

**Unexpected Metallosite-Selective CO Substitution of
Heteronuclear Tetrahedral (μ_3 -S)FeCoM (M = Mo, W)
Carbonyl Clusters with Cyclohexyl Isocyanide: ^{59}Co
NMR and ^{57}Fe Mössbauer Spectra of
(μ_3 -S)FeCoMo(CO) $_{8-n}$ (η^5 -C $_5$ H $_4$ COMe)(C $_6$ H $_{11}$ NC) $_n$ (n = 1–3)
and Crystal Structures of
(μ_3 -S)FeCoM(CO) $_{8-n}$ (η^5 -C $_5$ H $_4$ R)(C $_6$ H $_{11}$ NC) $_n$ (M = Mo, W; R
= MeCO, MeO $_2$ C; n = 1, 2)**

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We have first studied the selective CO substitution reactions of heteronuclear tetrahedral clusters of the type (μ_3 -S)FeMCo(CO) $_8$ (η^5 -C $_5$ H $_4$ R) (M = Mo, W) with cyclohexyl isocyanide CyNC. It was found that while clusters (μ_3 -S)FeMCo(CO) $_8$ (η^5 -C $_5$ H $_4$ R) (M = Mo, W; R = MeCO) react with 1 equiv of CyNC in THF at room temperature to give mono-CyNC-substituted products (μ_3 -S)FeMCo(CO) $_7$ (CyNC)(η^5 -C $_5$ H $_4$ COMe) (**1a**, M = Mo; **1b**, M = W) in 63% and 79% yields, clusters of (μ_3 -S)FeMCo(CO) $_8$ (η^5 -C $_5$ H $_4$ R) (M = Mo, W; R = MeCO, MeO $_2$ C, H) react with 2 equiv of CyNC under similar conditions to afford di-CyNC-substituted products (μ_3 -S)FeMCo(CO) $_6$ (CyNC) $_2$ (η^5 -C $_5$ H $_4$ R) (**2a**, M = Mo; R = MeCO; **2b**, M = W, R = MeCO; **2c**, M = Mo, R = MeO $_2$ C; **2d**, M = W, R = MeO $_2$ C; **2e**, M = Mo, R = H) in 56–68% yields. Similarly, tri-CyNC-substituted derivatives (μ_3 -S)FeMoCo(CO) $_5$ (CyNC) $_3$ (η^5 -C $_5$ H $_4$ R) (**3a**, R = MeCO; **3b**, R = MeO $_2$ C) are produced by reaction of clusters (μ_3 -S)FeMoCo(CO) $_8$ (η^5 -C $_5$ H $_4$ R) (R = MeCO, MeO $_2$ C) with 3 equiv of CyNC in 37% and 39% yields. The combined use of spectroscopic techniques (IR, ^1H and ^{59}Co NMR, and ^{57}Fe Mössbauer spectroscopy) with crystal X-ray diffraction analyses for **1a,b** and **2c,d** has established that the CyNC ligand in **1a,b** is bonded to M (M = Mo, W), the two CyNC ligands in **2a–e** are bound to M (Mo, W) and Fe, and the three CyNC ligands in **3a,b** are attached to Mo, Fe, and Co, respectively. Thus, the metallosite selectivity toward CyNC in the reaction of this type of cluster system decreases obviously in the order of η^5 -RC $_5$ H $_4$ (CO) $_2$ M (M = Mo, W) > Fe(CO) $_3$ > Co(CO) $_3$.

Introduction

It is known that the study on metallosite selectivity in carbonyl substitution of heteronuclear tetrahedral clusters is of considerable interest and has shown that the selectivity could be influenced by several factors, such as the nature of the metals in clusters, the type of both existing and attacking ligands, etc. For example, (i) while clusters HMCo $_3$ (CO) $_{12}$ (M = Fe, Ru) react with primary phosphine PCyH $_2$ (Cy = cyclohexyl) to give monosubstituted products in which PCyH $_2$ is bonded respectively to Co or Ru¹, they react with secondary and tertiary phosphines to afford monosubstituted deriva-

tives in which the phosphine ligand is always bonded to Co;^{2–4} (ii) while HRuCo $_3$ (CO) $_{12}$ reacts with Me $_2$ Te to yield a monosubstituted product in which Me $_2$ Te is bonded to Ru,⁵ HRuRh $_3$ (CO) $_{12}$ reacts with PR $_3$ to produce monosubstituted derivatives in which PR $_3$ is attached to Rh;⁶ (iii) in the disubstituted product HRuCo $_3$ (CO) $_{10}$ (PMe $_2$ Ph) $_2$ the second PMe $_2$ Ph is substituted at Ru,⁴ whereas in HRuCo $_3$ (CO) $_{10}$ (PPh $_3$) $_2$ each PPh $_3$ is bonded to Co;⁷ (iv) while trisubstitution of

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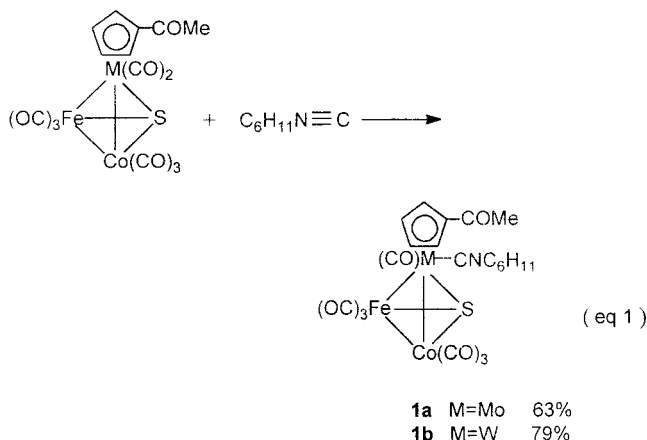
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HFeCo₃(CO)₁₂ with P(OMe)₃ occurs at each axial site of the three Co atoms,⁸ that of HFeCo₃(CO)₁₂ with PMe₂-Ph or HRuCo₃(CO)₁₂ with various phosphines affords products in which the third ligand is attached to Fe⁹ or Ru,⁴ respectively.

