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Selective CO oxidation of heterometallic carbonyl clusters with the oxygen transfer reagent (p-$CH_3OC_6H_4)_2TeO$. Crystal structures of (μ_3-S)FeCoMo$(CO)_7(\eta^5$-$C_5H_4COCH_3)(PPh_3)$ and (μ_3-Se)FeCoMo$(CO)_7(\eta^5$-$C_5H_4COCH_3)(PPh_3)$

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Abstract

The oxygen transfer reaction of the heterometallic carbonyl cluster (μ_3-S)$FeCo_2(CO)_9$ with bis(p-methoxyphenyl)telluroxide (BMPTO) gives bis(p-methoxyphenyl)telluride (BMPT) coordinated metal cluster products (μ_3-S)$FeCo_2(CO)_8$(BMPT) (**1a**) and (μ_3-S)$FeCo_2(CO)_7(BMPT)_2$ (**1b**), which react further with PPh_3 to afford Ph_3P-substituted derivatives (μ_3-S)$FeCo_2(CO)_8(PPh_3)$ (**1c**) and (μ_3-S)$FeCo_2(CO)_7(PPh_3)_2$ (**1d**), respectively. Similarly, the reactions of heterometallic clusters (μ_3-S)FeCoM$(CO)_8(\eta^5$-$C_5H_4R)$ or (μ_3-Se)FeCoM$(CO)_8(\eta^5$-$C_5H_4R)$ with BMPTO afford (μ_3-S)FeCoM$(CO)_7(\eta^5$-$C_5H_4R)$(BMPT) (**2a**, M = Mo, R = H; **2b**, M = Mo, R = $COCH_3$; **2c**, M = Mo, R = CO_2CH_3; **2d**, M = Mo, R = $C(CH_3)NNHC_6H_3(NO_2)_2$-2,4; **2e**, M = W, R = H; **2f**, M = W, R = $COCH_3$) and (μ_3-Se)FeCoM$(CO)_7(\eta^5$-$C_5H_4R)$(BMPT) (**2g**, M = Mo, R = $COCH_3$; **2h**, M = W, R = $C(CH_3)NNHC_6H_3(NO_2)_2$-2,4), whereas **2a**–**2d** and **2g** react with PPh_3 to produce (μ_3-S)FeCoMo$(CO)_7(\eta^5$-$C_5H_4R)(PPh_3)$ (**3a**, R = H; **3b**, R = $COCH_3$; **3c**, R = CO_2CH_3; **3d**, R = $C(CH_3)NNHC_6H_3(NO_2)_2$-2,4) and (μ_3-Se)FeCoMo$(CO)_7(\eta^5$-$C_5H_4COCH_3)(PPh_3)$ (**3e**). The products have been characterized by elemental analyses, IR, ^{1}H-NMR ^{125}Te-NMR and FAB-MS spectroscopies. The X-ray diffraction analyses for **3b** and **3e** have not only confirmed their structures, but also proved such oxygen transfer reactions to be highly selective towards Co atoms in those heterometallic carbonyl cluster substrates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Oxygen transfer reagent; Carbonyl; Heterometallic cluster; Crystal structure

1. Introduction

It is well known that oxygen transfer reactions (OTR) with oxygen transfer reagents, such as Me_3NO, C_6H_5IO and bis(p-methoxyphenyl)telluroxide (BMPTO), are of great interest [1] and have been widely utilized to synthesize various organic, inorganic and organometallic compounds [2,3], as well as biologically relevant substances [4]. In such reactions BMPTO is one of the most commonly used oxygen transfer reagents, particularly for the oxidation of CO ligands in mononuclear and homomultinuclear metal carbonyl complexes [5,6]. However, the oxygen transfer reactions of heteronuclear metal carbonyl complexes with BMPTO, to our knowledge, have not been reported in the literature so far. On the basis of our recent work on the synthetic methodology for mixed-metal carbonyl cluster complexes [7], we initiated a study on oxygen transfer reactions of such clusters with BMPTO to see (i) if the O-atom trasfer from BMPTO to CO ligand (resulting in CO oxidation) is selective with respect to different transition metals; (ii) if the novel (p-$CH_3OC_6H_4)_2$Te(BMPT) (generated in situ from BMPTO) coordinated heterometallic clusters could be synthesized; (iii) if the BMPT ligand in such heterometallic clusters could be easily replaced by PPh_3 ligand with respect to the coexistent CO ligands. Herein we wish to answer these questions by describing the synthesis and characterization of a series of μ_3-S or μ_3-Se heterotrimetallic carbonyl clusters containing

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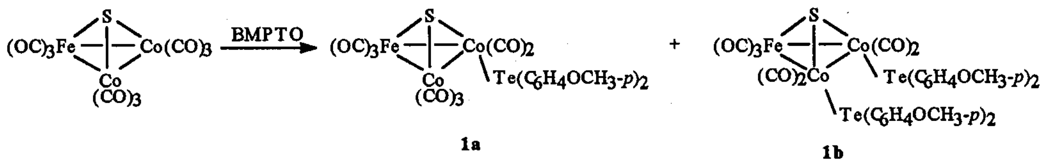
BMPT and PPh_3 ligands, as well as the X-ray crystal structures of (μ_3-S)$FeCoMo(CO)_7(\eta^5-C_5H_4COCH_3)(PPh_3)$ and (μ_3-Se)$FeCoMo(CO)_7(\eta^5-C_5H_4COCH_3)(PPh_3)$.

2. Results and discussion

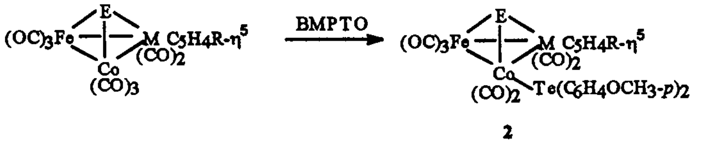
*2.1. Oxygen transfer reactions of metal clusters with BMPTO. Synthesis and characterization of BMPT-coordinated metal clusters **1a**,**b** and **2a**–**2h***

We found that the starting mixed-metal carbonyl cluster (μ_3-S)$FeCo_2(CO)_9$ reacted with BMPTO in 1:1 CH_2Cl_2–CH_3OH at room temperature to give mono-BMPT-coordinated product **1a** and bis-BMPT-coordinated product **1b** (Scheme 1). However, clusters (μ_3-E)$FeCoM(CO)_8(\eta^5-C_5H_4R)$ (E = S, Se; M = Mo, W; R = H, $COCH_3$, CO_2CH_3, $C(CH_3)NNHC_6H_3(NO_2)_2$-2,4) reacted with BMPTO in 1:1 CH_2Cl_2–CH_3OH at room temperature or in toluene at 80°C to give only mono-BMPT-coordinated products **2a**–**2h** (Scheme 2).

