

REACTIVITY OF $[M_4(CO)_{12}(\mu\text{-pymS})_4]$ (M = Mn, Re; pymS = PYRIMIDINE-2-THIOLATE) WITH BIS(TRIPHENYLPHOSPHINO)NICKEL(II) DICARBONYL: X-RAY CRYSTAL STRUCTURE OF $[Re(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$

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ABSTRACT

The reaction between the tetranuclear compound $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (**1**) and $(PPh_3)_2Ni(CO)_2$ at room temperature resulted in the cleavage of the square to afford the dinuclear complex $[Mn_2(CO)_5(\mu\text{-pymS})_2(PPh_3)]$ (**2**) (19%) along with two mononuclear complexes *fac*- $[Mn(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**3**) (43%) and $[Mn(CO)_2(\kappa^2\text{-pymS})(PPh_3)_2]$ (**4**) (24%). In contrast, a similar reaction of $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (**5**) with $(PPh_3)_2Ni(CO)_2$ at 25°C did not afford any dinuclear compound leading instead to the monophosphine substituted mononuclear compound *fac*- $[Re(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**6**) (72%). Compound **4** is also formed when a toluene solution of **3** is treated with PPh_3 at elevated temperature (100°C). A similar treatment of **6** with triphenylphosphine in refluxing toluene gave $[Re(CO)_2(\kappa^2\text{-pymS})(PPh_3)_2]$ (**7**) (60%). All the new compounds have been characterized by elemental analysis, IR, ¹H NMR and ³¹P{¹H} NMR spectroscopy and mass spectrometry along with single crystal X-ray diffraction analysis for **6**. Compound **6** consists of a single rhenium atom with three carbonyls, a triphenylphosphine ligand and a chelating pyrimidinethiolate ligand.

Key words: Tetranuclear, Dinuclear, Pyrimidine-2-thiolate, Triphenylphosphine, X-ray structure

INTRODUCTION

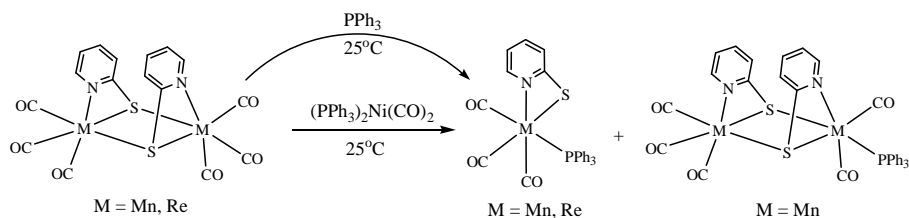
Interest in the chemistry of transition metal complexes containing heterocyclic-thiolate ligands stems from their structural diversity (Ghosh *et al.* 2009, Kitagawa *et al.* 1990, Azam *et al.* 2002, Deeming *et al.* 1988, 1990, 1988, Kabir *et al.* 1996, Brodie *et al.* 1986), biological relevance (Canzoniero *et al.* 2003, Hwu *et al.* 2002, Katiyar *et al.* 2003) and candidacy as precursors for metal-sulfide materials (Berardini *et al.* 1995). Pyridine-2-thiol and pyrimidine-2-thiol are versatile ligands known to exhibit a variety of coordination geometries and mono-, di- and polynuclear metal complexes containing these ligand have been shown to display a range of different structural types (Kabir *et al.*