Recently, we reported a type of monosubstitution metallosite-selective reaction of heteronuclear tetrahedral clusters (μ_3 -E)FeMCo(CO)₈(η^5 -C₅H₄R) (M = Mo, W; E = S, Se) with (*p*-MeOC₆H₄)₂TeO (BMPTO);¹⁰ this reaction has proved to produce a series of monosubstituted derivatives (μ_3 -E)FeMCo(CO)₇(BMPT)(η^5 -C₅H₄R), whose BMPT (generated in situ from BMPTO by O atom transfer reaction), i.e., (*p*-MeOC₆H₄)₂Te, ligand is substituted at the Co atom.¹⁰ To know the relative affinity of the three different transition metals (Fe, Mo, Co or Fe, W, Co) in the same cluster system in metallosite-selective reactions, we carried out the reactions of (μ_3 -S)FeMCo(CO)₈(η^5 -C₅H₄R) (M = Mo, W) with cyclohexyl isocyanide, CyNC. As a result, in contrast to the above-mentioned derivatives (μ_3 -E)FeMCo(CO)₇(BMPT)(η^5 -C₅H₄R), in the resulting mono-CyNC-substituted products the ligand CyNC is bonded to M (M = Mo, W) but not to Co. In addition, in disubstituted products the two CyNC are respectively bonded to M and Fe, and in trisubstituted derivatives the three CyNC are attached to M, Fe, and Co, respectively. It follows that the affinity of these transition metals toward CyNC in such reactions decreases in the order η^5 -RC₅H₄(CO)₂M (M = Mo, W) > Fe(CO)₃ > Co(CO)₃. Herein we report these interesting results, along with the synthesis and characterization of a series of new CyNC-substituted cluster complexes obtained from this study.

Results and Discussion

Synthesis and Structural Characterization of Mono-CyNC-Substituted Derivatives 1a,b Obtained by Reaction of (μ_3 -S)FeMCo(CO)₈(η^5 -C₅H₄R) with 1 equiv of CyNC. Interestingly, we found that the tetrahedral heteronuclear clusters (μ_3 -S)FeMCo(CO)₈(η^5 -C₅H₄R) (M = Mo, W; R = MeCO) reacted with 1 equiv of cyclohexyl isocyanide in THF at room temperature for 4 h to give corresponding mono-CyNC-substituted derivatives (μ_3 -S)FeMCo(CO)₇(CyNC)(η^5 -C₅H₄COMe) (**1a,b**), in which the ligand CyNC is bonded to Mo and W atoms (eq 1).



The ¹H NMR spectra of **1a,b** showed a multiplet in the range 1.29–1.90 ppm for the 10 hydrogen atoms of

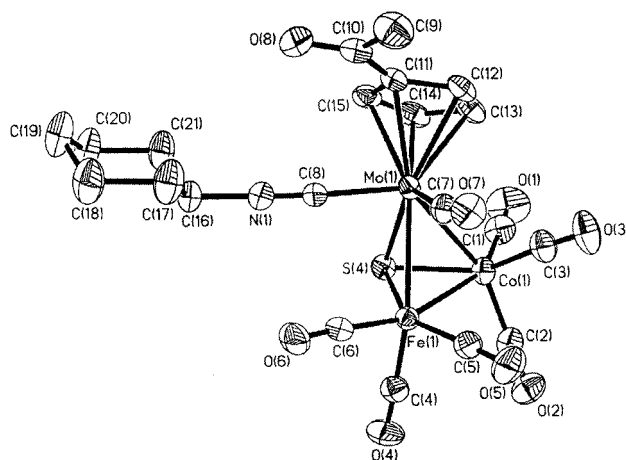


Figure 1. ORTEP drawing of **1a** with atom-labeling scheme.

H²–H⁶ in cyclohexyl, a singlet at 2.35 or 2.36 ppm for COCH₃, and a broad singlet at 3.75 or 3.87 ppm for the hydrogen atom on the carbon attached to the isocyanide group. The two sets of resonance signals in the higher and lower fields were respectively assigned to H^{3,4} and H^{2,5} on the substituted Cp ring, since the substituent COCH₃ is electron-withdrawing.¹¹ The IR spectra of **1a,b** displayed five to six metal–carbonyl absorption bands in the range 2055–1857 cm⁻¹,¹² and one acetyl absorption band at ca. 1681 cm⁻¹. In addition, the stretching frequencies of N≡C in **1a,b** appeared at 2183 and 2176 cm⁻¹, respectively. That these $\nu_{N\equiv C}$ appear at higher values than that of free CyNC (2138 cm⁻¹)¹³ is obviously due to the synergetic effects of the stronger σ -donor CyNC and the stronger π -acceptor CO coordinated to the same transition metals, which makes the C≡N σ - and π -systems in the isocyanide N≡C: group both inductively strengthened.¹⁴

To unambiguously confirm the structures of the monosubstituted products **1a,b**, the X-ray crystal diffraction analyses of **1a,b** were undertaken. Since **1a** is isostructural with **1b**, only the ORTEP drawing of the molecular structure of **1a** is shown in Figure 1. Table 1 lists the selected bond lengths and angles of **1a**. As can be seen in Figure 1, the carbon atom C(8) of the isocyanide ligand in **1a** is indeed attached to the Mo atom; that is, the CO substitution by C₆H₁₁NC occurred selectively at the Mo atom. Also, the X-ray diffraction analysis for **1b** revealed that the corresponding carbon atom of the isocyanide ligand in **1b** is attached to the W atom, and thus the CO substitution took place selectively at the W atom. This is unexpected since CO monosubstitution in the same type of tetrahedral (μ_3 -

