Synthesis and Structural Characterization of the μ-η^1:η^5-$Ph_2PC_5H_4$ Ligand-Containing Transition-Metal Cluster and Dinuclear Complexes (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-S)MFeCo$(CO)_7$ (M = Mo, W), (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-RC)$MCo_2(CO)_7$ (M = Mo, W; R = Me, Ph), and (μ-η^1:η^5-$Ph_2PC_5H_4$)$CpMo_2(CO)_5$ Obtained from the Studied Isolobal Displacement Reactions

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The isolobal displacement reaction of tetrahedral cluster (μ_3-S)$FeCo_2(CO)_9$ with isolobal reagents η^5-$Ph_2PC_5H_4(CO)_3MLi$ (M = Mo, W) in THF at about 60 °C was found to give the μ-η^1:η^5-$Ph_2PC_5H_4$-containing tetrahedral clusters (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-S)MFeCo$(CO)_7$ (**1**, M = Mo; **2**, M = W), whereas tetrahedral clusters (μ_3-RC)$Co_3(CO)_9$ (R = Me, Ph) reacted with η^5-$Ph_2PC_5H_4(CO)_3MLi$ under the same conditions to afford the corresponding tetrahedral clusters (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-MeC)$MCo_2(CO)_7$ (**3**, M = Mo; **4**, M = W) and (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-PhC)$MCo_2(CO)_7$ (**5**, M = Mo; **6**, M = W). However, it was found that when tetrahedral cluster $CpMoCo_3(CO)_{11}$ reacted with isolobal reagent η^5-$Ph_2PC_5H_4(CO)_3$-MoLi under similar conditions, the corresponding tetrahedral cluster (μ-η^1:η^5-$Ph_2PC_5H_4$)$CpMo_2Co_2(CO)_9$ (**7**) was not produced, but instead the dinuclear complex (μ-η^1:η^5-$Ph_2PC_5H_4$)$CpMo_2(CO)_5$ (**8**) was obtained unexpectedly. While **1**−**6** and **8** have been characterized by elemental analysis and spectroscopy, as well as by X-ray crystallography for **1**−**3** and **8**, the possible pathways for formation of these products are suggested.

Introduction

The synthesis and characterization of transition-metal dinuclear and cluster complexes have received considerable attention, because of their interesting chemistry and particularly their important applications in catalysis and material and life sciences.[1−11] In recent years we have prepared a variety of transition-metal tetrahedral cluster complexes through isolobal displacement reactions under the guidance of the principle of isolobal analogy.[12] These complexes include, for example, the single tetrahedral (μ_3-E)MFe_2 (E = S, Se; M = Mo, W) cluster complexes obtained from the corresponding single isolobal displacement reactions,[13] the double tetrahedral (μ_3-S)MFeCo (M = Mo, W) cluster complexes produced from the corresponding double isolobal displacement reactions,[14] and the single or double tetrahedral (μ_3-S)M_2Fe (M = Mo, W) cluster core-containing macrocyclic complexes yielded from the cyclization isolobal displacement reactions.[15−17] On the basis of our previous studies, we recently carried out a study on isolobal reactions of the tetrahedral (μ_3-S)$FeCo_2$, (μ_3-RC)Co_3, (R = Me, Ph), or $MoCo_3$ cluster core-containing complexes with isolobal reagents η^5-$Ph_2PC_5H_4(CO)_3MLi$ (M = Mo, W). The main purpose of this study is (i) to see the scope and limitations of the common isolobal displacement reactions between d^9-ML_3 and d^5-ML_5 fragments present in the substrates and the isolobal reagents; (ii) to see if the Ph_2P-substituted Cp ring of the isolobal reagents could influence the isolobal reactions to give unexpected cluster products; and (iii) to develop synthetic methodology for preparation of transition-metal cluster complexes. Herein we report our results obtained from this study.

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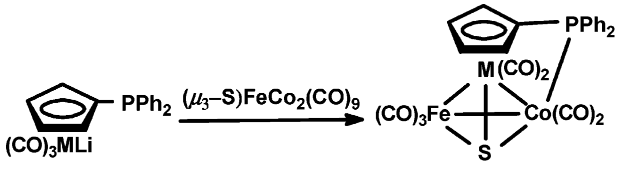
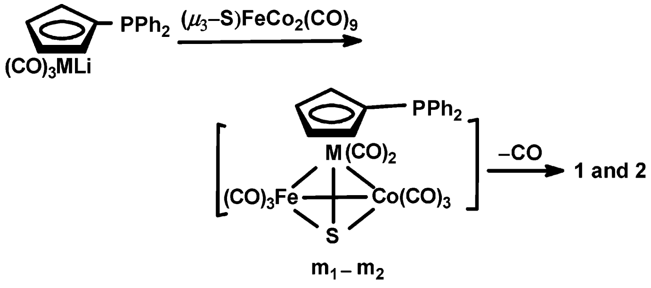
Scheme 1