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2000). The reactions of $M_2(CO)_{10}$ ($M = Re, Mn$) with pySH at $25^\circ C$ in the presence of Me_3NO gave dinuclear pyridine-2-thiolate complexes $[M_2(CO)_6(\mu-pyS)_2]$, while that of with pymSH afforded the tetranuclear pyrimidine-2-thiolato complexes $[Mn_4(CO)_{12}(\mu-pymS)_4]$. These complexes serve as versatile precursors for mononuclear complexes of the general formula $[M(CO)_3(\mu-L)]_n$ ($M = Mn, Re$; $L =$ heterocyclic-thiolate; $n = 2, 4$) (Islam *et al.* 1999, 2000, Ara *et al.* 2003, Kabir *et al.* 2009, Ghosh *et al.* 2009, 2009, 2010, 2010, 2011, 2012, 2009). Treatment of $[M_4(CO)_{12}(\mu-pymS)_4]$ ($M = Re, Mn$) with various mono- and bidentate ligands resulted in breakdown of the square to give mononuclear species within which the coordination geometry of the pyrimidine-2-thiolate ligand varies. The authors have also reported the synthesis of a variety of mixed metal complexes from the reactions of $[M_2(CO)_6(\mu-pyS)_2]$ and $[M_4(CO)_{12}(\mu-pymS)_4]$ ($M = Mn, Re$) with $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(NCMe)_2]$ (Kabir *et al.* 2009, Ghosh *et al.* 2010). Recently, we reported the first example of a PPh_3 substituted derivative of $[Mn(CO)_6(\mu-pyS)]$ from the reaction of $[Mn_2(CO)_6(\mu-pyS)]$ with $(PPh_3)_2Ni(CO)_2$ (Scheme 1) (Rahman *et al.* 2012).



Scheme 1

With this observation in mind we now investigated the reactions of the tetranuclear complexes $[M_4(CO)_{12}(\mu-pymS)_4]$ ($M = Re, Mn$) with $(PPh_3)_2Ni(CO)_2$ in order to synthesize PPh_3 substituted derivatives of these square type complexes without the cleavage of M-S bond.

MATERIALS AND METHODS

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Reagent grade solvents were dried using appropriate drying agents before use. IR spectra were recorded on a Shimadzu FTIR-8101 spectrophotometer. NMR spectra were recorded on a Bruker-DPX 400 instrument and mass spectra were recorded on a Varian Mat 312 mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratories of the Wazed Miah Science Research Centre at Jahangirnagar University. $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $(PPh_3)_2Ni(CO)_2$ were purchased from Strem Chemicals Inc. and used as received. Pyrimidine-2-thiol (pymSH) was purchased from Acros Chemicals Inc. and used as received. The starting complexes $[M_4(CO)_{12}(\mu-pymS)_4]$ ($M = Mn$, **1**; Re , **5**) were prepared according to the literature

procedures (Kabir *et al.* 2009). Preparative thin-layer chromatography was carried out on 1 mm plates prepared from silica gel GF254 (type 60, E. Merck).

Reaction of $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (1) with $(PPh_3)_2Ni(CO)_2$: A dichloromethane solution (20 ml) of **1** (100 mg, 0.101 mmol) and $(PPh_3)_2Ni(CO)_2$ (256 mg, 0.401 mmol) was stirred at room temperature for 5 days during which time the colour of the solution changed from yellow to red. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with dichloromethane/cyclohexane (7 : 3, v/v) developed five bands. The second band gave $[Mn_2(CO)_5(\mu\text{-pymS})_2(PPh_3)]$ (**2**) (14 mg, 19%) as red crystals from hexane/dichloromethane at 4°C. The fourth band gave the previously reported compound *fac*- $[Mn(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**3**) (22 mg, 43%) while the fifth band afforded $[Mn(CO)_2(\kappa^2\text{-pymS})(PPh_3)_2]$ (**4**) (18 mg, 24%) as yellow crystals after recrystallization from hexane/dichloromethane at 4°C. The first and third bands were unreacted $(PPh_3)_2Ni(CO)_2$ (trace) and **1** (trace), respectively. Spectral data for **2**: Anal. Calcd. for $C_{31}H_{21}Mn_2N_4O_5PS_2$: C, 50.69; H, 2.88; N, 7.63. Found: C, 50.96; H, 2.98; N, 7.81%. IR (ν CO, CH_2Cl_2): 2024 vs, 1935 vs, 1859 w cm^{-1} . 1H NMR ($CDCl_3$): δ 8.85 (m, 1H), 8.65 (m, 1H), 8.47 (m, 1H), 7.98 (m, 1H), 7.50 (m, 15H), 6.62 (m, 1H), 6.10 (m, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 87.5 (s). FAB MS: m/z 734 (M^+). Spectral data for **4**: Anal. Calcd. for $C_{42}H_{33}MnN_2O_2P_2S$: C, 67.56; H, 4.45; N, 3.75. Found: C, 67.83; H, 4.62; N, 3.85%. IR (ν CO, CH_2Cl_2): 1926 vs, 1853 vs cm^{-1} . 1H NMR ($CDCl_3$): δ 7.79 (d, $J = 5.8$ Hz, 1H), 7.51 (m, 15H), 7.24 (m, 15H), 7.01 (dd, $J = 5.8, 5.2$ Hz, 1H), 6.50 (d, $J = 5.2$ Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.5 (s). FAB MS: m/z 746 (M^+).

