S. Mok,J. Chem. Soc. A (1971) 1644.

[35] (a) E.E. Isaacs, W.A.G. Graham, Inorg. Chem. 14 (1975) 2560; (b) A. Blagg, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc., Dalton Trans. (1987) 769.

[36] (a) T.E. Burrow, A.J. Lough, R.H. Morris, A. Hills, D.L. Hughes, J.D. Lane, R.L. Richards, J. Chem. Soc., Dalton Trans. (1991) 2519; (b) P.K. Baker, M.G.B. Drew, E.E. Parker, N. Robertson, A.E. Underhill, J. Chem. Soc., Dalton Trans. (1997) 1429; (c) S. Tsukada, N. Abe, T.

Gunji, Polyhedron 117 (2016) 73; (d) T.E. Burrow, D.L. Hughes, A.J. Lough, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans. (1995) 1315.

[37] (a) R. Hoffmann, J.M. Howell, A.R. Rossi, J. Am. Chem. Soc. 98 (1976) 2484; (b) P. Kubácek, R. Hoffmann, J. Am. Chem. Soc. 103 (1981) 4320; (c) M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, S. Otsuka, J. Am. Chem. Soc. 103 (1981) 5772.
[38] (a) P.K. Baker, A.I. Clark, M.G.B. Drew, M.C. Durrant, R.L. Richards, Inorg. Chem. 38 (1999) 821; (b) S. Tsukada, N. Abe, T. Gunji, Polyhedron 117 (2016) 73; (c) S.K. Mohapatra, Y. Zhang, B. Sandhu, M.S. Fonari, T.V. Timofeeva, S.R. Marder, S. Barlow, Polyhedron 116 (2016) 88.

[39] Crystals of **10** were triclinic, space group *P*-1, with a = 11.669 Å, b = 12.393 Å, c = 15.401 Å; $\alpha = 112.69^{\circ}$, $\beta = 101.33^{\circ}$, $\gamma = 106.26^{\circ}$. The thin needles were weakly diffracting and produced diffraction data best described as poor, yielding structures with *R*₁ values > 10.

Compound	3	6	7	9
CCDC	1888840	1888841	1888842	1888844
Empirical formula	$C_{73.5}H_{56}Cl_3Mo_3N_6O_6P_3S_3$	$C_{34}H_{28}MoN_4OP_2S_2$	$C_{40}H_{30}Cl_2Mo_2N_4O_6P_2S_2$	$C_{40}H_{34}Cl_2MoO_2P_2S_2$
Formula weight	1702.50	730.60	1051.52	839.57
Temperature (K)	150(1)	150(1)	150(1)	150(1)
Wavelength (Å)	0.71073	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P 2_1/n$	$P 2_1/c$	$P 2_1/c$
Unit cell dimensions:				
a (Å)	14.6215(3)	10.83720(10)	11.23513(6)	10.85737(11)
<i>b</i> (Å)	26.1466(5)	28.02280(18)	17.15723(9)	18.69783(15)
<i>c</i> (Å)	38.0544(7)	11.68248(12)	21.83475(16)	18.89739(15)
α (°)	90	90	90	90
β (°)	93.5139(17)	117.3289(12)	91.0216(6)	96.8660(8)
γ (°)	90	90	90	90
Volume (Å ³)	14520.9(5)	3151.85(6)	4208.28(4)	3808.83(6)
Z	8	4	4	4
Density (calculated) (Mg/m ³)	1.558	1.540	1.660	1.464
Absorption coefficient (mm ⁻¹)	0.829	5.885	8.128	6.197
F(000)	6856.0	1488.0	2104.0	1712.0
Crystal size (mm ³)	0.2 imes 0.18 imes 0.1	0.3 imes 0.28 imes 0.04	0.2 imes 0.2 imes 0.04	$0.24 \times 0.16 \times 0.12$
2θ Range for data collection (°)	5.444 to 56.932	6.308 to 152.748	6.552 to 152.926	6.674 to 147.398
Reflections collected	111247	64899	87251	63863
Independent reflections $[R_{int}]$	16672 [$R_{\rm int} = 0.0386$]	6561 [$R_{int} = 0.0571$]	$8780 [R_{int} = 0.0383]$	7619 [$\mathbf{R}_{int} = 0.0315$]
Data / restraints / parameters	16672/0/892	6561/0/397	8780/0/542	7619/0/442
Goodness-of-fit on F^2	1.137	1.222	1.046	1.061
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0493, wR_2 = 0.0821$	$R_1 = 0.0470, wR_2 = 0.1097$	$R_1 = 0.0246, wR_2 = 0.0621$	$R_1 = 0.0566, wR_2 = 0.1464$
<i>R</i> indices (all data)	$R_1 = 0.0638, wR_2 = 0.0877$	$R_1 = 0.0475, wR_2 = 0.1099$	$R_1 = 0.0269, wR_2 = 0.0639$	$R_1 = 0.0590, wR_2 = 0.1483$
Largest diff. peak and hole (e $Å^{-3}$)	1.16/-1.19	1.34/-1.01	0.52/-0.55	1.75/-2.05
		22		