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a

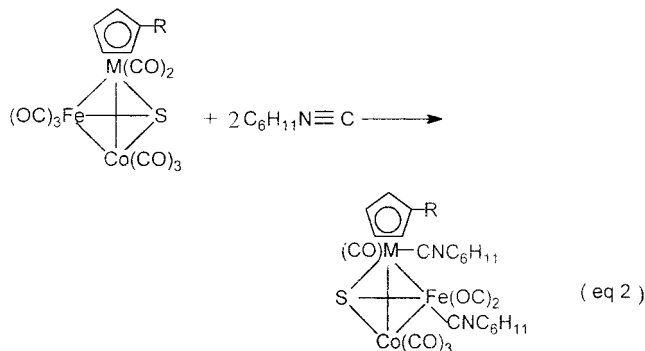
Co(1)–S(1)	2.2037(12)	Mo(1)–C(8)	2.068(5)
Co(1)–Fe(1)	2.5433(9)	Mo(1)–C(11)	2.287(4)
Co(1)–Mo(1)	2.7520(7)	Mo(1)–S(1)	2.3568(11)
Fe(1)–C(6)	1.771(5)	N(1)–C(8)	1.141(5)
Fe(1)–S(1)	2.1917(12)	N(1)–C(16)	1.461(5)
Fe(1)–Mo(1)	2.7840(7)	C(10)–C(11)	1.465(6)
S(1)–Co(1)–Fe(1)	54.43(3)	S(1)–Mo(1)–Fe(1)	49.62(3)
S(1)–Co(1)–Mo(1)	55.47(3)	Co(1)–Mo(1)–Fe(1)	54.69(2)
Fe(1)–Co(1)–Mo(1)	63.29(2)	Fe(1)–S(1)–Co(1)	70.71(4)
S(1)–Fe(1)–Co(1)	54.87(3)	Fe(1)–S(1)–Mo(1)	75.38(4)
S(1)–Fe(1)–Mo(1)	55.00(3)	Co(1)–S(1)–Mo(1)	74.15(4)
Co(1)–Fe(1)–Mo(1)	62.013(19)	C(8)–N(1)–C(16)	175.9(5)

S)FeMCo (M = Mo, W) cluster system by BMPT as mentioned above took place completely at the Co atom.¹⁰ The bond length of N(1)–C(8) in **1a** and corresponding bond length N–C in **1b** are respectively equal to 1.141(5) and 1.149(13) Å, which are comparable with those of corresponding mononuclear isocyanide complexes.^{15,16} The bond length of C(8)–Mo(1) (2.068(5) Å) in **1a** and corresponding C–W bond length (2.052(12) Å) in **1b** are close to those of the corresponding C–Mo (2.101(7) Å) in the mononuclear Mo complex [Mo(MeNC)₂(Ph₂PCH₂-CH₂PPh₂)]^{15c} and the corresponding C–W (average 2.113(13) Å) in mononuclear W complex [(t-BuNC)₃W(CO)₂I₂].¹⁶ The bond angles C(8)–N(1)–C(16) in **1a** and corresponding bond angle C–N–C in **1b** are 175.9(5)° and 169.8(15)°, which means that the terminal isocyanide C₆H₁₁NC displays a slight bending or nearly linear mode, although some terminal isocyanides may take a severe bending mode in their corresponding complexes.^{15,16} In addition, it can be seen from Figure 1 intuitively that the cyclohexyl group in the CyCN ligand lies in a stable chair-form conformation. Among the seven carbonyls attached to metal atoms in **1a** or **1b**, the carbonyl C(7)O(7) attached to Mo in **1a** and the corresponding carbonyl bonded to W in **1b** are semibridging (their asymmetric parameters α equal 0.40 and 0.41, respectively)¹⁷ and the others are terminal. The existence of both terminal and bridging CO's confirmed by X-ray diffraction analyses is consistent with the IR spectra of **1a,b** described above. The substituted Cp rings in **1a,b** are tilted to their triangular S–Co–Fe planes to give a dihedral angle of 42.57° and 41.10°, respectively. Since the dihedral angle between the Cp ring and the acetyl plane C(10)–O(8)–C(9) in **1a** or the corresponding angle in **1b** is rather small (4.42° and 5.80°, respectively), the π -system of the acetyl would be quite well conjugated with the Cp ring π -system, and thus the bond lengths of C(11)–C(10) (1.465(6) Å) in **1a** and the corresponding C–C bond length (1.466(15) Å) in **1b** become much shorter than a normal C–C single bond.

Synthesis and Structural Characterization of Di-CyNC-Substituted Derivatives **2a–e** Obtained by Reaction of (μ_3 -S)FeMCo(CO)₈(η^5 -C₅H₄R) with 2 equiv of CyNC.

We further found that when clusters

(μ_3 -S)FeMCo(CO)₈(η^5 -C₅H₄R) (M = Mo, W; R = MeCO, MeO₂C, H) reacted with 2 equiv of cyclohexyl isocyanide under similar conditions, the corresponding di-CyNC-substituted products (μ_3 -S)FeMCo(CO)₆(CyNC)₂(η^5 -C₅-H₄R) (**2a–e**) were obtained, in which the two ligands CyNC are bonded to Mo or W and Fe atoms, respectively (eq 2).



	2a	2b	2c	2d	2e
M	Mo	W	Mo	W	Mo
R	MeCO	MeCO	MeO ₂ C	MeO ₂ C	H
Yield	63%	56%	68%	60%	63%

The IR and ¹H NMR spectra of the disubstituted products **2a–e** showed the presence of their respective ligands η^5 -C₅H₄R, CO, and C₆H₁₁NC, and they are very similar to those of monosubstituted derivatives **1a,b**. However, compared to **1a,b**, both NC and CO stretching frequencies of **2a–e** appear in a lower region; for example, for **1a** and **2a** the ν_{NC} and ν_{CO} values are 2183/2055–1876 cm⁻¹ and 2157/2030–1831 cm⁻¹, respectively. Obviously, such shifts toward lower frequencies could be attributed to both the increase in the number of CyNC and the corresponding decrease of the number of CO. This is because isocyanide behaves generally as a stronger σ -donor and a weaker π -acceptor, when compared to the CO ligand.¹⁴ To unequivocally confirm the structures of the disubstituted derivatives **2a–e** and particularly to confirm the metallosites to which both CyNC ligands are attached, we carried out X-ray crystal diffraction analyses for **2c** and **2d**. Since **2c** and **2d** are isostructural, only the ORTEP drawing of the molecular structure of **2c** is shown in Figure 2. Table 2 presents the selected bond lengths and angles of **2c**. As can be seen from Figure 2, while the first CyNC is still bonded to the Mo(1) atom, the second CyNC is bonded to the Fe(1) atom and is located trans to the Fe(1)–Co(1) bond. The X-ray diffraction analysis for **2d** revealed that the first CyNC is bonded to the W atom and the second CyNC is bonded to the Fe atom and trans to the corresponding Fe–Co bond. This means that in these CO substitution reactions the affinity of CyNC toward metals is in the order of η^5 -RC₅H₄(CO)₂M (M = Mo, W) > Fe(CO)₃. In addition, the X-ray diffraction analyses for **2c** and **2d** showed that (i) the carbonyls C(6)O(6) attached to Mo(1) in **2c** and the corresponding carbonyl bound to W in **2d** are semibridging (their α 's all equal 0.38),¹⁷ while the others are terminal; (ii) the dihedral angles between the substituted Cp ring and the trian-