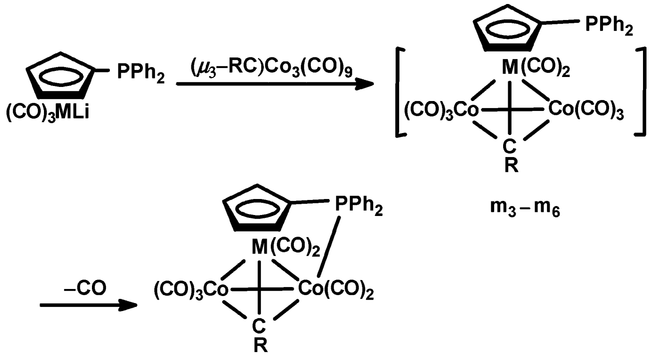


	1	2
M	Mo	W

Scheme 2



Scheme 3



	3	4	5	6
M	Mo	W	Mo	W
R	Me	Me	Ph	Ph

Results and Discussion

Synthesis and Spectroscopic Characterization of the μ-η^1:η^5-$Ph_2PC_5H_4$-Containing Tetrahedral Clusters 1−6 and Dinuclear Complex 8. We found that the η^5-$Ph_2PC_5H_4$-containing isolobal reagents η^5-$Ph_2PC_5H_4(CO)_3MLi$ (M = Mo, W) prepared from $M(CO)_6$ and diphenylphosphinocyclopentadienyllithium could react in situ with tetrahedral cluster (μ_3-S)$FeCo_2(CO)_9$ in THF at about 60 °C to afford the μ-η^1:η^5-$Ph_2PC_5H_4$-containing tetrahedral cluster complexes **1** and **2** in 41% and 38% yields, respectively (Scheme 1).

So far, the mechanism for formation of **1** and **2** is not clear to us. However, according to the previously reported similar isolobal reactions[14,15,18] and those well-documented transition-metal-bound CO substitutions by heteroatom ligands,[19−21] we might suggest a possible pathway to account for the formation of **1** and **2** (Scheme 2). As shown in Scheme 2, the reactions would first give the intermediates $\mathbf{m_1}$ and $\mathbf{m_2}$ via the intermolecular d^9-ML_3/d^5-ML_5 isolobal displacement of the $Co(CO)_3$ fragment in (μ_3-S)$FeCo_2(CO)_9$ by the η^5-$Ph_2PC_5H_4M(CO)_2$ fragment generated from η^5-$Ph_2PC_5H_4(CO)_3MLi$, and then the intramolecular substitution of the cobalt-attached CO in $\mathbf{m_1}$ or $\mathbf{m_2}$ by its P atom affords the final products **1** and **2**. It is interesting to note that **1** and **2** are actually the first transition-metal tetrahedral cluster complexes containing a μ-η^1:η^5-$Ph_2PC_5H_4$ ligand, although some homo- and heterodinuclear complexes containing such a ligand were previously reported.[22−25]

Products **1** and **2** are air-stable solids, which have been characterized by elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopy. For example, the IR spectra of **1** and **2** showed three absorption bands in the range 2047−1893 cm^{-1} for their carbonyls attached to transition metals. In addition, the ^1H NMR spectra of **1** and **2** displayed three and four singlets in the range 4.64−6.00 ppm for their monosubstituted cyclopentadienyl rings.[14,26] The ^{31}P NMR spectra of **1** and **2** each exhibited one singlet at 39.70 or 35.13 ppm for their P atoms attached to cobalt atoms. It is worth pointing out that these two singlets were broadened by the quadrupole effects of ^{59}Co nuclei[27] to give a half-height width $W_{h/2}$ = 1303 or 1208 Hz, respectively.

In order to show the generality of this synthetic methodology for preparation of such μ-η^1:η^5-$Ph_2PC_5H_4$-containing transition-metal clusters, we further carried out reactions of η^5-$Ph_2PC_5H_4(CO)_3MLi$ with another type of tetrahedral clusters, (μ_3-RC)$Co_3(CO)_9$ (R = Me, Ph), under similar conditions. As a result, the expected μ-η^1:η^5-$Ph_2PC_5H_4$ ligand-containing cluster complexes **3**−**6** were produced in 32−61% yields. Obviously, the possible pathway for formation of **3**−**6** is similar to that suggested for formation of **1** and **2**, in which the corresponding intermediates $\mathbf{m_3}$−$\mathbf{m_6}$ are first generated by the above-mentioned intermolecular d^9-ML_3/d^5-ML_5 isolobal displacement, and then the final products **3**−**6** can be produced by intramolecular coordination of their P atoms to cobalt atoms followed by loss of their CO ligands (Scheme 3).