Table 1. Crystal data and structure refinement details for compounds 3, 6, 7 and 9.



Fig. 1. ORTEP drawing of the molecular structure of $[Mo_2(CO)_4(\mu,\kappa^2 pymS)_2(\kappa^1-PPh_3)_2]$ (**3**) (left) and the DFT-optimized structure **A** (right). The thermal ellipsoids in the solid-state structure are at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected crystallographic bond lengths (Å) and angles (°): Mo(1)-Mo(2) 2.9552(4), Mo(1)-S(1) 2.5031(8), Mo(1)-S(2) 2.4557(8), Mo(2)-S(1) 2.4646(8), Mo(2)-S(2) 2.5032(8), Mo(1)-P(1) 2.4863(8), Mo(2)-P(2) 2.4855(8), Mo(1)-N(1) 2.262(3), Mo(2)-N(3) 2.254(3), S(1)-Mo(1)-Mo(2) 52.897(19), S(2)-Mo(1)-Mo(2) 54.16(2), S(2)-Mo(1)-S(1) 105.23(3), S(2)-Mo(1)-P(1) 170.36(3), P(1)-Mo(1)-Mo(2) 134.27(2), P(1)-Mo(1)-S(1) 84.19(3), N(1)-Mo(1)-Mo(2) 85.63(7), N(1)-Mo(1)-S(1) 65.24(7), N(1)-Mo(1)-S(2) 95.67(7), N(1)-Mo(1)-P(1) 90.12(7).



Fig. 2. ORTEP drawing of the molecular structure of $[Mo(CO)(\kappa^2-pymS)_2(\kappa^2-dppm)]$ (6), and the DFT-optimized structure **B** (right). The thermal ellipsoids in the solid-state structure are at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected crystallographic bond lengths (Å) and angles (⁹): Mo(1)–S(1) 2.5587(10), Mo(1)–S(2) 2.4949(10), Mo(1)–P(1) 2.4739(10), Mo(1)–P(2) 2.4500(10), Mo(1)–N(1) 2.223(3), Mo(1)–N(3) 2.267(3), S(2)–Mo(1)–S1138.52(3), P(1)–Mo(1)–S(1) 77.99(3), P(1)–Mo(1)–S2 134.78(4), P(2)–Mo(1)–S(1) 143.26(3), P(2)–Mo(1)–S(2) 75.26(3), P(2)–Mo(1)–P(1) 65.31(3), N(1)–Mo(1)–S(1) 63.94(9), N(1)–Mo(1)–S(2) 81.65(9), N(1)–Mo(1)–P(1) 141.63(9), N(1)–Mo(1)–P(2) 152.15(9), N(1)–Mo(1)–N(3) 82.88(12), N(3)–Mo(1)–S(1) 87.46(9), N(3)–Mo(1)–S(2) 64.85(9), N(3)–Mo(1)–P(1) 100.88(9), N(3)–Mo(1)–P(2) 100.78(9), Mo(1)–P(1)–P(2) 56.91(3), Mo(1)–P(2)–P(1) 57.78(3).