Since in these products each of the BMPT ligands is coordinated to a Co atom (vide infra), the CO ligands attached to Co atoms in starting clusters must have much higher reactivity than those attached to Fe, Mo and W atoms in such oxygen transfer reactions, thus making them highly selective towards Co atoms. Although the mechanism for production of **1a**,**b** and **2a**–**2h** has not been studied in detail as yet, a possible pathway, as exemplified by the formation of **2a**–**2h**, is as proposed in Scheme 3, according to the mechanism and kinetics studies on similar reaction systems [5,6]. First, the nucleophilic O atom of BMPTO attacks at the carbon atom of a CO ligand bound to a Co atom. Then, the attacked carbonyl converts to CO_2 to be released from the starting clusters. Finally, the BMPT generated in situ by loss of an oxygen atom from

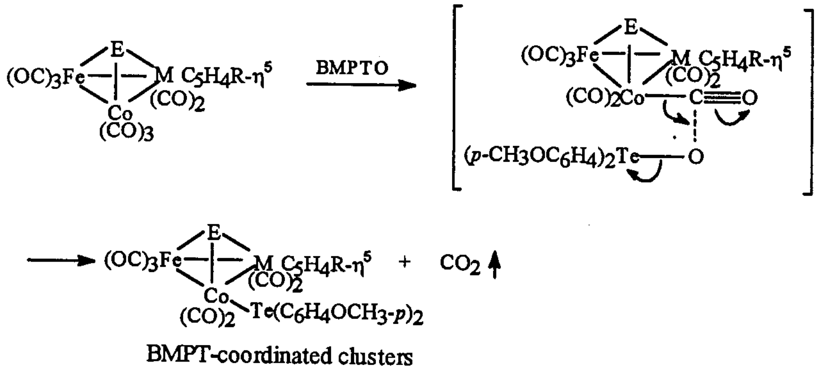


Scheme 1.



	2a	2b	2c	2d	2e	2f	2g	2h
E	S	S	S	S	S	S	Se	Se
M	Mo	Mo	Mo	Mo	W	W	Mo	W
R	H	$COCH_3$	CO_2CH_3	$C(CH_3)NNH$- $C_6H_3(NO_2)_2$-2,4	H	$COCH_3$	$COCH_3$	$C(CH_3)NNH$- $C_6H_3(NO_2)_2$-2,4

Scheme 2.



Scheme 3.

Table 1
^{125}Te-NMR data of BMPT-coordinated metal clusters, BMPT and BMPTO

	δ (ppm) ($CHCl_3$, Me_2Te)
1a	660.5(s)
2a	673.4(s)
2b	657.0(s)
2c	662.0(s)
2d	662.8(s)
2g	663.9(s)
BMPT	631.2(s)
BMPTO	1462.6(s)

BMPTO attacks at the coordinatively unsaturated Co atom to afford BMPT-coordinated clusters **2a**–**2h**.

It is worth noting that the yields of **1a**,**b** and **2a**–**2h** produced from the O-atom transfer reactions could be improved by using excess BMPTO. For example, for the reaction of (μ_3-S)FeCoMo(CO)$_8$(η^5-$C_5H_4COCH_3$) with BMPTO in 1:1 CH_2Cl_2–CH_3OH at room temperature for 4 h, when the molar ratio of starting cluster to BMPTO increased from 1:2 to 1:3, the yield of **2b** increased from 49% to 63%. In addition, the solvent used may influence the yields greatly. For example, when the reaction of (μ_3-Se)FeCoMo(CO)$_8$(η^5-$C_5H_4COCH_3$) with BMPTO in 1:2 molar ratio was carried out in toluene or in 1:1 CH_2Cl_2–CH_3OH at room temperature for 2 h, the yields of **2g** were 21% and 61%, respectively. This influence is obviously due to the better solubility of BMPTO in the mixed 1:1 CH_2Cl_2–CH_3OH solvent.

The BMPT-coordinated products **1a**,**b** and **2a**–**2h** are air stable in solid, but slowly decompose to give free ligand BMPT in solution. These products are new and were characterized by elemental analyses, IR and ^{1}H-NMR spectroscopies; for **1a**, **2a**–**2d**, **2g** ^{125}Te-NMR and for **1a**, **2a**,**b**, **2d** and **2g** FAB-MS spectrometry were also used. For example, in IR spectra, while all the products showed the metal-bonded carbonyl absorption bands [8], products **2b**–**2d** and **2f**–**2h** displayed the corresponding acetyl carbonyl, ester carbonyl and the C=N functionality absorption bands, respectively. In addition, the IR spectra of all the products also showed an absorption band in the finger region, characteristic of the *para*-disubstituted phenyl groups of the BMPT ligands [9]. The ^{1}H-NMR spectra of all these products indicated the presence of BMPT ligand by showing one singlet for the two methoxy groups of BMPT and two singlets, two doublets or two multiplets for the two disubstituted phenyl groups of BMPT. While the five protons for each of the unsubstituted cyclopentadienyls in **2a** and **2e** displayed one singlet, the four protons for each of the substituted cyclopentadienyls in **2b**–**2d** and **2f**–**2h** exhibited two multiplets (for **2c** one broad singlet and one multiplet), the upfield one being assigned to H^3 and H^4 protons and the downfield one being attributed to H^2 and H^5 protons [10,11]. In addition, the ^{1}H-NMR spectra of **2b**–**2d** and **2f**–**2h** showed corresponding signals assignable to their acetyl, methoxycarbonyl and 2,4-$(NO_2)_2C_6H_3NHN(CH_3)C$ substituents.

^{125}Te-NMR spectroscopy has now become an important tool for characterizing tellurium-containing organometallic clusters [12–17]. Table 1 lists the ^{125}Te-NMR spectral data of **1a**, **2a**–**2d** and **2g** along with those of BMPT and BMPTO, which further demonstrate the presence of BMPT ligands in all the products derived from the O-atom transfer reactions. As seen in Table 1 ^{125}Te-NMR signals of the coordinated BMPT in those clusters appear in the range 657–673 ppm, whereas those of the free BMPT ligand and starting material BMPTO appear at 631.2 and 1463.6 ppm, respectively. The ^{125}Te-NMR downfield shift of the coordinated BMPT relative to free BMPT may imply that the μ_3-E bridged metal carbonyl cluster moieties are electron withdrawing. Furthermore, the FAB-MS spectral data of **1a**, **2a**,**b**,**d** and **2g** are given in Table 2, which have been reasonably assigned to their molecular ion peaks and corresponding fragment ion peaks.