Products **3**−**6** are also air-stable solids and have been characterized by elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopy. In fact, the IR, ^1H NMR, and ^{31}P NMR spectra of **3**−**6** are very similar to those displayed by **1** and **2**. For instance, the IR spectra of **3**−**6** also showed four absorption bands around 2000 cm^{-1} for their carbonyls attached to transition metals. The ^1H NMR spectra of **3**−**6** exhibited three and four singlets in the region 3.93−5.87 ppm for their monosubstituted Cp rings.[14,26] The ^{31}P NMR spectra of **3**−**6** each displayed one broad singlet in the range 40−45 ppm with a $W_{h/2}$ value in the region 84−168 Hz for their tertiary P atoms coordinated to cobalt atoms.[27] In addition, similar to **1** and **2**, the ^{31}P chemical shifts of the Mo complexes **3** and **5** are greater than those of the W complexes **4** and **6**, implying the influence of the transition metals directly attached to the μ-η^1:η^5-$Ph_2PC_5H_4$ ligand.

On the basis of synthesizing the μ-η^1:η^5-$Ph_2PC_5H_4$-containing tetrahedral (μ_3-S)MFeCo and (μ_3-RC)MCo_2 cluster complexes **1**−**6**, an attempt has been made to prepare the tetrahedral Mo_2-

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Scheme 4

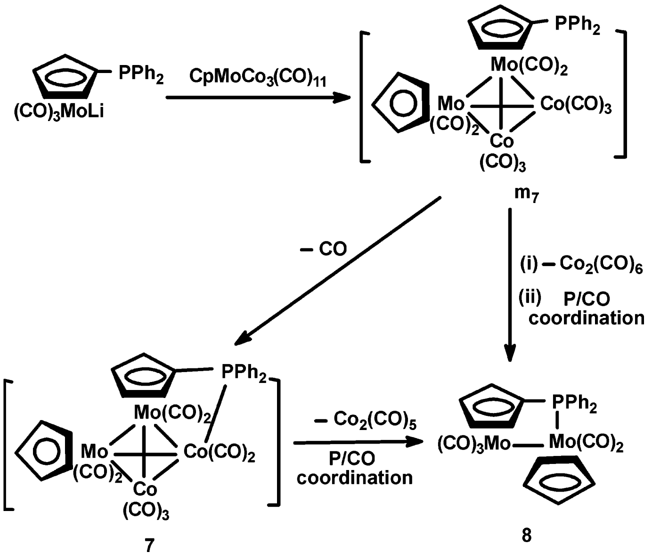

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−3 and 8

	1		
Mo(1)−S(1)	2.371(2)	Co(1)−S(1)	2.198(2)
Mo(1)−Co(1)	2.730(2)	Co(1)−P(1)	2.205(2)
Mo(1)−Fe(1)	2.814(1)	Fe(1)−S(1)	2.197(2)
S(1)−Fe(1)−Co(1)	54.51(5)	S(1)−Mo(1)−Co(1)	50.46(5)
S(1)−Fe(1)−Mo(1)	54.82(4)	S(1)−Co(1)−P(1)	104.45(5)
Fe(1)−S(1)−Mo(1)	75.96(4)	S(1)−Co(1)−Mo(1)	56.29(3)
	2		
W(1)−S(1)	2.357(2)	Co(1)−P(1)	2.198(2)
W(1)−Co(1)	2.720(2)	Co(1)−Fe(1)	2.556(2)
W(1)−Fe(1)	2.792(2)	Fe(1)−S(1)	2.197(2)
S(1)−Fe(1)−Co(1)	54.51(6)	S(1)−W(1)−Co(1)	50.74(6)
S(1)−Fe(1)−W(1)	54.83(6)	P(1)−Co(1)−S(1)	104.03(6)
Fe(1)−S(1)−Co(1)	71.09(5)	S(1)−Co(1)−W(1)	56.06(4)
	3		
Mo(1)−C(8)	2.120(5)	Co(1)−C(8)	1.918(6)
Mo(1)−Co(1)	2.650(1)	Co(1)−P(1)	2.229(2)
Mo(1)−Co(2)	2.695(1)	Co(1)−Co(2)	2.483(1)
Co(1)−Co(2)−Mo(1)	61.40(3)	P(1)−Co(1)−Co(2)	105.95(5)
C(10)−P(1)−Co(1)	101.82(2)	Co(2)−Co(1)−Mo(1)	63.24(3)
C(8)−Mo(1)−Co(1)	45.77(2)	Co(1)−C(8)−Mo(1)	81.9(2)
	8		
Mo(1)−Mo(2)	3.253(7)	Mo(1)−P(1)	2.427(6)
Mo(1)−C(1)	1.932(2)	P(1)−C(12)	1.821(2)
Mo(1)−C(18)	2.382(3)	P(1)−C(23)	1.805(2)
C(1)−Mo(1)−C(2)	76.95(9)	C(23)−P(1)−Mo(1)	107.00(6)
C(1)−Mo(1)−P(1)	81.78(7)	C(12)−P(1)−Mo(1)	122.63(6)
C(2)−Mo(1)−P(1)	116.01(6)	C(24)−Mo(2)−C(23)	36.26(7)