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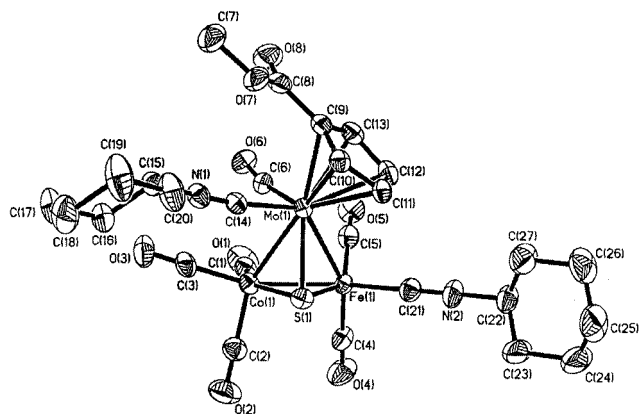


Figure 2. ORTEP drawing of **2c** with atom-labeling scheme.

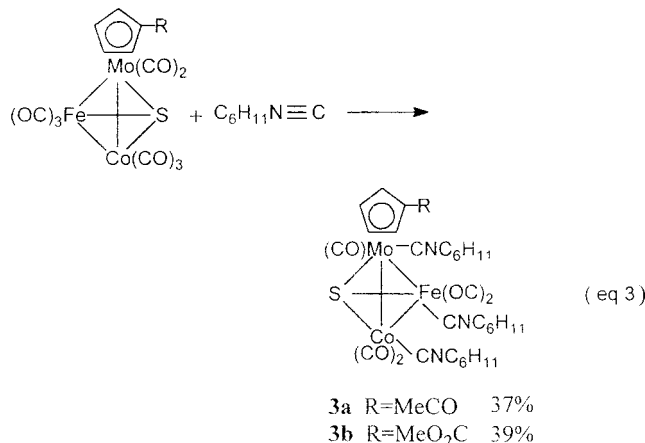
Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2c**

Co(1)–S(1)	2.1984(12)	N(1)–C(14)	1.153(5)
Co(1)–Fe(1)	2.5341(8)	N(1)–C(15)	1.435(5)
Co(1)–Mo(1)	2.7918(7)	N(2)–C(21)	1.159(5)
Fe(1)–S(1)	2.1965(12)	N(2)–C(22)	1.455(6)
Fe(1)–Mo(1)	2.7502(6)	C(7)–O(7)	1.443(6)
Mo(1)–S(1)	2.3531(11)	O(7)–C(8)	1.342(6)
S(1)–Co(1)–Fe(1)	54.75(3)	Fe(1)–Mo(1)–Co(1)	54.414(18)
S(1)–Co(1)–Mo(1)	54.72(3)	Fe(1)–S(1)–Co(1)	70.42(4)
Fe(1)–Co(1)–Mo(1)	61.958(19)	Fe(1)–S(1)–Mo(1)	74.30(4)
S(1)–Fe(1)–Co(1)	54.82(3)	Co(1)–S(1)–Mo(1)	75.58(4)
C(5)–Fe(1)–Mo(1)	83.65(15)	C(14)–N(1)–C(15)	175.1(4)
S(1)–Fe(1)–Mo(1)	55.45(3)	C(21)–N(2)–C(22)	177.8(5)
Co(1)–Fe(1)–Mo(1)	63.63(2)	N(2)–C(21)–Fe(1)	177.9(4)

gular plane S(1)–Co(1)–Fe(1) in **2c** and the corresponding angles in **2d** are 42.65° and 42.60°, respectively; (iii) the dihedral angle between the Cp ring and the plane C(8)–O(8)–O(7) of the methoxycarbonyl group in **2c** and the corresponding angle in **2d** are 3.83° and 3.50°, and thus the π -system of the methoxycarbonyl would be well conjugated with the Cp ring π -system and in turn makes the bond length of C(8)–C(9) (1.478(6) Å) in **2c** and corresponding C–C bond length (1.420(16) Å) in **2d** become much shorter than a normal C–C single bond. It follows that the structures of **2c,d** are very similar to those of **1a,b**. This can be also seen, for example, from the comparison of some of the geometric parameters associated with the terminal CyNC ligand in **1a** and **2c** (Table 3). Additionally, similar to **1a,b** in the two CyNC ligands of **2c,d** the cyclohexyl rings are all in stable chair-form conformations.

Synthesis and Structural Characterization of Tri-CyNC-Substituted Derivatives **3a,b Obtained by Reaction of $(\mu_3\text{-S})\text{FeMCo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})$ with 3 equiv of CyNC.** Interestingly, when 3 equiv of cyclohexyl isocyanide reacted with $(\mu_3\text{-S})\text{FeMoCo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})$ (R = MeCO, MeO₂C) in THF at room temperature for a prolonged time (12 h), tri-CyNC-substituted clusters $(\mu_3\text{-S})\text{FeMCo}(\text{CO})_5(\text{CyNC})_3(\eta^5\text{-C}_5\text{H}_4\text{R})$ (**3a,b**) were produced, in which each CyNC is attached to Mo, Fe, and Co, respectively (eq 3).

