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Electrophilic Additions of Metal Fragments Containing 11- and 12-Group Elements to the Anion Carbide Cluster $[Fe_5MoC(CO)_{17}]^{2-}$. X-ray Crystal Structures of $(NEt_4)[Fe_5MoAuC(CO)_{17}(PMe_3)]$ and $[Fe_5MoAu_2C(CO)_{17}(dppm)]$[†]

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The reaction of $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ with cationic metal fragments gives a series of clusters whose most striking structural feature is the selective addition of the incoming metal units on the triangular Fe_2Mo face of the starting anion. The use of $Au_2(dppm)^{2+}$ (dppm = diphenylphosphinomethane) gives the cluster $[Fe_5MoAu_2C(CO)_{17}(dppm)]$ in which the di-gold fragment adopts an unprecedented bonding mode.

Introduction

Although they belong to the same group, iron and ruthenium show marked differences in their cluster chemistry. Ruthenium clusters are far more common than those of iron, given the higher thermodynamic stability of their species and the ease with which they crystallize. The difference in thermodynamic stability between the iron and ruthenium clusters is shown, for example, in the reaction of the hexanuclear carbide anions $[M_6C(CO)_{16}]^{2-}$ with $(ClAu)_2$dppm (M = Fe,[1] Ru[2]). Thus, for M = Fe, the cluster $[Fe_4Au_2C(CO)_{12}(dppm)]$ was formed after partial cleavage of the octahedral iron anion, while the ruthenium anion gave the species $[Ru_6Au_2C(CO)_{16}(dppm)]$ in which the Ru_6 octahedron is unaltered. On the other hand, the ruthenium anion clusters are much more reactive to electrophilic species, such as $AuPPh_3^+$. For example, while $[Fe_6C(CO)_{16}]^{2-}$ reacts with an excess of $AuPPh_3^+$ to give the anion $[Fe_6AuC(CO)_{16}(PPh_3)]^-$, the analogous $[Ru_6C(CO)_{16}]^{2-}$ can incorporate up to two gold units and give the neutral compound $[Ru_6Au_2C(CO)_{16}(PMePh_2)_2]$.[3,4]

Here we describe the reaction of the heteronuclear anion $[Fe_5MoC(CO)_{17}]^{2-}$ with the electrophilic fragments $MPPh_3^+$ (M = Au, Cu, Ag), $AuPMe_3^+$, $Au_2(diphos)^{2+}$, $HgMo(CO)_3Cp^+$, and $HgW(CO)_3Cp^+$ and compare the results with those given by the use of the close anions $[Fe_6C(CO)_{16}]^{2-}$ and $[Ru_5WC(CO)_{17}]^{2-}$.

Results and Discussion

$(NEt_4)_2[Fe_5MoC(CO)_{17}]$ reacted with $ClAuPPh_3$ in tetrahydrofuran to give air-stable red crystals of $(NEt_4)[Fe_5MoAuC(CO)_{17}(PPh_3)]$, (NEt_4)[**1**] (Scheme 1). Although we were unable to grow single crystals of them, the cluster $(NEt_4)[Fe_5MoAuC(CO)_{17}(PMe_3)]$, (NEt_4)[**2**], obtained by the same method, gave suitable crystals for an X-ray crystal structure determination. The structure of the anion is shown in Figure 1, together with the atomic numbering scheme; the most significant bond distances and angles are given in Table 1. The structure may be regarded as derived from that of $[Fe_5MoC(CO)_{17}]^{2-}$ [5] with one Fe_2Mo triangular face of the octahedron capped by the $AuPMe_3^+$ moiety. The carbide is roughly equidistant from the five iron atoms with Fe−C distances in the range 1.871(8)−1.954(7) Å, not significantly different from those reported for the starting anion. Fifteen carbonyls are terminal, and two bridge the Fe(4)−Fe(2) and Mo−Fe(5) edges unsymmetrically. The products obtained by the reaction between the iron cluster $[Fe_5MoC(CO)_{17}]^{2-}$ and the ruthenium analogue $[Ru_5WC(CO)_{17}]^{2-}$ with gold halide complexes are different. In the first case, only the mono-gold derivative is obtained despite the use of an excess of the gold reagent, while in the second case the di-gold species $[Ru_5WAu_2C(CO)_{17}(PEt_3)_2]$ is isolated.[4] However, the most intriguing structural feature arises from the fact that the gold fragment caps an Fe_2Mo triangular face of the Fe/Mo anion; in contrast, an Ru_3 face of the Ru/W cluster is capped. Although the higher Mo−Au bonding energy in comparison with that of the Fe−Au could be

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[†] Dedicated to Prof. Rafael Usón on the occasion of his 75th birthday.