Co_2 cluster complex (μ-η^1:η^5-$Ph_2PC_5H_4$)$CpMo_2Co_2(CO)_9$ (**7**) by means of this synthetic method. However, it was found that upon treatment of $CpMoCo_3(CO)_{11}$ with η^5-$Ph_2PC_5H_4(CO)_3$-MoLi in THF at 50−60 °C, the dinuclear complex (μ-η^1:η^5-$Ph_2PC_5H_4$)$CpMo_2(CO)_5$ (**8**) was unexpectedly obtained in 35% yield, without any isolable **7** being observed. When **8** was fully characterized by us using elemental analysis, ^1H NMR and ^{31}P NMR spectroscopy, and particularly X-ray crystallography, we knew that **8** is a known complex.[23] Up to now, we did not clearly understand the mechanism of formation of **8**. However, based on the above-proposed pathways for formation of **1**−**6**, it is reasonable to suggest that **8** is most likely produced by loss of its $Co_2(CO)_5$ from **7** or simply from $\mathbf{m_7}$ by loss of its $Co_2(CO)_6$ (presumably due to the strong steric repulsions between the two bulky Cp and substituted Cp rings) followed by coordination of the P atom and the CO ligand present in the reaction system with the two Mo atoms, respectively (Scheme 4).

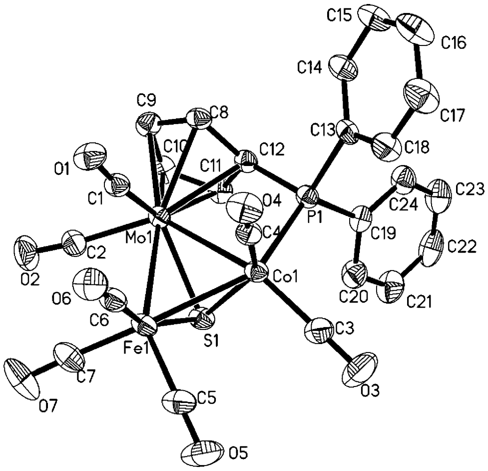

Figure 1. Molecular structure of **1** with 30% probability level ellipsoids.

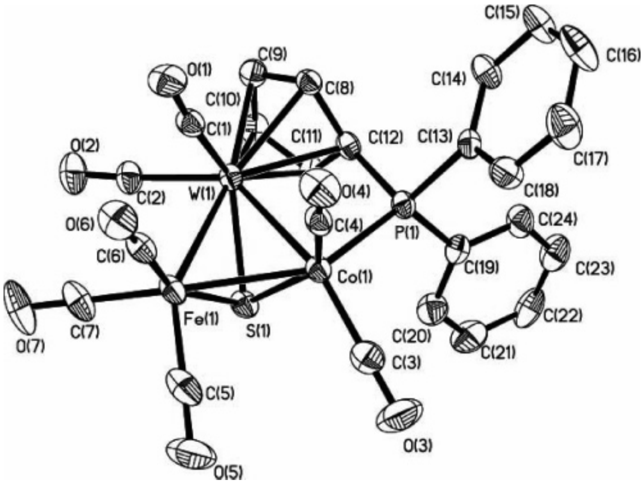

Figure 2. Molecular structure of **2** with 30% probability level ellipsoids.

X-ray Crystallography of 1−3 and 8. In order to unambiguously confirm the structures of tetrahedral clusters **1**−**6** and dinuclear complex **8**, we carried out the X-ray crystal diffraction analyses of **1**−**3** and **8**. Their selected bond lengths and angles are listed in Table 1, while Figures 1−4 show their molecular structures. As shown in Figures 1 and 2, clusters **1** and **2** indeed contain a tetrahedral cluster core (μ_3-S)MoFeCo or (μ_3-S)-WFeCo that bears seven carbonyls and an η^1:η^5-$Ph_2PC_5H_4$ ligand bridged between Mo and Co or W and Co atoms. Among the seven carbonyls attached to the metals, two carbonyls attached to the Mo atom are semibridging and the others terminal. For semibridging carbonyls Curtis's definition is $0.1 \leq \alpha = (d_2 - d_1)/d_2 \leq 0.6$.[28] For cluster **1**, the calculated α values of C(1)O(1) and C(2)O(2) attached to Mo are 0.41 and 0.37. For cluster **2**, the calculated α values of C(1)O(1) and C(2)O(2) attached to W are 0.32 and 0.37. So, they all fall into the range of α values for semibridging carbonyls. The existence of both terminal and semibridging CO's confirmed by X-ray diffraction analysis is consistent with the IR spectra of **1** and **2** described above. In fact, the overall geometry of **1** and **2** is very similar to that of the known clusters Cp(μ_3-S)MoFeCo-$(CO)_7$L and Cp(μ_3-S)WFeCo$(CO)_7$L (L = MePrPhP).[29]