The IR and ¹H NMR spectra of **3a,b** are consistent with their structures shown in eq 3 and very similar to the corresponding spectra of mono- and disubstituted derivatives. However, it is worthy of note that on the basis of the same reason as mentioned for **2a–e** both of the NC and CO stretching frequencies of **3a,b** continue to shift toward lower values,¹⁴ and the ν_{NC} and



ν_{CO} values for these substitution derivatives may be arranged in the order **1a,b** > **2a–e** > **3a,b**. Now, the question is how to further establish the structures of **3a,b**, particularly how to establish which metal is bonded to the third CyNC in these trisubstituted derivatives (so far, we cannot get single crystals of **3a,b** suitable for X-ray diffraction analysis). First, it is believed that the first and second CyNC ligands in **3a,b** are still attached respectively to Mo and Fe atoms. This is because that the CO substitution by CyNC follows the order $\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{M}$ (M = Mo, W) > Fe(CO)₃ in mono- and disubstitution reactions, and this has been confirmed by crystal structures of the mono- and disubstituted derivatives **1a,b** and **2c,d**. Second, the presence of the IR bands at 1813 cm⁻¹ for **3a** and 1832 cm⁻¹ for **3b** implies the retention of the semibridging CO attached to the Mo atom in **3a,b**,¹⁷ and thus the third CyNC is not bound to the Mo atom, but would be attached to the Fe or to Co atom. However, it is well-known that in CO substitution reactions of transition metal clusters the second CO ligand attached to the same metal is generally much more difficult to replace by another ligand.¹⁸ So, in this case the third CyNC would preferentially replace the CO ligand attached to the Co atom, but not the second CO attached to the Fe atom. To prove this, we determined the ⁵⁹Co NMR spectra of **1a–3a** and their parent compound $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COMe})$, as well as the ⁵⁷Fe Mössbauer spectra of **1a–3a**. The ⁵⁹Co NMR data of **1a–3a** and those corresponding to some other cobalt-containing clusters³ are presented in Table 4.

It is worthy of note that the ⁵⁹Co NMR spectra of the tetrahedral $(\mu_3\text{-S})\text{FeCoMo}$ clusters **1a–3a** and their parent cluster each show a singlet in the range from –1777 to –1244 ppm, whereas those (Co–CO) of the tetrahedral MCo₃ (M = Fe, Ru) clusters³ listed in Table 4 each display a single resonance in the range of much higher field from –2464 to –2760 ppm. This reflects the ⁵⁹Co NMR spectral characteristics for these two distinct cluster systems and may be applied for characterizing such cluster complexes. More interestingly, for **1a–3a** and their parent compound the ⁵⁹Co NMR spectra and the corresponding data presented in Table 4 may further provide the information that allows us to ascertain which metal atom (Fe or Co) is bonded to the third

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Table 3. Comparison of Some Geometric Parameters Related to CyNC in 1a and 2c

1a		2c			
CyNC coordinated to Mo(1)		CyNC coordinated to Mo(1)		CyNC coordinated to Fe(1)	
Bond Lengths (Å)					
N(1)–C(8)	1.141(5)	N(1)–C(14)	1.153(5)	N(2)–C(21)	1.159(5)
C(8)–Mo(1)	2.068(5)	C(14)–Mo(1)	2.078(4)	C(21)–Fe(1)	1.859(5)
Bond Angles (deg)					
C(16)–N(1)–C(8)	175.9(5)	C(15)–N(1)–C(14)	175.1(4)	C(21)–N(2)–C(22)	177.8(5)
N(1)–C(8)–Mo(1)	176.8(4)	N(1)–C(14)–Mo(1)	173.7(3)	N(2)–C(21)–Fe(1)	177.9(4)

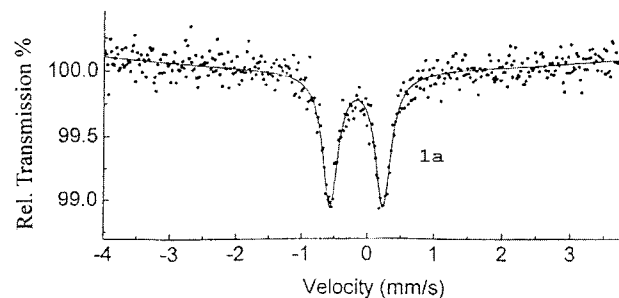
Table 4. Selected ⁵⁹Co NMR Data

cluster	NMR δ ⁵⁹ Co(Δν _{1/2} , Hz) ^a
(μ ₃ -S)FeCoMo(CO) ₈ (η ⁵ -C ₅ H ₄ COMe)	–1525(1700) (Co–CO)
(μ ₃ -S)FeCoMo(CO) ₇ (η ⁵ -C ₅ H ₄ COMe)- (CyNC) (1a)	–1640(3800) (Co–CO)
(μ ₃ -S)FeCoMo(CO) ₆ (η ⁵ -C ₅ H ₄ COMe)- (CyNC) ₂ (2a)	–1777(2570) (Co–CO)
(μ ₃ -S)FeCoMo(CO) ₅ (η ⁵ -C ₅ H ₄ COMe)- (CyNC) ₃ (3a)	–1244(3660) (Co–CyNC)
HFeCo ₃ (CO) ₁₂	–2720(420) (Co–CO) ¹
HRuCo ₃ (CO) ₁₂	–2760(1700) (Co–CO) ^b
HFeCo ₃ (CO) ₁₁ (NMe ₃)	–2730(800) (Co–CO) ^b
HRuCo ₃ (CO) ₁₁ (NMe ₃)	–2747(2000) (Co–CO) ^b
HRuCo ₃ (CO) ₁₀ (PPh ₃) ₂	–2464(10600) (Co–CO) ^b
HRuCo ₃ (CO) ₁₀ (SEt ₂) ₂	–2710(4800) (Co–CO) ^b

^a Measured at 293 K in CDCl₃; sample concentrations (1–2) × 10^{–2} mol/L; reference K₃[Co(CN)₆] in D₂O (±25 ppm). ^b See ref 3.