*2.2. Substitution of BMPT in metal clusters with PPh_3. Synthesis and characterization of clusters **1c**,**d** and **3a**–**3e***

We found that the ligand BMPT in the above mentioned metal clusters, such as **1a**,**b**, **2a**–**2d** and **2g** could be easily displaced by PPh_3 in CH_2Cl_2 at room temperature to give a series of corresponding PPh_3-substituted clusters **1c**,**d** (Scheme 4) and **3a**–**3e** (Scheme 5) in high yields. Interestingly, such PPh_3-substituted clusters could also be prepared by one pot reaction of the three components (μ_3-S)FeCo$_2$(CO)$_9$ or (μ_3-E)FeCoM(CO)$_8$(η^5-C_5H_4R) (E = S, Se; M = Mo, W), BMPTO and PPh_3. For instance, when a mixture of (μ_3-S)FeCoMo(CO)$_8$(η^5-C_5H_4R) (R = H; CO_2CH_3), BMPTO and PPh_3 in molar ratio 1:1:1 was stirred for 2 h, after work-up, the PPh_3-substituted products **3a** and **3c** were obtained in 84% and 82% yields, respectively. Apparently, this type of one pot reaction involves the BMPT-coordinated clusters (in the above two cases they are **2a** and **2c**) as intermediates generated by O-atom transfer reaction between starting clusters and BMPTO. Then, these intermediates undergo in situ substitution of their BMPT by a stronger ligand PPh_3 to give the PPh_3-substituted clusters. In addition, it is worth noting that although the PPh_3-substituted clusters might be prepared by direct substitution of the CO ligand in starting mixed clusters with PPh_3 [18–20], our one pot reaction method in the presence of BMPTO would have some advantages, such as mild reaction conditions and much higher yields.

Table 2
FAB-MS data of BMPT-coordinated metal clusters

Assignment	m/z [a] (relative intensity)				
	1a	**2a**	**2b**	**2d**	**2g**
$[M]^+$	774 (11.5)	850 (9.5)	892 (3.6)	1072 (12.0)	940 (28.4)
$[M-CO]^+$	746 (7.0)	822 (4.5)	864 (19.4)	1044 (2.0)	912 (1.6)
$[M-2CO]^+$	718 (5.2)	794 (6.4)	836 (12.0)	1016 (2.2)	884 (8.2)
$[M-3CO]^+$	690 (60.0)	766 (12.2)	808 (6.0)	988 (4.6)	856 (14.0)
$[M-4CO]^+$	662 (19.5)	738 (19.0)	780 (23.0)	960 (4.0)	828 (9.0)
$[M-5CO]^+$	634 (34.6)	710 (16.0)	752 (22.0)	932 (12.0)	800 (10.2)
$[M-6CO]^+$	606 (29.4)	682 (25.0)	724 (100.0)	904 (5.0)	772 (14.0)
$[M-7CO]^+$	578 (49.5)	654 (100.0)	696 (56.2)	876 (6.0)	744 (100.0)
$[M-8CO]^+$	550 (62.8)				
$[M-7CO\text{–}CH_3OC_6H_4]^+$	443 (16.8) [b]	547 (14.0)	589 (20.0)	769 (4.8)	637 (15.5)
$[M-7CO\text{–}2CH_3OC_6H_4]^+$	336 (45.4) [c]	440 (31.2)	482 (55.8)	662 (18.0)	530 (35.8)
$[TeFeCoMo]^+$		343 (25.0)		343 (92.5)	343 (52.0)
$[TeC_6H_4OCH_3]^+$	237 (14.8)	237 (23.4)	237 (5.0)	237 (44.4)	237 (28.0)
$[(C_6H_4OCH_3)_2]^+$	214 (100.0)	214 (30.2)		214 (60.8)	214 (18.5)

[a] Calculated according to the most abundant isotopes, such as ^{56}Fe, ^{59}Co, ^{98}Mo, ^{80}Se and ^{130}Te.

[b] $[M-8CO\text{–}CH_3OC_6H_4]^+$.

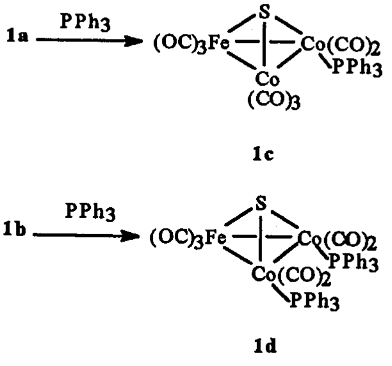
[c] $[M-8CO\text{–}2CH_3OC_6H_4]^+$.

While products **1c**,**d** were previously reported [18], **3a**–**3e** are new and have been characterized by elemental analyses, IR and ^{1}H-NMR spectroscopies. For the new PPh$_3$-substituted derivatives **3a**–**3e** the IR spectra showed several absorption bands for the metal-bonded carbonyls [8], and two absorption bands in the finger regions for the monosubstituted phenyl groups in PPh$_3$ ligand [9]. In addition, while the IR spectra of **3b** and **3e** each displayed an absorption band for the acetyl group, those of **3c** and **3d** each exhibited a corresponding absorption band for its methoxycarbonyl or C=N double bond, respectively. It is worth noting that while the ^{1}H-NMR spectrum of **3a** displayed a singlet for the five protons of its Cp ring, those spectra of **3b**–**3e** displayed two singlets, two doublets, three triplets or two singlets and one doublet for the four protons of the corresponding substituted cyclopentadienyl ring. In fact, ^{1}H-NMR spectra of monosubstituted cyclopentadienyl rings in transition metal complexes vary greatly in complexity, such as a singlet, an A_2B_2 or $A_2B'_2$ pattern or a multiplet pattern, mainly depending on the nature of the substituent and transition metals or metal cluster cores [10,11]. In addition, just like their precursors **2b**–**2d** and **2g**, the ^{1}H-NMR spectra of PPh$_3$-substituted derivatives **3b**–**3e** also displayed corresponding resonance signals for the acetyl, methoxycarbonyl and 2,4-$(NO_2)_2C_6H_3NHN(CH_3)C$ substituents.

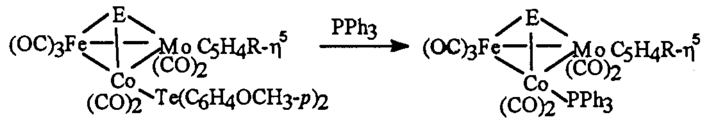
2.3. X-ray structural analyses for **3b** and **3e**

Although the structures of the BMPT-coordinated clusters derived from O-atom transfer reactions could not be directly confirmed by X-ray diffraction analyses due to their easy decomposition in solution and thus lack of suitable single crystals, those of PPh$_3$-substituted clusters derived from the BMPT-coordinated clusters were directly confirmed by X-ray diffraction analyses of the single crystals of **3b** and **3e** and therefore gave evidence for the structures of those corresponding BMPT-coordinated clusters. The ORTEP plots of **3b** and **3e** are presented in Figs. 1 and 2; Table 3 lists selected bond lengths and bond angles.

As seen in Figs. 1 and 2, **3a** and **3e** are all composed of a tetrahedral (μ_3-E)FeCoMo (E = S for **3b**; E = Se for **3e**) cluster core, that carries one acetylcyclopentadienyl and two carbonyls bonded to Mo atom, three carbonyls bound to Fe atom and two carbonyls and one PPh$_3$ attached to Co atom. Obviously, since the PPh$_3$ ligand in **3b** and **3e** is coordinated to the Co atom, the replaced BMPT ligand is originally bonded to this Co atom and the CO oxidation is highly selective in the O-atom transfer reactions described above. In **3b**, among the seven carbonyls attached to metals, two carbonyls attached to the Mo atom, i.e. C(1)O(1) and



Scheme 4.