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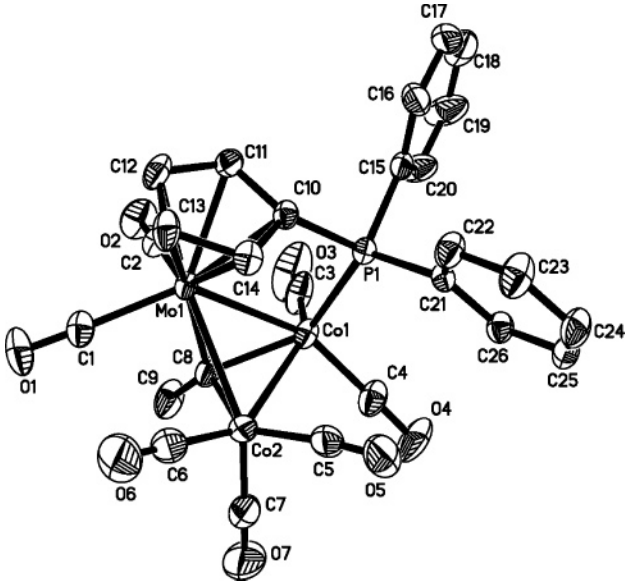

Figure 3. Molecular structure of **3** with 30% probability level ellipsoids.

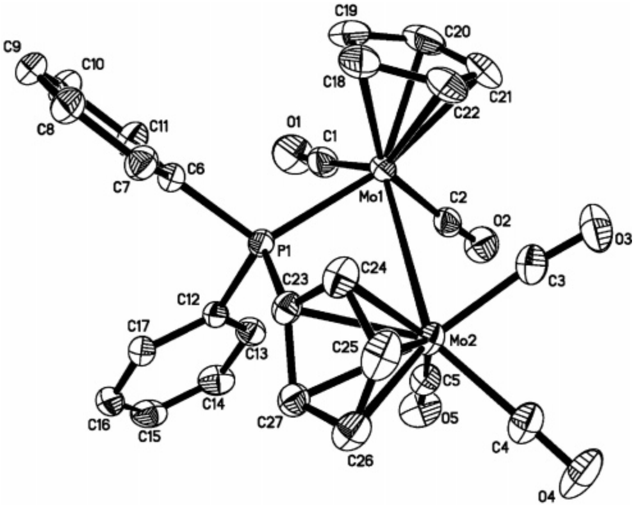

Figure 4. Molecular structure of **8** with 30% probability level ellipsoids.

Figure 3 demonstrates that cluster **3** is similar to **1** and **2**, which consists of a tetrahedral cluster core (μ_3-MeC)$MoCo_2$, seven metal-bound carbonyls, and an η^1:η^5-$Ph_2PC_5H_4$ ligand bridged between Mo and Co atoms. However, among the seven carbonyls, only one carbonyl, namely, C(1)O(1) ($\alpha = 0.41$), is semibridging and the others terminal. In addition, the dihedral angle between the substituted Cp ring and triangle plane C(8)−Co(1)−Co(2) in **3** is 35.8(9)°, which is much smaller than that (52.4(1)°) between the substituted Cp ring and triangle plane Fe(1)−Co(1)−S(1) in its analogous cluster **1**.

The crystal structure of **8** as shown in Figure 4 is composed of an η^1:η^5-$Ph_2PC_5H_4$ ligand bridged between the two molybdenum atoms; in addition, Mo(2) is coordinated by three carbonyls and Mo(1) by two carbonyls and a Cp ring. Actually, all the geometric parameters of our complex are nearly the same as those previously reported for this complex. For example, the metal−metal Mo(1)−Mo(2) bond length and the bond angle between the two *cis* carbonyls C(3)−Mo(2)−C(5) in our complex are 3.253(7) Å and 100.17(9)°, whereas the corresponding values previously reported are 3.255(2) Å and 100.2(6)°,[23] respectively.