CyNC in trisubstituted derivatives **3a,b**. First, the continuous change of the ⁵⁹Co NMR δ values of the unsubstituted cobalt nucleus toward upfield from –1525 ppm in the parent cluster to –1640 ppm in mono-CyNC-substituted derivative **1a** and then to –1777 ppm in di-CyNC-substituted derivative **2a** is consistent with CyNC being a stronger σ-donor and a weaker π-acceptor than CO¹⁴ and thus increasing the electron density at the unsubstituted Co nucleus. Then, the abruptly downfield change of the ⁵⁹Co NMR δ values from –1777 ppm in **2a** to –1244 ppm in **3a** (this means that the electron density at Co in **3a** is markedly decreased compared to that in **2a**) would be reasonably attributed to the third CyNC replacing the cobalt-CO ligand and then bonding to the cobalt atom. This is because further substitution of the iron-CO ligand in **2a** by CyNC would lead the ⁵⁹Co NMR δ values of **3a** to shift continuously toward a more upfield direction. However, at present we do not exactly know how the electron density at the cobalt nucleus in **3a** becomes much less than that at the unsubstituted Co nucleus in **1a** and **2a**. However, considering that the isocyanide CyNC is a stronger σ-donor and the carbonyl CO is a stronger π-acceptor,¹⁴ we might suggest a synergetic pull–push mechanism to account for this observation; that is, it is the enhanced π-accepting ability of the CO ligands caused by the third CyNC ligand, through the pull–push mechanism, that causes the electron density at the Co nucleus of **3a** to considerably decrease. It is worth noting that although the ⁵⁹Co NMR chemical shifts are not just a reflection of electron density but also include the “paramagnetic” contribution, for simplicity we roughly correlate the chemical shift with the major factor, namely, the electron density.

Furthermore, the ⁵⁷Fe Mössbauer spectra of **1a–3a** also demonstrate that in **3a,b** the third CyNC is bonded to the cobalt atom. The Mössbauer spectra of **1a–3a** are similar and all show a doublet with an equal intensity. As a representative, the Mössbauer spectrum of **1a** is shown in Figure 3, and the Mössbauer data of **1a–3a**

**Figure 3.** ⁵⁷Fe Mössbauer spectrum for **1a**.**Table 5. ⁵⁷Fe Mössbauer Data^a for 1a–3a**

parameter	1a	2a	3a
IS	–0.017	–0.054	–0.025
QS	0.803	0.747	0.750
Wh	0.155	0.131	0.170

^a Parameters in mm/s; errors within ±0.02 mm/s.

are given in Table 5. As can be seen from Table 5, the isomeric shift (IS) values increase from **1a** (–0.017 mm/s) to **2a** (–0.054 mm/s), and then the IS values decrease abruptly from **2a** to **3a** (–0.025 mm/s). So, similar to the discussion for the ⁵⁹Co NMR of **1a–3a**, this observation is consistent with the fact that the first CyNC is bonded to Mo, the second CyNC is bound to Fe, and the third CyNC is bonded to Co. This is because the IS value is proportional to the change in the electron density at the iron nucleus¹⁹ and CyNC ligand is a stronger σ-donor and a weaker π-acceptor. Obviously, it is due to the second CyNC being directly bonded to the Fe atom that the IS value of **2a** is 3 times that of **1a**. In addition, the abrupt decrease of the IS of **3a** can be attributed to the synergetic effects of the third CyNC and CO ligands at the cobalt atom, which makes the electron density at the Co atom and then at the Fe atom remarkably decreased. It is noteworthy that the quadrupole splittings (QS) of **1a–3a** are very close to those of similar tetrahedral clusters, such as (μ₃-S)FeCo₂(CO)₈(PPh₃) (0.78 mm/s)¹⁹ and (μ₃-S)FeCo₂(PPh₃)₂ (0.86 mm/s).¹⁹ This means that the symmetry of the electron cloud of the octahedral Fe atom in these clusters is similar.^{19,20}

Conclusions

The study of metallosite-selective CO substitution of the tetrahedral (μ₃-S)FeMCo (M = Mo, W) clusters (μ₃-S)FeMCo(CO)₈(η⁵-C₅H₄R) with CyNC has resulted in the formation of a series of new CyNC-substituted heteronuclear transition metal clusters with a general

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formula $(\mu_3\text{-S})\text{FeMCo}(\text{CO})_{8-n}(\text{CyNC})_n(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($\text{M} = \text{Mo}$, $n = 1\text{--}3$; $\text{M} = \text{W}$, $n = 1, 2$). Probably, the site of substitution is determined by kinetics rather than thermodynamics, since TLC showed that the R_f values of the CyNC-substituted products are unchanged during the course of reactions, although the quantity of the products increases with a given period of reaction time. More interestingly, the structural characterization of these CyNC-substituted products using crystal X-ray diffraction techniques along with IR, ^1H NMR, ^{59}Co NMR, and ^{57}Fe Mössbauer spectroscopic methods has shown that this type of CO substitution reaction with CyNC under studied conditions occurred selectively in replacing only one CO at each metal and following the ease of the substitution order $\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{M}$ ($\text{M} = \text{Mo}$, W) $>$ $\text{Fe}(\text{CO})_3$ $>$ $\text{Co}(\text{CO})_3$. Such unexpected results demonstrate again the important influences of the metals in the cluster core and the nature of the existing and attacking ligands upon the metallosite-selective substitution and would be very useful in the synthesis of the other ligand-substituted novel cluster complexes.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. THF was dried and distilled from sodium/benzophenone ketyl. Column chromatography and preparative TLC were carried out using silica gel of 300–400 mesh and silica gel G of 10–40 μm , respectively. Starting materials $\text{C}_6\text{H}_{11}\text{NC}^{13}$ and $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($\text{R} = \text{H}^{21}$, MeCO^{22} , $\text{MeO}_2\text{C}^{11}$) and $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($\text{R} = \text{MeCO}^{11}$, $\text{MeO}_2\text{C}^{11}$) were prepared according to the literature. IR spectra were recorded on a Nicolet 170 FTIR spectrophotometer, and ^1H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer, whereas ^{59}Co NMR spectra were measured on a Mercury VX 300 (Varian) spectrometer. Elemental analyses were performed using an Elemento Vario EL analyzer. The chemical shifts reported for ^{59}Co are negative high frequency from the external reference $\text{K}_3[\text{Co}(\text{CN})_6]$ saturated in D_2O . Standard parameters are as follows: pulse width 2 μs , sweep width 100 kHz, scan frequency 70.963 MHz, number of scans between 256 and 5000. The Mössbauer spectra were recorded on a MS-500 Mössbauer spectrometer using ^{57}Co diffused in a Pd matrix as radiation source. The isomeric shifts were recorded relative to natural iron foil at 293 K. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_7(\eta^5\text{-C}_5\text{H}_4\text{COME})(\text{CN-C}_6\text{H}_{11})_2$ (1a**).** A 100 mL two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with 0.285 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COME})$, 0.055 g (0.50 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$, and 20 mL of THF. The mixture was stirred for 4 h at room temperature. Solvent was removed in vacuo, and the residue was subjected to TLC using 4:1 (v/v) CH_2Cl_2 /petroleum ether as eluent. The first main band afforded 0.206 g (63%) of **1a** as a brown solid, mp 97–98 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{FeCoMoNO}_8\text{S}$: C, 38.50; H, 2.77; N, 2.14. Found: C, 38.58; H, 2.79; N, 2.15. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2183(vs); $\nu_{\text{C}=\text{O}}$ 2055(vs), 2017(vs), 1980(vs), 1957(vs), 1876(vs); $\nu_{\text{C}=\text{N}}$ 1682(s); $\nu_{\text{C}-\text{N}}$ 1276(s) cm^{-1} . ^1H NMR (CDCl_3): 1.29–1.90(m, 10H, H^{2-6} of Cy), 2.35(s, 3H, COCH_3), 3.75(br s, 1H, CNCH), 5.26(d, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_7(\eta^5\text{-C}_5\text{H}_4\text{COME})(\text{CN-C}_6\text{H}_{11})_2$ (1b**).** A procedure similar to that for **1a** was followed.