2a-d, 2g **3**

	3a	3b	3c	3d	3e
E	S	S	S	S	Se
R	H	$COCH_3$	CO_2CH_3	$C(CH_3)NNH-C_6H_3(NO_2)_2$-2,4	$COCH_3$

Scheme 5.

C(2)O(2) are semibridging and the others terminal. For the semibridging carbonyls, the asymmetry parameter α [21,22] is 0.49 for C(1)O(1) and 0.38 for C(2)O(2). Since the bond angles of C(1)–Mo(1)–Co(1) and C(2)–Mo(1)–Fe(1) are 75.71(9)° and 66.31(8)°, the carbonyl C(1)O(1) is bridged across the Mo(1)–Co(1) bond, whereas C(2)O(2) is bridged across the Mo(1)–Fe(1) bond, respectively. Another asymmetry factor θ, i.e. the bond angle of semibridging carbonyl to its bonded metal [21], is 174.5(3)° for C(1)O(1) and 168.7(3)° for C(2)O(2). The cyclopentadienyl ring is tilted to the triangular plane S(1)–Co(1)–Fe(1) and gives a dihedral angle of 45.71(9)°. The Mo–Cp ring centroid distance is 1.9961(12) Å. Since the dihedral angle between the cyclopentadienyl ring and the plane C(9)–C(8)–O(8) is rather small, 7.27(49)°, the π-system of the acetyl group would be quite well conjugated with the Cp ring π-system and thus the bond lengths of C(11)–C(8) (1.488(4) Å) and C(8)–C(9) (1.508(5) Å) become much shorter than a normal C–C single bond.

Similarly, in **3e** those two carbonyls attached to the Mo atom, i.e. C(1)O(1) ($\alpha = 0.39$, $\theta = 171.1(10)°$) and C(7)O(7) ($\alpha = 0.50$, $\theta = 173.5(10)°$) are semibridging and the other five carbonyls are terminal. While the dihedral angle between the cyclopentadienyl ring and triangular plane Se(1)–Co(1)–Fe(1) is 42.66(34)°, a value slightly less than the corresponding value in **3b**, the distance from Mo to Cp ring centroid (2.0138 Å) in **3e** is almost the same as that in **3b**. In addition, the π-system of the acetyl group is also well conjugated with the cyclopentadienyl ring π-system, since the dihedral angle between the plane C(8)–O(8)–C(9) and Cp ring is quite small (6.96°). The bond lengths of C(11)–C(8) (1.494(16) Å) and C(8)–C(9) (1.474(17) Å) are both shorter than a normal C–C single bond, reflecting this conjugation.

The bond lengths in cluster cores of **3b** and **3e** are given in Table 4, which are comparable with those of reported similar clusters [23,24]. In addition, the P–Co bond lengths of **3b** (2.214(7) Å) and **3e** (2.223(3) Å) are also comparable with those of the reported clusters $(\eta^5\text{-}C_5H_5)MoFeCo(CO)_7(MePrPhP)(\mu_3\text{-}S)$ (2.240(3) Å) [23], $(\eta^5\text{-}C_5H_5)WFeCo(CO)_7(MePrPhP)(\mu_3\text{-}S)$ (2.212(4) Å) [23], and $(\eta^5\text{-}C_5H_4COCH_3)MoFeCo(CO)_6(Ph_2PCH_2CH_2PPh_2)(\mu_3\text{-}S)$ (2.196(2) Å) [24].

3. Experimental

All reactions were carried out under prepurified nitrogen atmosphere using standard Schlenk or vacuum-line techniques. Toluene was dried and deoxygenated by distillation from sodium–benzophenone ketyl, CH_2Cl_2 from P_2O_5 and CH_3OH from Mg/I_2. All solvents were bubbled with N_2 prior to use. Column chromatography and preparative TLC were carried out using silica gel of 300–400 mesh and silica gel G of 10–40 μm, respectively. PPh_3 was purchased from Stream Chemicals Inc. $(\mu_3\text{-}S)FeCo_2(CO)_9$ [25], BMPTO [26], $(\mu_3\text{-}S)FeCoMo(CO)_8(\eta^5\text{-}C_5H_4R)$ ($R = H$ [27], $COCH_3$ [28], CO_2CH_3 [7b], 2,4-$(NO_2)_2C_6H_3NHN(CH_3)C$ [7e]), $(\mu_3\text{-}S)FeCoW(CO)_8(\eta^5\text{-}$

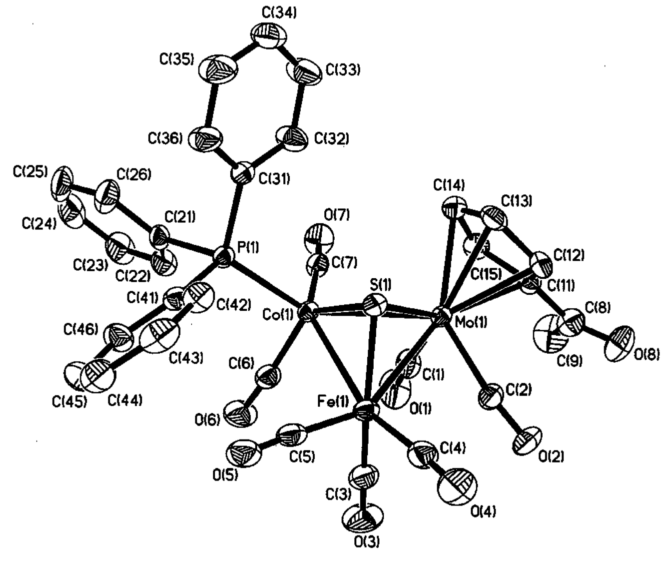


Fig. 1. Molecular structure of **3b** with atom-labeling scheme.

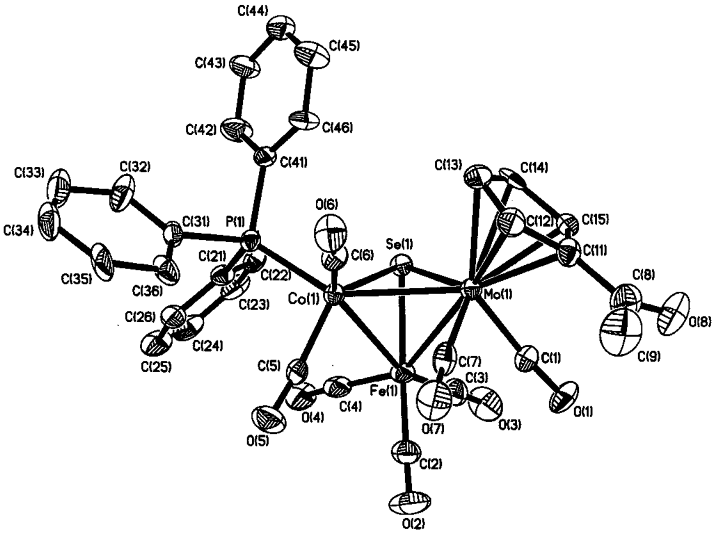


Fig. 2. Molecular structure of **3e** with atom-labeling scheme.