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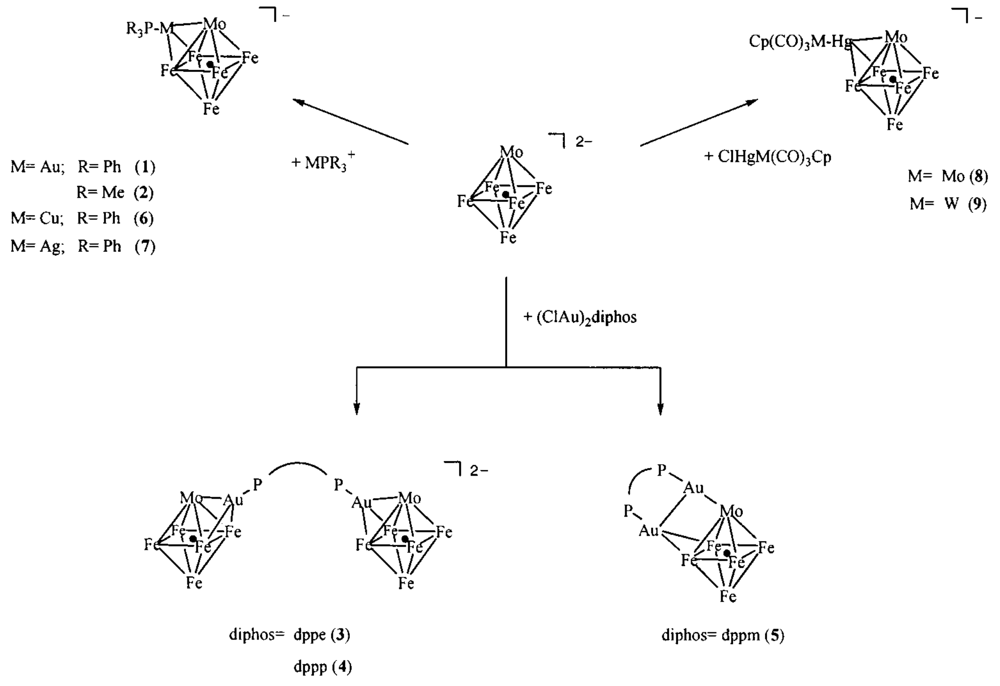
Scheme 1



the driving force to explain this result, it is not clear why the $AuPEt_3$ does not cap the Ru_2W face instead of the Ru_3.