Reaction of $[Mn(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (3) with triphenylphosphine: A toluene solution (20 ml) of **3** (20 mg, 0.039 mmol) and triphenylphosphine (11 mg, 0.039 mmol) was heated at 100°C (bath temp.) for 4 h. The solvent was removed *in vacuo* and the residue chromatographed by TLC on silica gel. Elution with dichloromethane/cyclohexane (7:3, v/v) developed three bands. The third band gave $[Mn(CO)_2(\kappa^2\text{-pymS})(PPh_3)_2]$ (**4**) (13 mg, 60%) as yellow crystals after recrystallization from hexane/dichloromethane at 4°C. The first and second bands were unreacted PPh_3 and **3** (trace), respectively.

Reaction of $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (5) with $(PPh_3)_2Ni(CO)_2$: A dichloromethane solution (20 ml) of $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (**5**) (100 mg, 0.065 mmol) and $(PPh_3)_2Ni(CO)_2$ (168 mg, 0.263 mmol) was stirred at room temperature for 5 days. The solvent was rotary evaporated and the residue chromatographed by TLC on silica gel. Elution with dichloromethane/cyclohexane (7:3, v/v) developed four bands. The third band gave *fac*- $[Re(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**6**) (30 mg, 72%) as yellow crystals from dichloromethane/hexane at 4°C. The first and the second bands were unreacted $(PPh_3)_2Ni(CO)_2$ and **5** (trace), respectively. The fourth band was too small for complete characterization. Spectral data for **6**: Anal. Calcd. for $C_{25}H_{18}ReN_2O_3PS$: C, 46.65; H, 2.82; N, 4.35. Found: C, 46.92; H, 2.98; N, 4.53%. IR (ν CO, CH_2Cl_2): 2024 vs, 1936 vs,

1905 vs cm^{-1} . ^1H NMR (CDCl_3): δ 8.02 (m, 1H), 7.61 (m, 1H), 7.51 (m, 6H), 7.36 (m, 9H), 6.46 (m, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.3 (s). FAB MS: m/z 644 (M^+).

Table 1. Crystallographic data and structure refinement for $[\text{Re}(\text{CO})_3(\kappa^2\text{-pymS})(\text{PPh}_3)]$ (6**).**

Compound	6
Identification code	Sid054
Empirical formula	$\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_3\text{PReS}$
Formula weight	1285.30
Temp (K)	232(2)
Wavelength (\AA)	0.71075
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	9.9844(7)
$b/\text{\AA}$	10.3846(7)
$c/\text{\AA}$	23.1831(16)
$\alpha/^\circ$	90
$\beta/^\circ$	95.614(7)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2392.2(3)
Z	2
D_{calc} (kg m^{-3})	1.784
μ (Mo $K\alpha$) (mm^{-1})	5.262
$F(000)$	1248
Crystal size (mm^3)	0.27 x 0.19 x 0.17
θ range ($^\circ$)	3.03 to 27.48
Index ranges	$-12 \leq h \leq 12$ $-13 \leq k \leq 13$, $-30 \leq l \leq 29$
Reflections collected	24771
Independent reflections (R_{int})	5471 (0.03691)
Max. and min. transmission	0.4682 and 0.3308
Data/restraints/parameters	5471 / 0 / 298
Goodness-of-fit on F^2	0.965
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0225$, $wR_2 = 0.0484$
R indices (all data)	$R_1 = 0.0285$, $wR_2 = 0.0509$
Largest difference in peak and hole (e \AA^{-3})	0.769 and -1.333