C_5H_4R) (R = H [7h], $COCH_3$ [7b]) and (μ_3-Se)$FeCoM(CO)_8(\eta^5\text{-}C_5H_4R)$ (M = Mo, R = $COCH_3$ [7f]; M = W, R = $2,4\text{-}(NO_2)_2C_6H_3NHN(CH_3)C$ [7g]) were prepared according to the literature. IR spectra were recorded on a Nicolet FT-IR 170SX IR spectrophotometer; ^{1}H- and ^{125}Te-NMR spectra were recorded on a Bruker AC-P200 or Bruker AC-400 NMR spectrometer. ^{125}Te-NMR spectra were referenced to Me_2Te (δ_0). Elemental analyses and FAB-MS determinations were performed on a Yanaco CHN Corder MT-3 analyzer and a Zabspec spectrometer, respectively. Melting points were determined on a Yanaco MP-500 micromelting point apparatus.

*3.1. Preparation of (μ_3-S)$FeCo_2(CO)_8$(BMPT) (**1a**) and (μ_3-S)$FeCo_2(CO)_7(BMPT)_2$ (**1b**)*

A 100 ml two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with 0.150 g (0.33 mmol) of (μ_3-S)$FeCo_2(CO)_9$, 0.120 g (0.33 mmol) of BMPTO, and 40 ml of 1:1 CH_2Cl_2–MeOH. The mixture was stirred at room temperature for 4 h, and then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the extracts were subjected to TLC separation using 1:1 CH_2Cl_2–petroleum ether as eluent. Three bands were developed. The first red band was starting cluster (μ_3-S)$FeCo_2(CO)_9$. The second green band gave 0.103 g (51%) of **1a** as a black syrup. Anal. Found: C, 34.35; H, 2.03. Calc. for $C_{22}H_{14}Co_2FeO_{10}STe$: C, 34.24; H, 1.83%. IR (KBr disk): terminal $C{\equiv}O$ 2077vs, 2025vs, 1981s, 1956s; $\nu_{\text{phenylene}}$ 822m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.81 (s, 6H, $2CH_3$), 6.89, 7.50 (broad s, s, 8H, $2C_6H_4$). The third green band gave 0.063 g (22%) of **1b** as a black powder, m.p. 46–47°C. Anal. Found: C, 38.66; H, 2.52. Calc. for $C_{35}H_{28}Co_2FeO_{11}STe_2$: C, 38.72; H, 2.60%. IR (KBr disk): terminal $C{\equiv}O$ 2044vs, 1991vs, 1930s, 1900s; $\nu_{\text{phenylene}}$ 821m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.79 (s, 12H, $4CH_3$), 6.84, 7.49 (d, d, 16H, $4C_6H_4$).

*3.2. Preparation of (μ_3-S)$FeCoMo(CO)_7$(BMPT)(η^5-C_5H_5) (**2a**)*

Similarly, from 0.460 g (0.82 mmol) of (μ_3-S)-$FeCoMo(CO)_8(\eta^5\text{-}C_5H_5)$, 0.310 g (0.86 mmol) of BMPTO and 40 ml of 1:1 CH_2Cl_2–MeOH, 0.463 g (63%) of **2a** was obtained as a black powder, m.p. 65–66°C. Anal. Found: C, 36.74; H, 2.29. Calc. for $C_{26}H_{19}O_9CoFeMoSTe$: C, 36.92; H, 2.26%. IR (KBr disk): terminal $C{\equiv}O$ 2071s, 2040vs, 1987vs, 1950s, 1860s; $\nu_{\text{phenylene}}$ 820m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.80 (s, 6H, $2CH_3$), 5.38 (s, 5H, C_5H_5), 6.76–6.86, 7.41–7.58 (m, m, 8H, $2C_6H_4$).

*3.3. Preparation of (μ_3-S)$FeCoMo(CO)_7$(BMPT)(η^5-$C_5H_4COCH_3$) (**2b**)*

Similarly, from 0.230 g (0.40 mmol) of (μ_3-S)-$FeCoMo(CO)_8(\eta^5\text{-}C_5H_4COCH_3)$, 0.287 g (0.80 mmol) of BMPTO and 40 ml of 1:1 CH_2Cl_2–CH_3OH, 0.173 g (49%) of **2b** was obtained. However, when using 0.100 g (0.17 mmol) of (μ_3-S)$FeCoMo(CO)_8(\eta^5\text{-}C_5H_4COCH_3)$ and 0.200 g (0.56 mmol) of BMPTO, 0.097 g (63%) of **2b** was obtained as a black powder, m.p. 44–45°C. Anal. Found: C, 37.58; H, 2.24. Calc. for $C_{28}H_{21}CoFeMoO_{10}STe$: C, 37.88; H, 2.38%. IR (KBr disk): terminal $C{\equiv}O$ 2041s, 1991vs, 1967vs, 1839s; acetyl carbonyl $C{=}O$ 1680s; $\nu_{\text{phenylene}}$ 819m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.28 (s, 3H, $COCH_3$), 3.76 (s, 6H, $2CH_3$), 5.20–5.48 (m, 2H, H^3/H^4), 5.76–5.96 (m, 2H, H^2/H^5), 6.68–6.96, 7.28–7.60 (m, m, 8H, $2C_6H_4$).

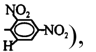
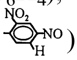
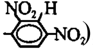
Table 3
Selected bond lengths (Å) and angles (°) for **3b** and **3e**

Complex **3b**			
Mo(1)–S(1)	2.3709(6)	Co(1)–P(1)	2.2148(7)
Co(1)–Fe(1)	2.5997(5)	Mo(1)–Co(1)	2.7397(4)
Fe(1)–S(1)	2.1821(7)	Mo(1)–Fe(1)	2.8184(4)
P(1)–C(21)	1.842(3)	Co(1)–S(1)	2.1874(7)
S(1)–Mo(1)–Co(1)	50.047(16)	Fe(1)–Co(1)–Mo(1)	63.658(12)
S(1)–Mo(1)–Fe(1)	48.799(17)	Co(1)–Fe(1)–Mo(1)	60.591(11)
Co(1)–Mo(1)–Fe(1)	55.751(11)	Fe(1)–S(1)–Co(1)	73.02(2)
S(1)–Co(1)–Fe(1)	53.397(19)	Fe(1)–S(1)–Mo(1)	76.36(2)
P(1)–Co(1)–Fe(1)	120.96(2)	Co(1)–S(1)–Mo(1)	73.76(2)
S(1)–Co(1)–Mo(1)	56.188(18)	S(1)–Fe(1)–Mo(1)	54.836(18)
Complex **3e**			
Mo(1)–Se(1)	2.5024(16)	Se(1)–Co(1)	2.3107(16)
Mo(1)–Co(1)	2.7767(17)	Co(1)–P(1)	2.223(3)
Mo(1)–Fe(1)	2.8493(18)	Co(1)–Fe(1)	2.629(2)
Se(1)–Fe(1)	2.3091(19)	P(1)–C(21)	1.829(10)
Se(1)–Mo(1)–Co(1)	51.60(4)	P(1)–Co(1)–Mo(1)	143.14(9)
Se(1)–Mo(1)–Fe(1)	50.62(5)	Se(1)–Co(1)–Mo(1)	58.07(5)
Co(1)–Mo(1)–Fe(1)	55.69(5)	Fe(1)–Co(1)–Mo(1)	63.56(5)
Fe(1)–Se(1)–Co(1)	69.36(6)	Se(1)–Fe(1)–Co(1)	55.35(5)
Fe(1)–Se(1)–Mo(1)	72.50(5)	Se(1)–Fe(1)–Mo(1)	56.89(5)
Co(1)–Se(1)–Mo(1)	70.34(5)	Co(1)–Fe(1)–Mo(1)	60.76(5)