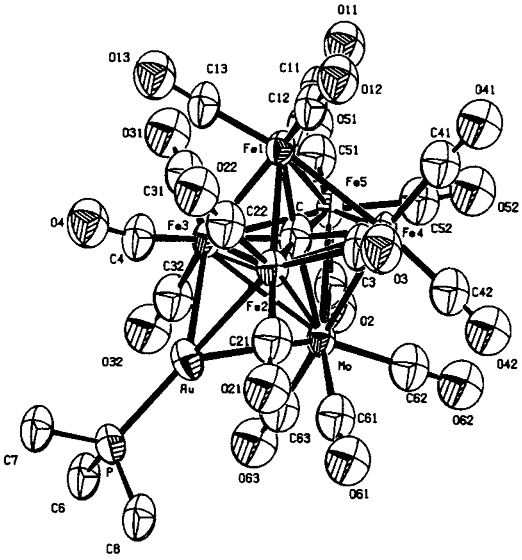


Figure 1. ORTEP view of the molecular structure of the anionic cluster **2** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Bimetallic $Au_2(diphos)^{2+}$ or trimetallic $Au_3(triphos)^{3+}$ cations as electrophilic species have been widely studied. This is because such units can be bound to a cluster anion through two gold atoms[6] or can link two[7] or three[8] cluster units together. The structure of the final product strongly depends on the bite angle of the diphosphine.[9] With this in mind, we analyzed the reaction between $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ and $(ClAu)_2$diphos (diphos = bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp)) (Scheme 1). We found that for $(ClAu)_2$diphos (diphos = dppe, dppp), the resulting species were $(NEt_4)_2[\{Fe_5MoAuC(CO)_{17}\}_2(dppe)]$, $(NEt_4)_2$[**3**], and $(NEt_4)_2[\{Fe_5MoAuC(CO)_{17}\}_2(dppp)]$, $(NEt_4)_2$[**4**], in which two "$Fe_5MoAuC(CO)_{17}$" are linked by the corresponding diphosphine, according to the IR and NMR spectroscopies and electrospray mass spectrometry. However, the X-ray crystal structure determination of dppm derivative revealed the neutral compound $[Fe_5MoAu_2C(CO)_{17}(dppm)]$, **5**. Its molecular structure is illustrated in Figure 2, together with the atomic numbering scheme; the most significant bond distances and angles are given in Table 2. The metal core geometry can be described as an Fe_5Mo octahedron in which an Fe−Fe edge is bridged by one gold atom, whereas the other is directly attached to the molybdenum center. This surprising coordination mode of the $Au_2(dppm)^{2+}$ moiety (μ^3-η^2) to the cluster anion has no precedent in the literature; the $Au_2(dppm)^{2+}$ units are usually attached to metal clusters through two μ_2- or μ_3-bonding modes.[6,7] The average distances between Fe(1)−Fe(4) and the carbide fall in the range 1.880(7)−1.949(7) Å, whereas the Fe(3)−C and the Mo−C lengths are somewhat higher, 2.023(10) and 2.058(10) Å, respectively. C(3)−O(3) and C(19)−(O19) are semibridging along the

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for (NEt$_4$)[2]

Au−Fe(2)	2.743(2)	Fe(1)−Fe(3)	2.623(2)
Au−Fe(3)	2.747(1)	Fe(1)−Fe(4)	2.648(2)
Au−Mo	2.963(3)	Fe(1)−Fe(5)	2.676(2)
Mo−Fe(5)	2.784(1)	Fe(1)−Fe(2)	2.684(1)
Mo−Fe(4)	2.894(2)	Fe(2)−Fe(4)	2.569(2)
Mo−Fe(2)	2.952(2)	Fe(2)−Fe(3)	2.841(3)
Mo−Fe(3)	3.014(2)	Fe(3)−Fe(5)	2.698(3)
		Fe(4)−Fe(5)	2.710(2)
P−Au−Fe(2)	149.92(6)	Fe(1)−Fe(2)−Au	115.34(5)
P−Au−Fe(3)	141.15(7)	Fe(1)−Fe(2)−Mo	91.47(4)
Fe(2)−Au−Fe(3)	62.33(4)	Au−Fe(2)−Mo	62.58(6)
P−Au−Mo	137.54(6)	Fe(1)−Fe(3)−Au	117.27(5)
Fe(2)−Au−Mo	62.15(6)	Fe(5)−Fe(3)−Au	119.44(5)
Fe(3)−Au−Mo	63.59(3)	Fe(1)−Fe(3)−Mo	91.29(8)
Fe(5)−Mo−Au	109.77(3)	Au−Fe(3)−Mo	61.69(4)
Fe(4)−Mo−Au	107.14(6)	Fe(5)−C(1)−Fe(2)	172.9(5)
Fe(4)−Fe(2)−Au	124.99(6)	Fe(3)−C(1)−Fe(4)	176.0(5)
		Fe(1)−C(1)−Mo	175.6(5)

edge Mo−Au(1), and C(6)−O(6) is semibridging along the edge Fe(2)−Au(2). This structural feature favors short Au−C bond distances in the range 2.454(8)−2.680(9) Å, as found in related metal clusters.[10] It is interesting to compare the structure of **5** with that found for [Fe$_4$Au$_2$C(CO)$_{12}$(dppm)], which is the result of the reaction between [Fe$_6$C(CO)$_{16}$]$^{2-}$ and (ClAu)$_2$dppm.[1] Formation of [Fe$_4$Au$_2$C(CO)$_{12}$(dppm)] results from the partial cleavage of the octahedral iron anion, whereas the presence of the molybdenum in [Fe$_5$MoC(CO)$_{17}$]$^{2-}$ seems to stabilize the metal core against the formation of the di-gold derivative.