*Reaction of fac- $[\text{Re}(\text{CO})_3(\kappa^2\text{-pymS})(\text{PPh}_3)]$ (**6**) with triphenylphosphine:* A toluene solution (20 ml) of **6** (25 mg, 0.065 mmol) and triphenylphosphine (10 mg, 0.263 mmol) was heated to reflux for 23 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/dichloromethane (6:4, v/v) developed three bands. The third band gave $[\text{Re}(\text{CO})_2(\kappa^2\text{-pymS})(\text{PPh}_3)_2]$ (**7**) (20 mg, 60%) as yellow crystals after recrystallization from dichloromethane/hexane at 4°C . The first band was unreacted ligand. The second band was too small for characterization.

Spectral data for **7**: Anal. Calcd. for $C_{42}H_{33}ReN_2O_2P_2S$: C, 57.46; H, 3.79; N, 3.19. Found: C, 57.63; H, 3.95; N, 3.27%. IR (ν_{CO} , CH_2Cl_2): 2027 s, 1923 vs, 1849 vs cm^{-1} . 1H NMR ($CDCl_3$): δ 7.57 (m, 12H), 7.27 (m, 19H), 6.64 (m, 1H), 5.66 (m, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.3 (s). FAB MS: m/z 878 (M^+).

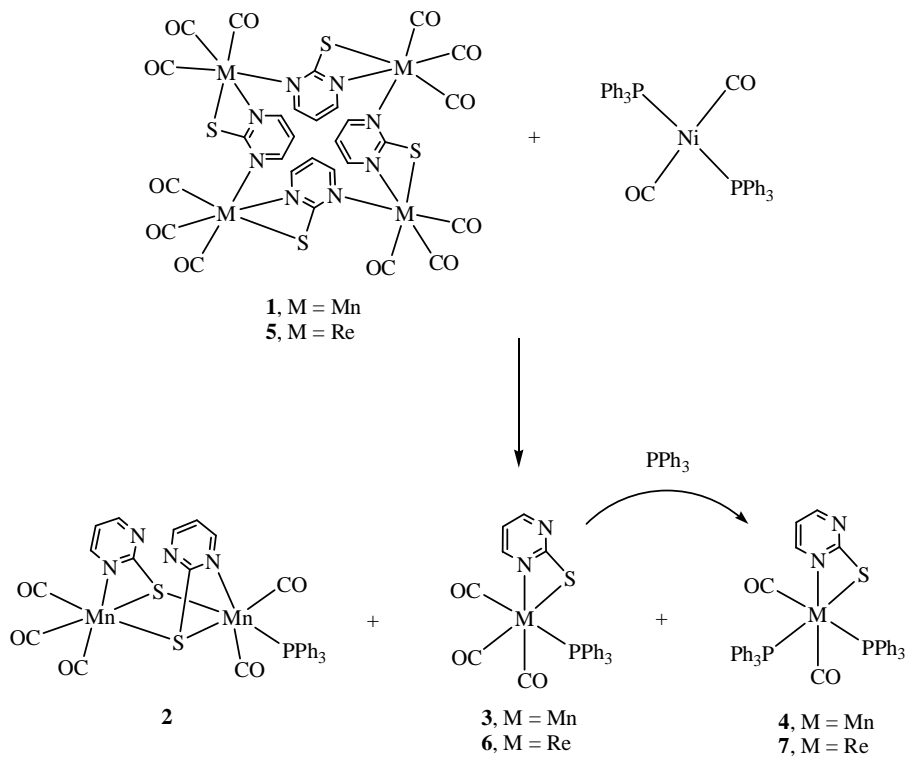
X-ray structure determination: Single crystals of **6** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at 4°C. Crystals were coated with Paraton N oil, suspended in a small MiTeGen loop with apeazon grease and placed in a cooled nitrogen gas stream at 232 K on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data were collected ω scans with 10 s frame exposures in 1° steps. Data collection and processing was carried out using CrystalClear (Rigaku 1999, Pflugrath 1999) software. The final cell parameters were determined from least-squares refinement on 24771 reflections. The structure was solved using the Direct methods and difference Fourier techniques (Sheldrick *et al.* 2008). Hydrogen atoms were placed their expected chemical positions using the HFIX command and were included in the cycles of least-squares with isotropic Uij 's related to the atom's ridden upon. Scattering factors and anomalous dispersion corrections are taken from the International Tables for X-ray crystallography (Wilson *et al.* 1992). The structure was solved by SHELXS97 (Sheldrick *et al.* 2008) and refined using SHELXL97 (Sheldrick *et al.* 2008) within the WINGX program suite (Farrugia 2012).