*3.4. Preparation of (μ_3-S)FeCoMo(CO)$_7$(BMPT)(η^5-$C_5H_4CO_2CH_3$) (**2c**)*

Similarly, from 0.380 g (0.64 mmol) of (μ_3-S)FeCoMo(CO)$_8$(η^5-$C_5H_4CO_2CH_3$), 0.345 g (0.96 mmol) of BMPTO and 40 ml of 1:1 CH_2Cl_2–CH_3OH, 0.299 g (51%) of **2c** was obtained as a black powder, m.p. 42–43°C. Anal. Found: C, 37.02; H, 2.24. Calc. for $C_{28}H_{21}CoFeMoO_{11}STe$: C, 37.21; H, 2.34%. IR (KBr disk): terminal C≡O 2075s, 2044vs, 1993vs, 1955vs, 1880s; ester carbonyl C=O 1722s; $\nu_{phenylene}$ 821m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.76 (s, 3H, CO_2CH_3), 3.81 (s, 6H, $2CH_3O$), 5.35–5.60 (m, 2H, H^3/H^4), 5.96 (broad s, 2H, H^2/H^5), 6.80–6.93, 7.45–7.61 (m, m, 8H, $2C_6H_4$).

*3.5. Preparation of (μ_3-S)FeCoMo(CO)$_7$-(BMPT)(η^5-$C_5H_4C(CH_3)NNHC_6H_3(NO_2)_2$-2,4) (**2d**)*

Similarly, from 0.260 g (0.34 mmol) of (μ_3-S)-FeCoMo(CO)$_8$(η^5-$C_5H_4C(CH_3)NNHC_6H_3(NO_2)_2$-2,4), 0.248 g (0.69 mmol) of BMPTO and 15 ml of 1:1 CH_2Cl_2–CH_3OH, 0.176 g (49%) of **2d** was obtained as a black powder, m.p. 82–83°C. Anal. Found: C, 38.13; H, 2.62; N, 5.40. Calc. for $C_{34}H_{25}CoFeMoN_4O_{13}STe$: C, 38.24; H, 2.36; N, 5.25%. IR (KBr disk): terminal C≡O 2072s, 2042vs, 1993vs, 1950vs, 1880s; $\nu_{C=N}$ 1616s; $\nu_{phenylene}$ 823m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.31, 2.42 (s, s, 3H, CH_3), 3.77, 3.80 (s, s, 6H, $2CH_3O$), 5.80–5.95 (m, 2H, H^3/H^4), 6.20–6.50 (m, 2H, H^2/H^5), 6.83–7.05, 7.55–7.70 (m, m, 8H, $2C_6H_4$), 8.05–8.10 (m, 1H, ), 8.25–8.30 (m, 1H, ), 8.90–8.95 (m, 1H, ), 11.26(broad s, 1H, NH).

*3.6. Preparation of (μ_3-S)FeCoW(CO)$_7$(BMPT)(η^5-C_5H_5) (**2e**)*

Similarly, when 0.198 g (0.32 mmol) of (μ_3-S)FeCoW(CO)$_8$(η^5-C_5H_5), 0.125 g (0.35 mmol) of BMPTO and 15 ml of toluene were stirred at 80°C for 1.5 h, 0.060 g (21%) of **2e** was obtained as a black powder, m.p. 49–51°C. Anal. Found: C, 33.07; H, 1.96. Calc. for $C_{26}H_{19}CoFeO_9STeW$: C, 33.45; H, 2.05%. IR (KBr disk): terminal C≡O 2039vs, 1986vs, 1959vs, 1870s; $\nu_{phenylene}$ 820m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.74 (s, 6H, $2CH_3$), 5.24 (s, 5H, Cp), 6.60–6.76, 7.28–7.60 (m, m, 8H, $2C_6H_4$).

*3.7. Preparation of (μ_3-S)FeCoW(CO)$_7$(BMPT)-(η^5-$C_5H_4COCH_3$) (**2f**)*

Similarly, from 0.218 g (0.33 mmol) of (μ_3-S)-FeCoW(CO)$_8$(η^5-$C_5H_4COCH_3$), 0.125 g (0.35 mmol) of BMPTO and 20 ml of toluene, 0.110 g (35%) of **2f** was obtained as a black powder, m.p. 40–41°C. Anal. Found: C, 34.32; H, 1.92. Calc. for $C_{28}H_{21}CoFeO_{10}STeW$: C, 34.47; H, 2.17%. IR (KBr disk): terminal C≡O 2043vs, 1993vs, 1967vs, 1873s; acetyl carbonyl C=O 1686s; $\nu_{phenylene}$ 823m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.30 (s, 3H, $COCH_3$), 3.75 (s, 6H, $2CH_3O$), 5.24–5.60 (m, 2H, H^3/H^4), 5.72–5.92 (m, 2H, H^2/H^5), 6.60–6.92, 7.20–7.60 (m, m, 8H, $2C_6H_4$).

Table 4
Comparison of the bond lengths (Å) of **3b** and **3e** with those of similar clusters

Cluster	Mo–Fe	Mo–Co	Fe–Co	Mo–S	Fe–S	Co–S	Reference
CpMoFeCo(CO)$_7$L(μ_3-S) [a]	2.793(2)	2.750(2)	2.568(2)	2.363(2)	2.182(3)	2.170(3)	[23]
Cp*MoFeCo(CO)$_6$L(μ_3-S) [b]	2.807(1)	2.743(1)	2.608(2)	2.372(2)	2.187(3)	2.197(3)	[24]
3b	2.8184(4)	2.7397(4)	2.5977(5)	2.3709(6)	2.1821(7)	2.1874(7)	
3e	2.8493(18)	2.7767(17)	2.629(2)				

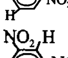
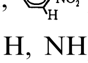
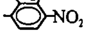
[a] Cp = η^5-C_5H_5, L = MePrPhP.