To extend our studies to other electrophilic species, the anion [Fe$_5$MoC(CO)$_{17}$]$^{2-}$ was allowed to react with IM(PPh$_3$) (M = Ag, Cu), ClHgMo(CO)$_3$Cp, and ClHgW(CO)$_3$Cp. The reaction was monitored by IR spectroscopy in the ν(CO) region and was completed after 1 h. The new compounds (NEt$_4$)[Fe$_5$MoMC(CO)$_{17}$(PPh$_3$)] (M = Cu, (NEt$_4$)[**6**]; M = Ag, (NEt$_4$)[**7**]), (NEt$_4$)[Fe$_5$MoHgMoC(CO)$_{20}$Cp], (NEt$_4$)[**8**], and (NEt$_4$)[Fe$_5$MoHgWC(CO)$_{20}$Cp], (NEt$_4$)[**9**], were characterized by ESMS and NMR spectroscopy. Although from the spectroscopic data it is not possible to deduce the site of attachment of the MPPh$_3^+$ and the mercury fragments units to the starting anion, the similarity of the pattern in the ν(CO) IR region displayed for the latter derivatives to that exhibited for (NEt$_4$)[**1**] and (NEt$_4$)[**2**] indicate that they have the same metal skeleton, which is consistent with the isolobal analogy[11] between AuPPh$_3^+$ and HgMo(CO)$_3$Cp$^+$, which has been illustrated in a large series of compounds.[12]

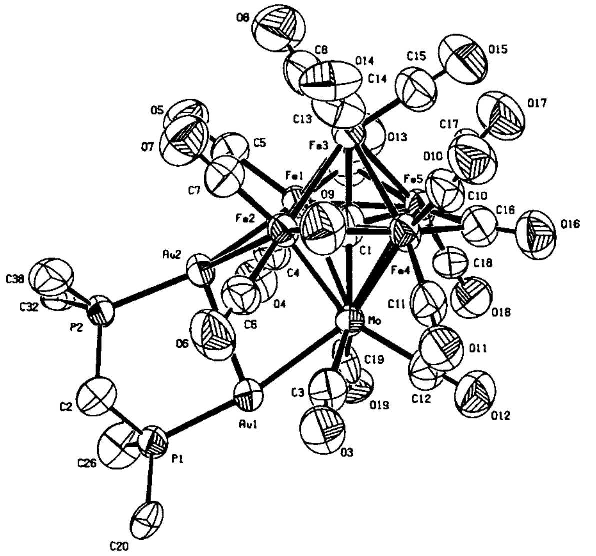

Figure 2. ORTEP view of the molecular structure of **5** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 5