Conclusion

We have developed a convenient "one-pot" synthetic route that leads to the first μ-η^1:η^5-$Ph_2PC_5H_4$ ligand-containing tetrahedral cluster complexes **1**−**6** and the known dinuclear complex **8**. This route for production of **1**−**6** involves a d^9-ML_3/d^5-ML_5 type of isolobal displacement reaction between isolobal reagents η^5-$Ph_2PC_5H_4(CO)_3MLi$ (M = Mo, W) and tetrahedral cluster (μ_3-S)$FeCo_2(CO)_9$, (μ_3-MeC)$Co_3(CO)_9$, or (μ_3-PhC)$Co_3(CO)_9$ to give intermediates $\mathbf{m_1}$−$\mathbf{m_6}$, followed by CO substitution of $\mathbf{m_1}$−$\mathbf{m_6}$ by heteroatom P of the Ph_2P-substituted Cp ring. This route leading to the unexpected dinuclear complex **8** includes the isolobal displacement reaction between isolobal reagent η^5-$Ph_2PC_5H_4(CO)_3MoLi$ and tetraherdal cluster $CpMoCo_3(CO)_{11}$ to give intermediates $\mathbf{m_7}$ and **7**, followed by extrusion of $Co_2(CO)_6$ or $Co_2(CO)_5$ and the P/CO coordination with their two Mo atoms. It follows that both the η^5-$Ph_2PC_5H_4$ ligand-containing isolobal reagents and the tetrahedral cluster substrates may exert great influence upon the isolobal reactions to give different types of products.

Experimental Section

General Comments. All reactions were carried out under prepurified nitrogen using standard Schlenk or vacuum-line techniques. THF and diglyme were distilled from sodium/benzophenone ketyl under nitrogen. $M(CO)_6$ (M = Mo, W) and Ph_2PCl were available from commercial suppliers without further purification. CpNa,[30] *n*-BuLi,[31] $Ph_2PC_5H_4Li$,[32] (μ_3-S)$FeCo_2(CO)_9$,[33] (μ_3-RC)$Co_3(CO)_9$ (R = Me, Ph),[34] and $CpMoCo_3(CO)_{11}$[35] were prepared by slight modifications of the published procedures. Products were separated by thin-layer chromatography on glass plates, 20 × 25 × 0.25 cm, coated with silica gel G (10−40 μm). IR spectra were taken on a Bruker Vector 22 infrared spectrophotometer, ^1H NMR on a Bruker AC-P 200 MHz NMR or a Bruker 300 MHz NMR spectrometer, and ^{31}P NMR on a Bruker 300 MHz NMR or a Varian Mercury Plus 400 MHz spectrometer. Elemental analyses were performed on an Elementar Vario EL analyzer, and melting points were determined on a Yanaco MP-500 apparatus, respectively.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-S)$MoFeCo(CO)_7$ (1). A 100 mL three-necked flask equipped with a magnetic stir-bar, two serum caps, and a reflux condenser topped with a nitrogen inlet tube was charged with a THF solution (20 mL) of CpNa (1.25 mmol), and then the solution was cooled to −78 °C by a dry ice/acetone bath. To this cooled solution was added Ph_2PCl (0.280 g, 1.25 mmol), and the mixture was warmed to room tempertature. After the mixture was stirred at this temperature for 0.5 h, it was cooled again to −78 °C, and then a hexane solution (0.70 mL) of *n*-BuLi (1.20 mmol) was added. The mixture was warmed again to room temperature and stirred at this temperature for 1 h to give a THF solution of $Ph_2PC_5H_4Li$ (ca. 1.0 mmol). To this THF solution

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Table 2. Crystal Data and Structural Refinements Details for 1−3 and 8

	1	**2**	**3**	**8**
mol formula	$C_{24}H_{14}CoFeMoO_7PS{\cdot}0.25CH_3C_6H_5$	$C_{24}H_{14}CoFeWO_7PS{\cdot}0.25CH_3C_6H_5$	$C_{26}H_{17}Co_2MoO_7P$	$C_{27}H_{19}Mo_2O_5P$
mol wt	711.14	799.05	686.17	646.27
temp/K	298(2)	293(2)	293(2)	293(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
a/Å	10.485(6)	10.485(7)	10.457(3)	8.097(2)
b/Å	12.409(7)	12.428(8)	14.716(4)	17.001(4)
c/Å	12.774(7)	12.748(9)	17.430(4)	18.226(4)
α/deg	67.847(9)	68.295(1)	90	90
β/deg	65.925(8)	65.845(1)	101.293(4)	100.351(3)
γ/deg	87.486(1)	87.589(1)	90	90
V/Å^3	1393.5(1)	1391.8(2)	2630.3(1)	2473.7(1)
Z	2	2	4	4
D_c/g cm^{-3}	1.695	1.907	1.733	1.735
abs coeff/mm^{-1}	1.719	5.399	1.820	1.115
F(000)	705	769	1360	1280
limiting indices	$-12 \le h \le 8$	$-6 \le h \le 12$	$-11 \le h \le 12$	$-10 \le h \le 10$
	$-12 \le k \le 14$	$-14 \le k \le 14$	$-17 \le k \le 17$	$-22 \le k \le 21$
	$-14 \le l \le 15$	$-15 \le l \le 15$	$-20 \le l \le 15$	$-24 \le l \le 12$
no.of rflns	5613	5735	13 511	16 476
no. of indep rflns	4728	4827	4638	5927
$2\theta_{max}$/deg	50.00	50.00	50.02	55.94
R	0.0352	0.0295	0.0350	0.0223
R_w	0.0860	0.0589	0.0663	0.0563
gooodness of fit	1.007	1.009	1.094	1.051
largest diff peak and hole/e Å^{-3}	0.977/−0.413	0.690/−0.587	0.497/−0.409	0.345/−0.408