Fig. 3. ORTEP drawing of the molecular structure of $[Mo_2(CO)_6(\mu,\kappa^1-pymS)_2(\mu,\kappa^2-dppm)]$ (7) (left) and the DFT-optimized structure C (right). The thermal ellipsoids in the solid-state structure are at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected crystallographic bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.9959(2), Mo(1)–S(1) 2.4859(5), Mo(1)–S(2) 2.4604(4), Mo(1)–P(1) 2.5543(5), Mo(2)–S(1) 2.4672(5), Mo(2)–S(2) 2.4546(5), Mo(2)–P(2) 2.5659(5), S(1)–Mo(1)–Mo(2) 52.498(11), S(1)–Mo(1)–P(1) 87.636(15), S(2)–Mo(1)–Mo(2) 52.357(11), S(2)–Mo(1)–S(1) 104.665(15), S(2)–Mo(1)–P(1) 88.030(15), P(1)–Mo(1)–Mo(2) 90.210(11), S(1)–Mo(2)–Mo(1) 53.067(11), S(1)–Mo(2)–P(2) 85.742(15), S(2)–Mo(2)–Mo(1) 52.532(11), S(2)–Mo(2)–S(1) 105.406(15), S(2)–Mo(2)–P(2) 90.510(15), P(2)–Mo(2)–Mo(1) 90.726(11), Mo(2)–S(1)–Mo(1) 74.435(13), Mo(2)–S(2)–Mo(1) 75.111(13).



Fig. 4. ORTEP drawing of the molecular structure of $[Mo(CO)_2(\kappa^2-dppm)]$ (9), showing 50% probability thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–S(1) 2.3696(12), Mo(1)–S(2) 2.3639(11), Mo(1)–P(1) Mo(1) - P(2)2.5216(10), 2.5272(10), Mo(1)-C(1)2.041(4), Mo(1)-C(2)2.020(4),S(1)–Mo(1)–P(1) 155.20(4), S(1)-Mo(1)-P(2)89.31(4), S(2)-Mo(1)-S(1)114.53(4), S(2)-Mo(1)-P(1)90.14(4), S(2)-Mo(1)-P(2)156.16(4), P(2)-Mo(1)-P(1)66.07(3), C(1)-Mo(1)-S(1)86.30(14), C(1)-Mo(1)-S(2)94.31(14), C(1)-Mo(1)-P(1)94.68(13), C(1)-Mo(1)-P(2)86.55(13), C(2)–Mo(1)–S(1) 94.04(13), C(2)–Mo(1)–S(2) 86.71(12), C(2)-Mo(1)-P(1) 84.49(13), C(2)-Mo(1)-P(2) 92.18(12), C(2)-Mo(1)-C(1) 178.68(18).

Graphical Abstract

Reactivity of $[Mo(CO)_3(NCMe)_3]$ towards pyrimidine-2-thiol (pymSH) and thiophenol (PhSH) in the presence of phosphine auxiliaries: Synthesis of mono- and dinuclear complexes bearing κ^2 and μ,κ^2 -pymS coordination motifs

Roknuzzaman, S.M. Tareque Abedin, Mohd. Rezaul Haque, Shishir Ghosh, Derek A. Tocher, Michael G. Richmond, Shariff E. Kabir

A number of new mono- and di-molybdenum complexes have been isolated and characterized from the reactions of $[Mo(CO)_3(NCMe)_3]$ with pmySH or PhSH in the presence of a phosphine.