Au(1)−Au(2)	2.8621(6)	Fe(1)−Fe(5)	2.654(1)
Au(2)−Fe(1)	2.680(1)	Fe(1)−Fe(3)	2.695(2)
Au(2)−Fe(2)	2.682(1)	Fe(1)−Fe(2)	2.877(1)
Mo−Fe(5)	2.885(1)	Fe(2)−Fe(4)	2.607(1)
Mo−Fe(4)	2.905(1)	Fe(2)−Fe(3)	2.641(1)
Mo−Fe(2)	2.946(1)	Fe(3)−Fe(4)	2.622(1)
Mo−Fe(1)	2.959(1)	Fe(3)−Fe(5)	2.673(2)
		Fe(4)−Fe(5)	2.609(1)
P(1)−Au(1)−Mo	167.62(7)	Au(2)−Fe(2)−Fe(1)	57.51(3)
P(2)−Au(2)−Fe(1)	155.16(5)	Fe(5)−C(1)−Fe(2)	169.3(6)
P(2)−Au(2)−Fe(2)	136.36(7)	Fe(4)−C(1)−Fe(1)	168.7(5)
Fe(1)−Au(2)−Fe(2)	64.91(4)	Fe(4)−C(1)−Mo	95.0(3)
Au(1)−Mo−Fe(5)	146.85(3)	Fe(5)−C(1)−Mo	93.5(4)
Au(1)−Mo−Fe(4)	145.51(4)	Fe(2)−C(1)−Mo	96.1(3)
Fe(5)−Fe(1)−Au(2)	131.94(4)	Fe(1)−C(1)−Mo	95.2(4)
Au(2)−Fe(1)−Fe(3)	110.71(5)	Fe(3)−C(1)−Mo	179.1(4)
Au(2)−Fe(1)−Fe(2)	57.58(3)	O(3)−C(3)−Mo	170.2(8)
Fe(4)−Fe(2)−Au(2)	133.46(7)	O(19)−C(19)−Mo	172.3(8)
Fe(3)−Fe(2)−Au(2)	112.32(5)		

In conclusion, we have shown that the heteronuclear anion [Fe$_5$MoC(CO)$_{17}$]$^{2-}$ incorporates only one electrophilic metal fragment, which caps an Fe$_2$Mo triangular face, in contrast to the cluster [Ru$_5$WC(CO)$_{17}$]$^{2-}$, which reacts with two metal fragments using the Ru$_3$ triangular faces. On the other hand, the substitution of an Fe(CO)$_3$ for an Mo(CO)$_5$ fragment in the cluster [Fe$_6$C(CO)$_{16}$]$^{2-}$ stabilizes the resulting mixed-metal cluster anion [Fe$_5$MoC(CO)$_{17}$]$^{2-}$. Consequently, the latter anion does not exhibit cleavage during the reaction with the di-gold complex (ClAu)$_2$dppm and the final compound displays an unprecedented (μ_3−η^2) Au$_2$(dppm)$^{2+}$ bonding mode.

Experimental Section

All manipulations were performed under prepurified N$_2$ using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Infrared spectra were recorded in THF solutions on an FT-IR 520 Nicolet spectrophotometer. ^{31}P{^{1}H} NMR (δ (85% H$_3$PO$_4$) = 0.0 ppm), ^{1}H NMR, and ^{13}C{^{1}H} NMR (δ (TMS) = 0.0 ppm) spectra were obtained on Bruker DXR 250 and Varian 200 spectrometers. Elemental analyses of C, H, and N were carried out at the Institut de Bio-Orgànica in Barcelona. FAB(−) and electrospray mass spectra were recorded on a Fisons VG Quattro spectrometer with methanol as the solvent. The compounds (NEt$_4$)$_2$[Fe$_5$MoC(CO)$_{17}$],[13] ClAuPPh$_3$,[14] IAgPPh$_3$,[15] ICuPPh$_3$,[16] ClHgMo(CO)$_3$-

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Table 3. Crystal Data and Structure Refinement for Compounds (NEt_4)[2] and 5

	(NEt_4)[**2**]	**5**
empirical formula	$C_{29}H_{29}AuFe_5MoNO_{17}P$	$C_{43}H_{22}Au_2Fe_5MoO_{17}P_2$
fw	1266.66	1641.67
temp (K)	293(2)	293(2)
wavelength (Å)	0.710 69	0.710 69
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	9.563(11)	10.8220(10)
b (Å)	34.989(4)	25.7800(10)
c (Å)	12.294(9)	17.8930(10)
α (deg)	90	90
β (deg)	92.63(7)	104.1130(10)
γ (deg)	90	90
V (Å^3)	4109(6)	4841.3(6)
Z	4	4
density (calcd) (g/cm^3)	2.047	2.252
abs coeff (mm^{-1})	5.673	7.876
F(000)	2448	3104
cryst size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Θ range for data collection (deg)	2.03−29.98	1.94−25.01
index ranges	$-13 < h < 13, 0 < k < 42, 0 < l < 17$	$-7 < h < 7, 0 < k < 30, 0 < l < 20$
no. rflns collected	12 193	15 460
no. indep rflns	11651 ($R_{int} = 0.0511$)	5281 ($R_{int} = 0.0654$)
refinement method	full-matrix least squares on F^2	
no. data/restraints/params	11651/10/244	5281/72/631
GOF on F^2	0.916	0.869
final R indices [$I > 2\sigma(I)$]	R1 = 0.0445, wR2 = 0.1185	R1 = 0.0268, wR2 = 0.0442
R indices (all data)	R1 = 0.1191, wR2 = 0.1481	R1 = 0.0803, wR2 = 0.0496
largest diff peak and hole (e/Å^3)	0.721 and −0.849	0.623 and −0.624