The reaction of 0.334 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COME})$ with 0.055 g (0.50 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ afforded 0.293 g (79%) of **1b** as a brown solid, mp 154–155 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{FeCoWNO}_8\text{S}$: C, 33.94; H, 2.44; N, 1.88. Found: C, 33.77; H, 2.22; N, 1.95. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2176(s); $\nu_{\text{C}=\text{O}}$ 2055(vs), 2016(vs), 1995(s), 1973(vs), 1953(s), 1857(s); $\nu_{\text{C}=\text{N}}$ 1680(s); $\nu_{\text{C}-\text{N}}$ 1272(s) cm^{-1} . ^1H NMR (CDCl_3): 1.29–1.68(m, 10H, H^{2-6} of Cy), 2.36(s, 3H, COCH_3), 3.87(br s, 1H, CNCH), 5.26, 5.45(2s, 2H, $\text{H}^{3.4}$ of Cp), 5.70(d, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_4\text{COME})(\text{CN-C}_6\text{H}_{11})_2$ (2a**).** The same procedure as that for **1a** was followed. The reaction of 0.285 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COME})$ with 0.109 g (1.0 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ afforded 0.232 g (63%) of **2a** as a brown solid, mp 118–119 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{FeCoMoN}_2\text{O}_7\text{S}$: C, 44.04; H, 3.97; N, 3.80. Found: C, 43.95; H, 3.89; N, 3.88. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2157(vs), $\nu_{\text{C}=\text{O}}$ 2030(vs), 1976(vs), 1961(vs), 1930(s), 1831(s); $\nu_{\text{C}=\text{N}}$ 1673(s); $\nu_{\text{C}-\text{N}}$ 1280(s) cm^{-1} . ^1H NMR (CDCl_3): 1.32–1.83(m, 20H, H^{2-6} of 2Cy), 2.29(s, 3H, COCH_3), 3.71(br s, 2H, 2CNCH), 5.14(br s, 2H, $\text{H}^{3.4}$ of Cp), 5.59(d, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_4\text{COCH}_3)(\text{CN-C}_6\text{H}_{11})_2$ (2b**).** The same procedure as that for **1a** was followed. The reaction of 0.334 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COME})$ with 0.109 g (1.0 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ afforded 0.230 g (56%) of **2b** as a brown solid, mp 145–146 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{FeCoWN}_2\text{O}_7\text{S}$: C, 39.35; H, 3.55; N, 3.40. Found: C, 39.36; H, 3.50; N, 3.42. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2155(s); $\nu_{\text{C}=\text{O}}$ 2027(vs), 1972(s), 1958(vs), 1926(s), 1830(s); $\nu_{\text{C}=\text{N}}$ 1675(m); $\nu_{\text{C}-\text{N}}$ 1276(w) cm^{-1} . ^1H NMR (CDCl_3): 1.35–1.85(m, 20H, H^{2-6} of 2Cy), 2.32(s, 3H, COCH_3), 3.79(br s, 2H, 2CNCH), 5.27(br s, 2H, $\text{H}^{3.4}$ of Cp), 5.59(d, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})(\text{CN-C}_6\text{H}_{11})_2$ (2c**).** Similarly, the reaction of 0.293 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})$ with 0.109 g (1.0 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ afforded 0.257 g (68%) of **2c** as a brown solid, mp 104–105 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{FeCoMoN}_2\text{O}_8\text{S}$: C, 43.11; H, 3.89; N, 3.72. Found: C, 42.90; H, 3.85; N, 3.91. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2158(vs); $\nu_{\text{C}=\text{O}}$ 2027(vs), 1966(vs), 1937(vs), 1851(s); $\nu_{\text{C}=\text{N}}$ 1721(s); $\nu_{\text{C}-\text{N}}$ 1287(s) cm^{-1} . ^1H NMR (CDCl_3): 1.34–1.68(m, 20H, H^{2-6} of 2Cy), 3.77(br s, 5H, COCH_3 , 2CNCH), 5.10–5.30(m, 2H, $\text{H}^{3.4}$ of Cp), 5.67(s, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})(\text{CN-C}_6\text{H}_{11})_2$ (2d**).** Similarly, the reaction of 0.342 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})$ with 0.109 g (1.0 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ gave 0.253 g (60%) of **2d** as a brown solid, mp 123–125 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{FeCoWN}_2\text{O}_8\text{S}$: C, 38.60; H, 3.48; N, 3.33. Found: C, 38.75; H, 3.39; N, 3.44. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2156(vs); $\nu_{\text{C}=\text{O}}$ 2022(vs), 1960(vs), 1931(vs), 1848(s); $\nu_{\text{C}=\text{N}}$ 1722(s); $\nu_{\text{C}-\text{N}}$ 1285(s) cm^{-1} . ^1H NMR (CDCl_3): 1.29–1.64(m, 20H, H^{2-6} of 2Cy), 3.75(br s, 5H, CO_2CH_3 , 2CNCH), 5.19(d, 2H, $\text{H}^{3.4}$ of Cp), 5.60(s, 2H, $\text{H}^{2.5}$ of Cp) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)(\text{CNC}_6\text{H}_{11})_2$ (2e**).** Similarly, the reaction of 0.266 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)$ with 0.109 g (1.0 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$ gave 0.220 g (63%) of **2e** as a brown solid, mp 124–125 °C. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{FeCoMoN}_2\text{O}_6\text{S}$: C, 43.25; H, 3.92; N, 4.03. Found: C, 43.35; H, 3.69; N, 4.33. IR (KBr disk): $\nu_{\text{N}=\text{C}}$ 2145(vs); $\nu_{\text{C}=\text{O}}$ 2016(vs), 1971(s), 1956(vs), 1928(s), 1843(s); $\nu_{\text{C}-\text{N}}$ 1262(w) cm^{-1} . ^1H NMR (CDCl_3): 1.30–1.67(m, 20H, H^{2-6} of 2Cy), 3.77(br s, 2H, 2CNCH), 5.17(s, 5H, C_5H_5) ppm.