of η^5-$Ph_2PC_5H_4Li$ was added $Mo(CO)_6$ (0.264 g, 1.0 mmol). The mixture was stirred at reflux for 16 h to give a red solution of η^5-$Ph_2PC_5H_4(CO)_3MoLi$. To this solution was added (μ_3-S)$FeCo_2(CO)_9$ (0.456 g, 1.0 mmol), and the mixture was stirred at about 60 °C for an additional 1 h. Solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC separation. Elution with CH_2Cl_2/petroleum ether (2:1 v/v) produced a red-brown band, from which 0.284 g (41%) of **1** as a brown-red solid was obtained, mp 110−112 °C. Anal. Calcd for $C_{24}H_{14}CoFeMoO_7PS$: C, 41.89; H, 2.05. Found: C, 42.20; H, 1.68. IR (KBr disk): $\nu_{C\equiv O}$, 2047 (s), 1992 (vs), 1904 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 4.64, 4.74 (2s, 2H, H^3, H^4), 5.43, 5.80 (2s, 2H, H^2, H^5), 7.45−7.98 (m, 10H, $2C_6H_5$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 39.70 (br s, $W_{h/2}$ = 1303 Hz) ppm.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-S)WFeCo(CO)$_7$ (2). The same THF solution of $Ph_2PC_5H_4Li$ as prepared by the procedure described in the preparation of **1** was evaporated to dryness at reduced pressure, and then the residue was redissolved in diglyme (20 mL). To this diglyme solution was added $W(CO)_6$ (0.352 g, 1.0 mmol), and the mixture was stirred and refluxed for 6 h to give a red solution of η^5-$Ph_2PC_5H_4(CO)_3WLi$. After diglyme was removed at reduced pressure, THF (20 mL) and (μ_3-S)$FeCo_2(CO)_9$ (0.456 g, 1.0 mmol) were added. The new mixture was stirred at about 60 °C for another 1 h. The same workup as that for **1** afforded 0.294 g (38%) of **2** as a brown-red solid, mp 126−128 °C. Anal. Calcd for $C_{24}H_{14}CoFeO_7PSW$: C, 37.15; H, 1.82. Found: C, 37.17; H, 1.95. IR (KBr disk): $\nu_{C\equiv O}$, 2046 (s), 1981 (vs), 1893 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 5.02 (s, 2H, H^3, H^4), 5.54, 6.00 (2s, 2H, H^2, H^5), 7.65−8.20 (m, 10H, $2C_6H_5$) ppm. ^{31}P NMR (161 MHz, $CDCl_3$, 85% H_3PO_4): 35.13 (br s, $W_{h/2}$ = 1208 Hz) ppm.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-MeC)MoCo$_2$(CO)$_7$ (3). The same procedure as for **1** was followed, but (μ_3-MeC)$Co_3(CO)_9$ (0.456 g, 1.0 mmol) was used instead of (μ_3-S)$FeCo_2(CO)_9$. A 0.334 g (50%) amount of **3** as a brown-green solid was obtained, mp 179 °C (dec). Anal. Calcd for $C_{26}H_{17}Co_2MoO_7P$: C, 45.51; H, 2.50. Found: C, 45.33; H, 2.58. IR (KBr disk): $\nu_{C\equiv O}$, 2042 (s), 1993 (vs), 1976 (vs), 1932 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 3.74 (s, 3H, CH_3), 4.04, 5.03 (2s, 2H, H^3, H^4), 5.64 (s, 2H, H^2, H^5), 7.43−7.92 (m, 10H, $2C_6H_5$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 44.47 (br s, $W_{h/2}$ = 93 Hz) ppm.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-MeC)WCo$_2$(CO)$_7$ (4). The same procedure as for **2** was followed, except that (μ_3-MeC)$Co_3(CO)_9$ (0.456 g, 1.0 mmol) was used instead of (μ_3-S)$FeCo_2(CO)_9$, and the mixture of (μ_3-MeC)$Co_3(CO)_9$ with η^5-$Ph_2PC_5H_4(CO)_3WLi$ was stirred at 60 °C for 6 h. A 0.469 g (61%) amount of **4** as a brown-green solid was obtained, mp 180 °C (dec). Anal. Calcd for $C_{26}H_{17}Co_2O_7PW$: C, 40.34; H, 2.21. Found: C, 40.38; H, 2.20. IR (KBr disk): $\nu_{C\equiv O}$, 2042 (s), 1993 (vs), 1975 (vs), 1926 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 3.71 (s, 3H, CH_3), 4.19, 5.08 (2s, 2H, H^3, H^4), 5.54, 5.69 (2s, 2H, H^2, H^5), 7.44−7.87 (m, 10H, $2C_6H_5$). ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 40.83 (br s, $W_{h/2}$ = 84 Hz) ppm.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-PhC)MoCo$_2$(CO)$_7$ (5). The same procedure as for **1** was followed, except that (μ_3-PhC)$Co_3(CO)_9$ (0.518 g, 1.0 mmol) was employed in place of (μ_3-S)$FeCo_2(CO)_9$, and the mixture of (μ_3-PhC)$Co_3(CO)_9$ with η^5-$Ph_2PC_5H_4(CO)_3MoLi$ was stirred at 60 °C for 2.5 h. A 0.245 g (33%) amount of **5** as a brown-green solid was obtained, mp 200 °C (dec). Anal. Calcd for $C_{31}H_{19}Co_2MoO_7P$: C, 49.76; H, 2.56. Found: C, 49.73; H, 2.77. IR (KBr disk): $\nu_{C\equiv O}$, 2064 (s), 2007 (vs), 1980 (vs), 1904 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 3.93, 5.01 (2s, 2H, H^3, H^4), 5.54, 5.84 (2s, 2H, H^2, H^5), 7.01−7.89 (m, 15H, $3C_6H_5$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 44.07 (br s, $W_{h/2}$ = 168 Hz) ppm.