Cp, and $ClHgW(CO)_3Cp$[17] were synthesized as described previously. The complexes $(ClAu)_2$(dppm), $(ClAu)_2$(dppe), and $(ClAu)_2$(dppp) were synthesized and isolated as solids from ClAu(tht) solutions[9,18] by adding the appropriate amount of the corresponding phosphine.

Syntheses of (NEt_4)[1], (NEt_4)[2], (NEt_4)[6], (NEt_4)[7]. Solid $ClAuPPh_3$ (0.16 g, 0.31 mmol) and $TlBF_4$ (0.09 g, 0.31 mmol) were added to a precooled (−5 °C) solution of $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ (0.36 g, 0.31 mmol) in 40 mL of THF. The reaction was monitored by IR, and after 1 h of stirring the salts (TlCl and NEt_4BF_4) were filtered off. Subsequent addition of 20 mL of diethyl ether and cooling 2 h at −30 °C afforded more salts. Then it was filtered through Celite and the solution was evaporated to dryness. The remaining solid was extracted with CH_2Cl_2 (10 mL), and hexane (8 mL) was added. The resulting solution was cooled to −30 °C overnight to induce the formation of the dark-red crystalline solid (NEt_4)[**1**]. Yield: 0.27 g (57%). IR (THF, cm^{-1}): ν(CO) 2047 (m), 1991 (vs). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 55.5 (s, PPh_3). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 7.50−7.48 (m, Ph), 3.11 (q, CH_2,^3J(H−H) = 7.50 Hz), 1.36 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 221.62 (s, CO), 134.08−129.24 (m, Ph), 53.63 (s, CH_2), 7.39 (s, CH_3). ESMS (M^-) m/z: calcd, 1322; found, 1324. Anal. Calcd: C, 36.34; H, 2.41; N, 0.96. Found: C, 36.39; H, 2.46; N, 1.02.

Compounds (NEt_4)[**2**], (NEt_4)[**6**], and (NEt_4)[**7**] were obtained by a similar procedure, but a molar ratio of 1:2:2 was used for (NEt_4)[**2**] and a ratio of 1:1.5:1.5 was used for (NEt_4)[**6**] instead of 1:1:1. (NEt_4)$[Fe_5MoC(CO)_{17}\{AuPMe_3\}]$: yield, 0.22 g (54%). IR (THF, cm^{-1}): ν(CO) 2046 (m), 1989 (vs), 1961 (s). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 16.5 (s, PPh_3). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 3.10 (q, CH_2,^3J(H−H) = 7.50 Hz), 1.58 (d, $P(CH_3)_3$, J(C−P) = 8.26), 1.29 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 221.86 (s, CO), 53.31 (s, CH_2) 17.60 (d, $P(CH_3)_3$, J(P−C) = 31.45), 7.19 (s, CH_3). ESMS (M^-) m/z: calcd, 1136; found, 1136. Anal. Calcd: C, 27.49; H, 2.30; N, 1.11. Found: C, 27.52; H, 2.35; N, 1.13. (NEt_4)$[Fe_5MoC(CO)_{17}\{CuPPh_3\}]$: yield, 0.23 g (55%). IR (THF, cm^{-1}): ν(CO) 2048 (m), 1990 (vs), 1965 (sh). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ(ppm)): 0.2 (s, PPh_3). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 7.50−7.54 (m, Ph), 3.17 (q, CH_2, ^3J(H−H) = 7.50 Hz), 1.36 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 475.65 (s, C), 221.02 (s, CO), 133.10−128.00 (m, Ph), 53.30 (s, CH_2), 7.14 (s, CH_3). ESMS (M^-) m/z: calcd, 1189; found, 1190. Anal. Calcd: C, 40.04; H, 2.65; N, 1.06. Found: C, 40.10; H, 2.69; N, 1.13. (NEt_4)$[Fe_5MoC(CO)_{17}\{AgPPh_3\}]$: yield, 0.25 g (58%). IR (THF, cm^{-1}): ν(CO) 2047 (m), 1988 (vs), 1967 (sh). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 13.2 (d, PPh_3, $J(^{109}Ag-P) = 526.5$, $J(^{107}Ag-P) = 456.6$). ^1H NMR (298 K, CD_2Cl_2, δ(ppm)): 7.39−7.51 (m, Ph), 3.11 (q, CH_2, ^3J(H−H) = 7.50 Hz), 1.30 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 221.16 (s, CO), 133−128 (m, Ph), 53.20 (s, CH_2), 7.19 (s, CH_3). ESMS (M^-) m/z: calcd, 1233; found, 1234. Anal. Calcd: C, 38.68; H, 2.60; N, 1.03. Found: C, 38.72; H, 2.73; N, 1.09.