[b] Cp* = η^5-$C_5H_4COCH_3$, L = $Ph_2PCH_2CH_2PPh_2$.

3.8. Preparation of $(\mu_3\text{-Se})FeCoMo(CO)_7(BMPT)(\eta^5\text{-}C_5H_4COCH_3)$ (**2g**)

Similarly, from 0.331 g (0.54 mmol) of (μ_3-Se)FeCoMo(CO)$_8$(η^5-C$_5$H$_4$COCH$_3$), 0.378 g (1.1 mmol) of BMPTO and 15 ml of 1:1 CH$_2$Cl$_2$–CH$_3$OH, 0.300 g (61%) of **2g** was obtained as a black powder, m.p. 34–36°C. Anal. Found: C, 35.99; H, 2.27. Calc. for $C_{28}H_{21}CoFeMoO_{10}SeTe$: C, 35.98; H, 2.26%. IR (KBr disk): terminal C≡O 2041vs, 1991vs, 1959vs, 1877s; acetyl carbonyl C=O 1680m; $\nu_{\text{phenylene}}$ 819m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.40 (s, 3H, COCH$_3$), 3.86 (s, 6H, 2CH$_3$O), 5.16–5.60 (m, 2H, H^3/H^4), 5.76–5.96 (m, 2H, H^2/H^5), 6.68–7.08, 7.32–7.88 (m, m, 8H, 2C$_6$H$_4$).

3.9. Preparation of $(\mu_3\text{-Se})FeCoW(CO)_7(BMPT)$-$(\eta^5\text{-}C_5H_4C(CH_3)NNHC_6H_3(NO_2)_2\text{-}2,4)$ (**2h**)

Similarly, from 0.105 g (0.12 mmol) of (μ_3-Se)-FeCoW(CO)$_8$(η^5 - C$_5$H$_4$C(CH$_3$)NNHC$_6$H$_3$(NO$_2$)$_2$ - 2,4), 0.045 g (0.13 mmol) of BMPTO and 15 ml of toluene, 0.045 g (31%) of **2h** was obtained as a black powder, m.p. 43–45°C. Anal. Found: C, 34.21; H, 2.51, N, 4.60. Calc. for $C_{34}H_{25}CoFeN_4O_{13}SeTeW$: C, 33.95; H, 2.10; N, 4.66%. IR (KBr disk): terminal C≡O 2035s, 1986s, 1960s; $\nu_{C=N}$ 1616m; $\nu_{\text{phenylene}}$ 823m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.20, 2.32 (s, s, 3H, CH$_3$), 3.76, 3.78 (s, s, 6H, 2CH$_3$O), 5.35–5.70 (m, 2H, H^3/H^4), 5.75–6.01 (m, 2H, H^2/H^5), 6.70–7.00, 7.30–7.60 (m, m, 8H, 2C$_6$H$_4$), 7.80–8.00 (m, 1H, ), 8.25–8.40 (m, 1H, ), 9.20 (broad s, 1H, ), 11.25 (broad s, 1H, NH).

3.10. Preparation of $(\mu_3\text{-S})FeCo_2(CO)_8(PPh_3)$ (**1c**)

A 100 ml two-necked flask equipped with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with 0.168 g (0.22 mmol) of **1a**, 0.054 g (0.21 mmol) of PPh$_3$ and 40 ml of CH$_2$Cl$_2$. The mixture was stirred at room temperature for 3 h and then the solvent was removed under reduced pressure. The residue was extracted with CH$_2$Cl$_2$ and the extracts were subjected to TLC separation using 1:1 CH$_2$Cl$_2$–petroleum ether as eluent. 0.134 g (89%) of **1c** was obtained as a black powder, m.p. 126–128°C. Anal. Found: C, 44.85; H, 2.20. Calc. for $C_{26}H_{15}Co_2FeO_8PS$: C, 45.12; H, 2.18%. IR (KBr disk): terminal C≡O 2078vs, 2013vs, 1968vs, 1945vs; ν_{phenyl} 692s, 747m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.43 (broad s, 15H, 3C$_6$H$_5$).

3.11. Preparation of $(\mu_3\text{-S})FeCo_2(CO)_7(PPh_3)_2$ (**1d**)

Similarly, from 0.041 g (0.038 mmol) of **1b**, 0.018 g (0.069 mmol) of PPh$_3$ and 30 ml of CH$_2$Cl$_2$, 0.029 g (83%) of **1d** was obtained as a black powder, m.p. 125–126°C. Anal. Found: C, 55.34; H, 3.16. Calc. for $C_{43}H_{30}Co_2FeO_7P_2S$: C, 55.75; H, 3.26‘%. IR (KBr disk): terminal C≡O 2046vs, 2013vs, 1984vs, 1945vs; ν_{phenyl} 695s, 745m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.41 (broad s, 30H, 6C$_6$H$_5$).

3.12. Preparation of $(\mu_3\text{-S})FeCoMo(CO)_7(PPh_3)(\eta^5\text{-}C_5H_5)$ (**3a**)

Similarly, from 0.152 g (0.18 mmol) of **2a**, 0.050 g (0.19 mmol) of PPh$_3$ and 30 ml of CH$_2$Cl$_2$, 0.124 g (90%) of **3a** was obtained as a black powder, m.p. 130°C dec. Anal. Found: C, 47.04; H, 2.63. Calc. for $C_{30}H_{20}CoFeMoO_7PS$: C, 47.03; H, 2.63%. IR (KBr disk): terminal C≡O 2042vs, 1977vs, 1953vs, 1916s, 1896s; ν_{phenyl} 695m, 747m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 5.26 (s, 5H, C$_5$H$_5$), 7.39–7.47 (m, 15H, 3C$_6$H$_5$).

3.13. Preparation of $(\mu_3\text{-S})FeCoMo(CO)_7(PPh_3)(\eta^5\text{-}C_5H_4COCH_3)$ (**3b**)

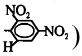
Similarly, from 0.070 g (0.08 mmol) of **2b**, 0.030 g (0.11 mmol) of PPh$_3$ and 20 ml of CH$_2$Cl$_2$, 0.054 g (85%) of **3b** was obtained as a black powder, m.p. 156–158°C. Anal. Found: C, 47.94; H, 2.67. Calc. for $C_{32}H_{22}CoFeMoO_8PS$: C, 47.56, H, 2.74%. IR (KBr disk): terminal C≡O 2049vs, 2002s, 1983vs, 1975vs, 1952vs, 1933s, 1916vs, 1888s; acetyl carbonyl C=O 1683s; ν_{phenyl} 694m, 745m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.30 (s, 3H, CH$_3$), 5.27 (s, 2H, H^3/H^4), 5.78 (s, 2H, H^2/H^5), 7.40 (broad s, 15H, 3C$_6$H$_5$).