RESULTS AND DISCUSSIONS

*Reaction of $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (**1**) with $(Ph_3P)_2Ni(CO)_2$: Synthesis of phosphine substituted di- and mononuclear complexes* : In order to examine whether one carbonyl group from the tetranuclear compound $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (**1**) could be replaced by triphenylphosphine, we investigated its reaction with bis(triphenylphosphino)nickel(II) dicarbonyl. Treatment of **1** with bis(triphenylphosphino)nickel(II) dicarbonyl in dichloromethane at room temperature afforded $[Mn_2(CO)_5(\mu\text{-pymS})_2(PPh_3)]$ (**2**) and $[Mn(CO)_2(\kappa^2\text{-pymS})(PPh_3)_2]$ (**4**) along with the previously reported compound *fac*- $[Mn(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**3**) (Rahman *et al.* 2012) in 19, 24 and 43% yields, respectively (Scheme 2). Compound **3** was previously reported from the reaction of **1** with PPh_3 at room temperature. The mononuclear compound **4** is also produced from an equimolar reaction between **3** and PPh_3 in toluene at 100°C.

As the present authors could not obtain single crystals of **2** suitable for X-ray diffraction, it has been characterized by elemental analysis, IR, 1H NMR, $^{31}P\{^1H\}$ NMR and mass spectroscopic data. The dinuclear nature of **2** is apparent from its mass spectrum which shows a molecular ion peak at m/z 734 and fragmentation peaks due to the sequential loss of five carbonyls. The pattern of the IR spectrum of **2** in the carbonyl

region [2024 vs, 1935 vs and 1859 w cm^{-1}] is very similar to that of structurally characterized $[\text{Mn}_2(\text{CO})_5(\mu\text{-pyS})_2(\text{PPh}_3)]$ (Rahman *et al.* 2012) indicating that they are isostructural. The ^1H NMR spectrum of compound **2** in the aromatic region displays discrete resonances centered at δ 8.85, 8.65, 8.47, 7.98, 7.50, 6.62, and 6.10 for the phenyl and pyrimidyl protons of the ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** exhibits a singlet at δ 87.5, assigned to the phosphorus nucleus of the PPh_3 ligand.



Scheme 2

Compound **4** has been characterized by a combination of elemental analysis, IR, ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and mass spectrometry. The infrared spectrum of the compound **4** in the carbonyl stretching region shows two characteristic terminal CO absorption bands at 1926 vs and 1852 vs cm^{-1} which is very similar to that observed for $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\kappa^2\text{-pyS})]$ (Rahman *et al.* 2012). The ^1H NMR spectrum of compound **4** in the aromatic region displays two multiplets centered at δ 7.51 and 7.24 with total integration of 15H, due to the aromatic protons of PPh_3 , two doublets and a doublet of doublets at δ 7.79, 6.50 and 7.01, respectively, attributable to the heterocyclic aromatic protons of the pyrimidine-2-thiolato ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** shows a singlet at δ 23.5 indicating presence of equivalent phosphorus nuclei. In addition, the

mass spectrum exhibits a molecular ion peak at m/z 746 together with the peaks due to sequential loss of two CO groups and a pymS group.

Reaction of $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (5) with $(Ph_3P)_2Ni(CO)_2$: Synthesis of phosphine substituted mononuclear complexes : The synthesis of the dinuclear compound **2** from the reaction of $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (**1**) with $(Ph_3P)_2Ni(CO)_2$ prompted us to investigate the reaction of the latter with **5**. Treatment of **5** with $(Ph_3P)_2Ni(CO)_2$ in dichloromethane at room temperature afforded *fac*- $[Re(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**6**) as orange crystals in 24% yield (Scheme 2), no dinuclear compound produced at all. The new compound **6** has been structurally characterized by IR, 1H NMR, $^{31}P\{^1H\}$ NMR and single crystal X-ray diffraction analysis.