Syntheses of (NEt_4)[8] and (NEt_4)[9]. Details of the synthesis of (NEt_4)[**8**] also apply to the synthesis of (NEt_4)[**9**]. To a precooled solution of $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ (0.31 g, 0.27 mmol) in THF (50 mL) at −5 °C, solid $ClHgMo(CO)_3Cp$ (0.13 g, 0.27 mmol) and $TlBF_4$ (0.08 g, 0.27 mmol) were added. The mixture was stirred for 2 h, and 15 mL of diethyl ether were added to ensure the total precipitation of the salts (TlCl and NEt_4BF_4). After filtration the remaining solution was taken to dryness and extracted with CH_2Cl_2 (10 mL). Addition of pentane (7 mL) by slow diffusion at −30 °C afforded (NEt_4)[**8**] as a dark-red solid. Yield: 0.23 g (49%). IR (THF, cm^{-1}): ν(CO) 2056 (m), 2002 (vs), 1982 (s). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 5.49 (s, Cp), 3.22 (q, CH_2, ^3J(H−H) = 7.50 Hz), 1.36 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 220.02 (s, CO), 89.21 (s, 5H, Cp), 53.73 (s, CH_2), 7.62 (s, CH_3). ESMS (M^-) m/z: calcd, 1309; found, 1308. Anal. Calcd: C, 28.36; H, 1.74; N, 0.97. Found: C, 28.47; H, 1.79; N, 1.08. (NEt_4)$[Fe_5MoC(CO)_{17}\{HgW(CO)_3Cp\}]$: yield, 0.23 g (47%). IR (THF, cm^{-1}): ν(CO) 2056 (m), 2001 (vs), 1982 (s). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 5.46 (s, 5H, Cp), 3.22 (q, CH_2, ^3J(H−H) = 7.50 Hz), 1.36 (t, CH_3, ^3J(H−H) = 6.25 Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ (ppm)): 220.28 (s, CO), 88.15 (s, Cp), 54.00 (s, CH_2), 7.92 (s, CH_3). ESMS (M^-) m/z: calcd, 1397; found, 1397. Anal. Calcd: C, 26.73; H, 1.64; N, 0.92. Found: C, 26.79; H, 1.69; N, 1.01.