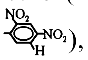
3.14. Preparation of $(\mu_3\text{-S})FeCoMo(CO)_7(PPh_3)(\eta^5\text{-}C_5H_4CO_2CH_3)$ (**3c**)

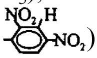
Similarly, from 0.163 g (0.18 mmol) of **2c**, 0.050 g (0.19 mmol) of PPh$_3$ and 30 ml of CH$_2$Cl$_2$, 0.131 g (88%) of **3c** was obtained as a black powder, m.p. 149–150°C. Anal. Found: C, 46.55; H, 2.76. Calc. for $C_{32}H_{22}CoFeMoO_9PS$: C, 46.63; H, 2.69%. IR (KBr disk): terminal C≡O 2037vs, 1989vs, 1969vs, 1948s, 1858s; ester carbonyl C=O 1727s; ν_{phenyl} 695m, 752m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.78 (s, 3H, CH$_3$), 5.18, 5.38 (t, t, 2H, H^3/ H^4), 5.86 (t, 2H, H^2/H^5), 7.40–7.46(m, 15H, 3C$_6$H$_5$).

3.15. Preparation of $(\mu_3\text{-S})FeCoMo(CO)_7(PPh_3)$-$(\eta^5\text{-}C_5H_4C(CH_3)NNHC_6H_3(NO_2)_2\text{-}2,4)$ (**3d**)

Similarly, from 0.060 g (0.056 mmol) of **2d**, 0.018 g (0.069 mmol) of PPh$_3$ and 20 ml of CH$_2$Cl$_2$, 0.034 g (61%) of **3d** was obtained as a black powder, m.p. 69–70°C. Anal. Found: C, 46.47; H, 2.58; N, 5.61. Calc. for $C_{38}H_{26}CoFeMoN_4O_{11}PS$: C, 46.17; H, 2.65;

N, 5.67%. IR (KBr disk): terminal C≡O 2045vs, 1988vs, 1974vs, 1936s, 1840s; $\nu_{C=N}$ 1615s; ν_{phenyl} 693m, 743m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.15 (s, 3H, CH$_3$), 5.36 (d, 2H, H^3/H^4), 5.80 (d, 2H, H^2/H^5), 7.39–7.48 (m, 15H, 3C$_6$H$_5$), 7.90 (d, 1H, 

), 8.26(d, 1H, 

), 9.12(d, 1H, 

), 11.19 (broad s, 1H, NH).

3.16. Preparation of (μ$_3$-Se)FeCoMo(CO)$_7$(PPh$_3$)(η^5-C$_5$H$_4$COCH$_3$) (3e)

Similarly, from 0.152 g (0.16 mmol) of **2g**, 0.043 g (0.16 mmol) of PPh$_3$ and 30 ml of CH$_2$Cl$_2$, 0.127 g (91%) of **3e** was obtained as a black powder, m.p. 159–160°C. Anal. Found: C, 45.03; H, 2.58. Calc. for C$_{32}$H$_{22}$CoFeMoO$_8$PSe: C, 44.94; H, 2.59%. IR (KBr disk): terminal C≡O 2047vs, 2001s, 1981vs, 1973vs, 1948vs, 1929s, 1911vs, 1888s; acetyl carbonyl C=O 1683s; ν_{phenyl} 693m, 744m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.33 (s, 3H, CH$_3$), 5.22, 5.38 (s, s, 2H, H^3/H^4), 5.72 (d, 2H, H^2/H^5), 7.39–7.49 (m, 15H, 3C$_6$H$_5$).

3.17. Preparation of 3a and 3c via one pot reaction of three components

A 100 ml two-necked flask equipped as described above was charged with 0.096 g (0.18 mmol) of (μ$_3$-S)FeCoMo(CO)$_8$(η^5-C$_5$H$_5$), 0.065 g (0.18 mmol) of BMPTO, 0.047 g (0.18 mmol) of PPh$_3$ and 15 ml of CH$_2$Cl$_2$. The mixture was stirred at room temperature for 2 h. Solvent was removed and the residue was subjected to TLC separation using 1:1 CH$_2$Cl$_2$–petroleum ether as eluent. From the black band 0.116 g (84%) of **3a** was obtained. Similarly, from 0.020 g (0.034 mmol) of (μ$_3$-S)FeCoMo (CO)$_8$(η^5-C$_5$H$_4$CO$_2$CH$_3$), 0.012 g (0.034 mmol) of BMPTO and 0.009 g (0.034 mmol) of PPh$_3$, 0.023 g (82%) of **3c** was obtained.

3.18. X-ray structural determinations of 3b and 3e

X-ray quality crystals of **3b** and **3e** were grown by slow evaporation of their solutions in 2:1 CH$_2$Cl$_2$–hexane at −5°C. Both crystals were in the form of black plates. The single-crystal of **3b** (0.30 × 0.20 × 0.05 mm) or **3e** (0.15 × 0.10 × 0.05 mm) was mounted on a glass fiber in an arbitrary orientation and determined on a Bruker Smart 1000 automated diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ radiation (λ = 0.71073 Å). Absorption corrections were performed using SADBS in the ω scanning mode. Details of the crystals, data collections, and structure refinements are

Table 5
Crystal data and structure refinement for **3b** and **3e**

	3b	**3e**
Molecular formula	C$_{32}$H$_{22}$CoFeMoO$_8$PS	C$_{32}$H$_{22}$CoFeMoO$_8$PSe
Molecular weight	808.25	855.15
Temperature (K)	293(2)	293(2)
Space group	$P2_1/n$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic
Unit cell parameters		
a (Å)	14.2448(9)	14.334(5)
b (Å)	9.4393(6)	9.485(3)
c (Å)	24.3505(17)	24.491(8)
α (°)	90	90
β (°)	90.448(2)	90.513(9)
γ (°)	90	90
V (Å^3)	3274.1(4)	3329(2)
Z	4	4
Density (g cm^{-3})	1.640	1.706
Absorption coefficient (mm^{-1})	1.476	2.482
F(000)	1616	1688
Limiting indices	$-12 \le h \le 17$, $-11 \le k \le 11$, $-22 \le l \le 30$	$-6 \le h \le 17$, $-11 \le k \le 10$, $-26 \le l \le 29$
No. of reflections	15053	11572
No. of independent reflections	6726 ($R_{int} = 0.0261$)	5867 ($R_{int} = 0.1427$)
Completeness to θ	$\theta = 26.42°$, 99.8%	$\theta = 25.05°$, 99.6%
Data/restraints/parameters	6726/0/406	5867/0/406
Goodness-of-fit on F^2	0.986	0.921
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0278$; $wR_2 = 0.0664$	$R_1 = 0.0601$; $wR_2 = 0.1169$
R indices (all data)	$R_1 = 0.0423$; $wR_2 = 0.0726$	$R_1 = 0.1410$; $wR_2 = 0.1598$
Largest difference peak and hole (e Å^{-3})	0.396 and −0.393	0.906 and −0.908
Weighing scheme	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$

summarized in Table 5. The structures were solved by a direct phase determination method (MULTAN 82). The final refinement was accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a Bruker Smart computer using the SHELX-97 program system.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 145880 for **3b** and no. 145881 for **3e**. 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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