Preparation of (μ-η^1:η^5-$Ph_2PC_5H_4$)(μ_3-PhC)WCo$_2$(CO)$_7$ (6). The same procedure as for **2** was followed, but (μ_3-PhC)$Co_3(CO)_9$ (0.518 g, 1.0 mmol) was utilized in place of (μ_3-S)$FeCo_2(CO)_9$. A 0.270 g (32%) amount of **6** as a brown-green solid was obtained, mp 200 °C (dec). Anal. Calcd for $C_{31}H_{19}Co_2O_7PW$: C, 44.53; H, 2.29. Found: C, 44.41; H, 2.33. IR (KBr): $\nu_{C\equiv O}$, 2051 (s), 2003 (vs), 1980 (vs), 1895 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 4.09, 5.08 (2s, 2H, H^3, H^4), 5.47, 5.87 (2s, 2H, H^2, H^5), 7.01−7.87 (m, 15H, $3C_6H_5$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 40.42 (br s, $W_{h/2}$ = 149 Hz) ppm.

Unexpected Formation of (μ-η^1:η^5-$Ph_2PC_5H_4$)CpMo$_2$(CO)$_5$ (8). The same procedure as for **1** was followed, except that $CpMoCo_3(CO)_{11}$ (0.730 g, 1.0 mmol) was used instead of (μ_3-S)$FeCo_2(CO)_9$, and the new mixture was stirred at 50 °C for 2 h and at 60 °C for 1 h. A 0.228 g (35%) amount of **8** as a brown solid was obtained, mp 182 °C (dec). Anal. Calcd for $C_{27}H_{19}Mo_2O_5P$: C, 50.18; H, 2.96. Found: C, 50.15; H, 2.90. IR (KBr): $\nu_{C\equiv O}$, 1975 (vs), 1915 (vs), 1870 (vs), 1842 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 3.20, 4.46 (2s, 2H, H^3, H^4), 4.96 (s, 5H, C_5H_5), 5.28, 5.50 (2s, 2H, H^2, H^5), 7.30−7.70 (m, 10H, $2C_6H_5$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 63.40 (s) ppm. This ^{31}P NMR chemical shift is relative to 85% H_3PO_4, which corresponds to −78.40 ppm relative to $P(OMe)_3$ (very close to that reported, −78.7 ppm),[23] since the ^{31}P NMR chemical shift of $P(OMe)_3$ is 141.8 ppm relative to 85% H_3PO_4.[36]

Crystal Structure Determinations of 1−3 and 8. Single crystals of **1** and **2** suitable for X-ray diffraction analyses were obtained by slow diffusion of toluene into their CH_2Cl_2 solutions at room temperature, while the X-ray-quality crystals of **3** and **8** were grown by slow diffusion of petroleum ether into their CH_2Cl_2 solutions at 4 °C, respectively. A single crystal of **1**, **2**, **3**, or **8** was mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω−ϕ scanning mode. Absorption correction was performed by the SADABS program.[37] The structures were solved by direct methods using the SHELXS-97 program[38] and refined by full-matrix least-squares techniques (SHELXL-97)[39] on F^2. Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 2.

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Supporting Information Available: Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **1**−**3** and **8** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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