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Synthesis of [Fe_5Mo $Au_2C(CO)_{17}$(dppm)] (5). Solid $(ClAu)_2$dppm (0.22 g, 0.26 mmol) and $TlBF_4$ (0.09 g, 0.31 mmol) were added to a solution of $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ (0.28 g, 0.25 mmol) in THF (35 mL). The mixture was stirred for 17 h at 0 °C, and the salts (TlCl and NEt_4BF_4) were filtered off. The solution was concentrated to dryness, and the residual solid was extracted with CH_2Cl_2 (8 mL). Slow layer diffusion of hexane (8 mL) at −30 °C afforded deep-red crystals of **5**. Yield: 0.17 g (54%). IR (THF, cm^{-1}): ν(CO) 2059 (m), 2009 (vs), 1979 (s). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 44.2 (d), 50.4 (d) (dppm, $J(P-P) = 74.3$ Hz). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 7.66−7.17 (m, Ph), 3.22 (t, CH_2, $^2J(H-P) = 9.19$). FABMS (M^-) *m/z*: calcd, 1641; found, 1640. Anal. Calcd: C, 31.44; H, 1.34. Found: C, 31.49; H, 1.38.

Syntheses of $(NEt_4)_2$[3] and $(NEt_4)_2$[4]. Details of synthesis of $(NEt_4)_2$[**4**] also apply to $(NEt_4)_2$[**3**]. Solid $(ClAu)_2$dppp (0.12 g, 0.14 mmol) and $TlBF_4$ (0.08 g, 0.27 mmol) were added to a solution of $(NEt_4)_2[Fe_5MoC(CO)_{17}]$ (0.30 g, 0.27 mmol) in THF (40 mL) at −10 °C. The mixture was stirred for 30 min, and the salts (TlCl and NEt_4BF_4) were filtered off. The resulting solution was then concentrated to dryness. The residue was extracted with CH_2Cl_2 (10 mL), and hexane (8 mL) was added. A dark-red solid was obtained in 51% yield (0.19 g). IR (THF, cm^{-1}): ν(CO) 2047 (m), 1991 (vs), 1965 (sh). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 26.7 (s, dppp). ^1H NMR (298 K, CD_2Cl_2, δ(ppm)): 7.30−7.61 (m, Ph), 3.20 (q, CH_2, $^3J(H-H) = 7.50$ Hz), 2.65 (m, CH_2CH_2P), 1.91 (m, CH_2CH_2P), 1.35 (t, CH_3, $^3J(H-H) = 6.25$ Hz). ^{13}C NMR (298 K, CD_2Cl_2, δ(ppm)): 221.41 (s, CO), 132.75−129.35 (m, Ph), 53.30 (s, CH_2-CH_3), 28.09 (dd, CH_2CH_2P), 23.27 (d, CH_2CH_2P), 7.92 (s, CH_3). ESMS ($M^{2-}/2$) *m/z*: calcd, 1266; found, 1267. Anal. Calcd: C, 33.95; H, 2.36; N, 1.00. Found: C, 34.05; H, 2.39; N, 1.04.

$(NEt_4)_2[\{Fe_5MoAuC(CO)_{17}\}_2(dppe)]$: reaction temperature was −10 °C and reaction time 2 h. Yield: 0.23 g (52%). IR (THF, cm^{-1}): ν(CO) 2047 (m), 1991 (vs), 1966 (sh). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ (ppm)): 53.3 (s, dppe). ^1H NMR (298 K, CD_2Cl_2, δ (ppm)): 7.59−7.46 (m, Ph), 3.21 (q, CH_2, $^3J(H-H) = 7.50$ Hz), 2.75 (s, CH_2P), 1.36 (t, CH_3, $^3J(H-H) = 6.25$ Hz). ESMS ($M^{2-}/2$) *m/z*: calcd, 1259; found, 1259. Anal. Calcd: C, 33.69; H, 2.30; N, 1.01. Found: C, 33.81; H, 2.38; N, 1.04.

X-ray Structure Determination of (NEt_4)[2] and 5. Red block crystals of compounds (NEt_4)[**2**] and **5** were selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Crystallographic and experimental details of both compounds are summarized in Table 3. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner.

The structures were solved by direct methods, using the SHELXS computer program, and were refined by a full-matrix least-squares method with the SHELX97 computer program.[19] The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0774P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$, and f, f', and f'' were taken from International Tables for X-Ray Crystallography.[20] All H atoms were computed and refined with an overall isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the atom and are linked using a riding model.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for compounds (NEt_4)[**2**] and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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