Preparation of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_5(\eta^5\text{-C}_5\text{H}_4\text{COME})(\text{CN-C}_6\text{H}_{11})_3$ (3a**).** The mixture of 0.285 g (0.50 mmol) of $(\mu_3\text{-S})\text{FeCoMo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{COME})$, 0.164 g (1.50 mmol) of $\text{C}_6\text{H}_{11}\text{NC}$, and 20 mL of THF in the flask described above was stirred at room temperature for 12 h, then the solvent was removed under reduced pressure. The residue was subjected to preparative TLC using 4:1 (v/v) CH_2Cl_2 /petroleum ether as eluent. The main band afforded 0.150 g (37%) of **3a** as a brown solid, mp 58–59 °C. Anal. Calcd for $\text{C}_{33}\text{H}_{40}\text{FeCoMoN}_3\text{O}_6\text{S}$: C, 48.49; H, 4.93; N, 5.14. Found: C, 48.25; H, 4.85; N, 5.16. IR (KBr

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Table 6. Crystal Data and Structural Refinements Details for 1a,b and 2c,d

	1a	1b	2c	2d
mol formula	C ₂₁ H ₁₈ CoFeMoNO ₈ S	C ₂₁ H ₁₈ CoFeNO ₈ SW	C ₂₇ H ₂₉ CoFeMoN ₂ O ₈	C ₂₇ H ₂₉ CoFeN ₂ O ₈ SW
mol wt	655.14	742.05	752.30	840.21
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P2(1)/n</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>
<i>a</i> /Å	22.447(3)	11.922(4)	8.3017(6)	8.301(2)
<i>b</i> /Å	11.7950(14)	13.501(4)	33.305(2)	33.285(9)
<i>c</i> /Å	21.122(2)	15.756(5)	11.4591(8)	11.489(3)
α /deg	90	90	90	90
β /deg	118.720(3)	99.662(6)	102.8190(10)	102.760(5)
γ /deg	90	90	90	90
<i>V</i> /Å ³	4904.4(10)	2500.0(13)	3089.3(4)	3096.0(14)
<i>Z</i>	8	4	4	4
<i>D</i> _c /g cm ⁻³	1.775	1.971	1.617	1.803
<i>F</i> (000)	2608	1428	1520	1648
abs coeff/mm ⁻¹	1.886	5.946	1.510	4.814
temp/K	298(2)	293(2)	298(2)	293(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{\max}$ /deg	50.04	50.06	50.06	50.06
no. of data/restraints/params	3975/0/307	4361/6/307	5447/0/370	5462/12/370
<i>R</i>	0.0334	0.0446	0.0357	0.0468
<i>R</i> _w	0.0685	0.0999	0.0900	0.0886
goodness of fit	0.960	0.926	0.996	0.917
largest diff peak and hole/e Å ⁻³	0.347 -0.301	0.888 -1.459	0.446 -0.645	0.709 -1.135

disk): $\nu_{\text{N=C}}$ 2136(vs); $\nu_{\text{C=O}}$ 2007(vs), 1992(vs), 1959(vs), 1813(s); $\nu_{\text{C=O}}$ 1670(s); $\nu_{\text{C-N}}$ 1280(s) cm⁻¹. ¹H NMR (CDCl₃): 1.28–1.90(m, 30H, H²⁻⁶ of 3Cy), 2.32(s, 3H, COCH₃), 3.71(br s, 3H, 3CNCH), 5.05–5.77(m, 4H, H²⁻⁵ of Cp) ppm.

Preparation of (μ_3 -S)FeCoMo(CO)₅(η^5 -C₅H₄CO₂Me)(CN-C₆H₁₁)₃ (3b). The same procedure as that for **3a** was followed. The reaction of 0.266 g (0.50 mmol) of (μ_3 -S)FeCoMo(CO)₈(η^5 -C₅H₅) with 0.164 g (1.5 mmol) of C₆H₁₁NC gave 0.160 g (39%) of **3b** as a brown solid, mp 49–50 °C. Anal. Calcd for C₃₃H₄₀-FeCoMoN₃O₇S: C, 47.56; H, 4.84; N, 5.04. Found: C, 47.58; H, 4.80; N, 5.01. IR (KBr disk): $\nu_{\text{N=C}}$ 2135(vs); $\nu_{\text{C=O}}$ 2003(vs), 1991(vs), 1955(vs), 1832(s); $\nu_{\text{C=O}}$ 1718(s); $\nu_{\text{C-N}}$ 1286(s) cm⁻¹. ¹H NMR (CDCl₃): 1.33–1.95(m, 30H, H²⁻⁶ of 3Cy), 3.75(br s, 6H, 3CNCH, OCH₃), 5.02–5.77(m, 4H, H²⁻⁵ of Cp) ppm.

X-ray Crystal Structure Determinations of 1a,b and 2c,d. Single crystals of **1a,b** and **2c,d** suitable for X-ray diffraction analyses were grown by slow evaporation of their solutions in 1:1 CH₂Cl₂/hexane at about 4 °C. Each single crystal 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 α radiation ($\lambda = 0.71073$ Å). Details of the crystals, data

collections, and structure refinements are summarized in Table 6. The structures were solved by a direct phase determination method (Mulan 82) and expanded by Fourier techniques. The final refinements were 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 SHELXTL-97 program system.

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Supporting Information Available: Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **1a,b** and **2c,d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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