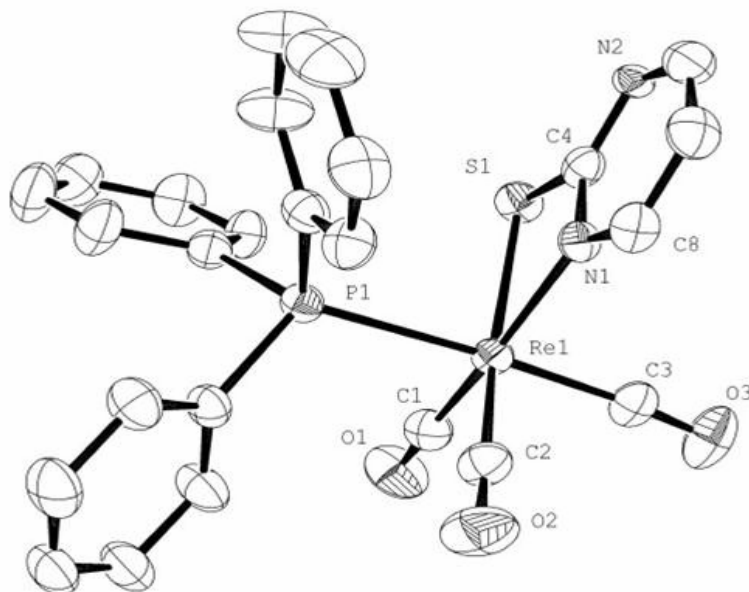


Fig. 1. The solid-state molecular structure of *fac*- $[Re(CO)_3(\kappa^2\text{-pymS})(PPh_3)]$ (**6**), showing 50% probability thermal ellipsoids. Ring hydrogen atoms are omitted for clarity.

The solid-state molecular structure of compound **6** is depicted in Fig. 1, crystal data and structure refinement parameters are given in Table 1 and selected bond distances and angles are collected in Table 2. The molecule consists of a single rhenium atom coordinated by three carbonyls, a PPh_3 ligand and a chelating pyrimidine-thiolate ligand. The coordination geometry around the rhenium atom is a distorted octahedron with three carbonyl groups arranged in a facial fashion. The distortion from octahedral coordination geometry is evident from the short N-Re-S chelate angle $[65.09(7)^\circ]$ created by the heterocyclic ligand which is similar to that observed in the tetrahydropyrimidine-2-thiolato analog *fac*- $[Re(CO)_3(\mu\text{-thpymS})(PPh_3)]$ (thpymS = tetrahydropyrimidine-2-

thiolato) (Ahmed *et al.* 2013). The Re-P, Re-S and Re-N bond distances [Re(1)-P(1) = 2.4876(8), Re(1)-S(1) = 2.5281(8), Re(1)-N(1) = 2.178(2) Å] as well as the overall molecular structure of **6** are very similar to *fac*-[Re(CO)₃(μ-thpymS)(PPh₃)] [Re(1)-P(1) = 2.4826(10), Re(1)-S(1) = 2.5542(10), Re(1)-N(1) = 2.156(3) Å] (Ahmed *et al.* 2013). In comparison with compound **3** the rhenium associated diatomic distances are significantly longer than that of manganese associated diatomic distances. This is due to the larger size of Re atom than Mn atom.

Table 2. Selected bond lengths and bond angles of *fac*-[Re(CO)₃(κ²-pymS)(PPh₃)] (6**).**

Bond lengths [Å]			
Re(1)-C(2)	1.908(3)	Re(1)-P(1)	2.4876(8)
Re(1)-C(1)	1.912(3)	Re(1)-S(1)	2.5281(8)
Re(1)-C(3)	1.946(3)	S(1)-C(4)	1.726(3)
Re(1)-N(1)	2.178(2)	N(1)-C(4)	1.356(4)
Bond angles [°]			
C(2)-Re(1)-C(1)	92.08(14)	N(1)-Re(1)-P(1)	91.03(7)
C(2)-Re(1)-C(3)	90.01(14)	C(1)-Re(1)-S(1)	101.95(10)
C(1)-Re(1)-C(3)	86.45(14)	C(3)-Re(1)-S(1)	91.92(10)
C(2)-Re(1)-N(1)	100.93(12)	N(1)-Re(1)-S(1)	65.09(7)
C(3)-Re(1)-N(1)	91.16(12)	P(1)-Re(1)-S(1)	91.44(3)
C(2)-Re(1)-P(1)	86.92(10)	C(4)-S(1)-Re(1)	80.57(10)
C(1)-Re(1)-P(1)	92.02(10)	N(1)-C(4)-S(1)	111.0(2)

The spectroscopic data of **6** are consistent with the solid-state structure. The infrared spectrum of compound **6** in the carbonyl stretching region shows absorption bands at 2024 vs, 1936 vs and 1905 vs cm⁻¹ indicating that all the carbonyl groups are terminally bonded. The ¹H NMR spectrum of compound **6** in the aromatic region displays five multiplets, three of which centered at δ 8.02, 7.61 and 6.46 (each integrating to 1H) are assigned to the protons of the pyrimidine-2-thiolate ligand while the multiplets centered at δ 7.51 and 7.36 are due to the phenyl protons of the PPh₃ ligand. The ³¹P{¹H} NMR spectrum of compound **6** shows a singlet at δ 21.3 indicating presence of one phosphorus nucleus.

Treatment of **6** with triphenylphosphine in refluxing toluene afforded [Re(CO)₂(κ²-pymS)(PPh₃)₂] (**7**) as yellow crystals in 60% yield (Scheme 2). The infrared spectrum of **7** in the carbonyl stretching region shows absorption bands at 2027 s, 1923 vs and 1849 vs cm⁻¹ indicating that all the carbonyl ligands are terminally coordinated and these values are very similar to those observed for compound **4**. The ¹H NMR spectrum of **7** in the aromatic region displays four multiplets centered at δ 7.57, 7.27, 6.64 and 5.66 with a relative intensity of 12 : 19 : 1 : 1 due to thirty phenyl and three pyrimidine-2-thiolate protons. The ³¹P{¹H} NMR spectrum of **7** shows a singlet at δ 26.3 implying the presence of equivalent phosphorus nuclei.

CONCLUSIONS

Tetrameric square-type pyrimidine-2-thiolate complex $[\text{Mn}_4(\text{CO})_{12}(\mu\text{-pymS})_4]$ (**1**) acts as a useful source of $\text{Mn}_2(\text{CO})_5(\mu\text{-pymS})_2$, $\text{Mn}(\text{CO})_3(\kappa^2\text{-pymS})$ and $\text{Mn}(\text{CO})_2(\kappa^2\text{-pymS})$ fragments, reacting with $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ to afford di- and mononuclear complexes $[\text{Mn}_2(\text{CO})_5(\mu\text{-pymS})_2(\text{PPh}_3)]$ (**2**), $[\text{Mn}(\text{CO})_3(\kappa^2\text{-pymS})(\text{PPh}_3)]$ (**3**) and $[\text{Mn}(\text{CO})_2(\kappa^2\text{-pymS})(\text{PPh}_3)_2]$ (**4**), behavior which partially parallels that reported for $[\text{Mn}_2(\text{CO})_6(\mu\text{-pyS})_2]$. In contrast, compound **5** reacts with $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ to afford $[\text{Re}(\text{CO})_5(\kappa^2\text{-pymS})(\text{PPh}_3)]$ (**6**) as the sole product. Compound **2** provides the first example of a dimeric complex of Gr VII metal carbonyls bearing pyrimidine-2-thiolate ligand. All the compounds of Gr VII metal carbonyls bearing pyrimidine-2-thiolate ligand so far reported are either tetranuclear or mononuclear.

ACKNOWLEDGMENTS

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SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, deposition number: CCDC 978335 for compound **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.ac.uk>).

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