Heterometallic Nitrido-Carbonyl Clusters − Synthesis and Characterization of $[Fe_5MN(CO)_{14}(C_5H_5)]^{2-}$, $[Fe_3M_3N(CO)_{18}]^{3-}$ (M = Mo, W) and $[HFe_5MoN(CO)_{16}]^{2-}$ and Solid-State Structures of $[Fe_5MoN(CO)_{14}(C_5H_5)]^{2-}$, $[Fe_5WN(CO)_{14}(C_5H_5)]^{2-}$, and $[Fe_3Mo_3N(CO)_{18}]^{3-}$

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The anionic clusters $[Fe_5MN(CO)_{14}Cp]^{2-}$ [M = Mo (**1**) or W (**2**)] were synthesized from $[Fe_4N(CO)_{12}]^-$ and $[MCp(CO)_3]^-$ in refluxing acetonitrile. The clusters $[Fe_3M_3N(CO)_{18}]^{3-}$ [M = Mo (**3**) or W (**4**)] were prepared by reaction of $[Fe_4N(CO)_{12}]^-$ with $[M_2(CO)_{10}]^{2-}$ under the same conditions. The molybdenum-containing anions **1** and **3** are obtained in higher yields than **2** and **4**. The reaction of the tetranuclear iron cluster with $[Mo(\eta^6\text{-}Me_3C_6H_3)(CO)_3]$ affords a mixture of $[Fe_3Mo_3N(CO)_{18}]^{3-}$ and $[HFe_5MoN(CO)_{16}]^{2-}$ (**5**). The solid state structures of the clusters **1**, **2** and **3** have been determined; they consist of six metal atoms, arranged in octahedral metal cages encapsulating a μ_6-N ligand. The cyclopentadienyl ligand is bound to Mo in **1** and to W in **2**; these anions have three edge-bridging carbonyl groups and eleven terminal carbonyl groups. The cluster **3** possesses three molybdenum atoms in a *fac* arrangement, and the carbonyl ligands are all terminal, or asymmetrically bridging. Inspection of the interatomic distances suggests that molybdenum interacts preferentially with the carbonyl and the nitrido ligands, whereas the iron atoms bind strongly with the other metal centres. The solid state structure of **5** could not be fully resolved owing to crystal disorder. Analytical and spectroscopic data (infrared and ^{1}H NMR) are all consistent with the proposed formula.

Introduction

The interest in heterometallic clusters is still growing, and several examples of their application in catalysis can be found in the literature.[1] In homogeneous catalysis, mixed metal species are preferred, due to the presence of polar metal−metal bonds which can tune electron density at the metal centres, thus modifying the reactivity of the coordinated ligands.[2] In the field of heterogeneous catalysis, mixed-metal species can be exploited for the formation of bimetallic particles which are extraordinarily uniform in their morphology and composition.[3] In this context, the stability of the cage due to the interstitial atoms can avoid sinterization during the absorption to the support and the decarbonylation. Heterometallic species often have unusual structures of remarkable stability due to the preference of the two elements for different chemical sites within the cluster.[4] In these compounds, the HOMO−LUMO gap can be small, and the frontier orbitals can be filled/depleted without decomposition. Therefore, heterometallic clusters with an odd number of valence electrons, and possibly displaying unusual magnetic properties, are not uncommon.[5]

For these reasons, we are studying the reactions of $[Fe_4N(CO)_{12}]^-$ with carbonyl complexes of different transition metals, aiming for the preparation of iron-based mixed-metal clusters stabilized by a nitrido ligand.[6,7] The interstitial atom plays an essential role in these syntheses, limiting the fragmentation of the starting material and directing the reconstruction of *closo* polyhedra. In order to prove the generality of this approach, and to expand this kind of chemistry as much as possible, we turned our investigations to the metals of groups 6, 7 and 10. We describe here the synthesis and characterization of several bimetallic species containing molybdenum or tungsten. These organometallic species may suggest a new approach to the preparation of transition metal nitrides,[8] which are widely investigated for their catalytic properties.[9]

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Results

Syntheses

$[Fe_5MoN(CO)_{14}(C_5H_5)]^{2-}$ (1) and $[Fe_5WN(CO)_{14}(C_5H_5)]^{2-}$ (2)

The carbido dianion $[Fe_4C(CO)_{12}]^{2-}$ reacts with a large variety of metal complexes acting as Lewis acids, to give metal-cage expansion.[10] In contrast, the nitrido species $[Fe_4N(CO)_{12}]^-$, because of the low specific charge, reacts only after reduction, possibly through the labilization of a carbonyl ligand.[11] Under these conditions, the nitride reagent is partially destroyed, and the iron carbonyl fragment can contribute to the construction of larger metal cages. We have already exploited this approach to obtain $[Fe_6N(CO)_{15}]^{3-}$ [6] and $[Fe_5RhN(CO)_{15}]^{2-}$.[7] While attempting the synthesis of heterometallic species containing molybdenum or tungsten, we tested first nucleophilic anionic metal complexes, such as $[M_2(CO)_{10}]^{2-}$ or $[M(CO)_3(C_5H_5)]^-$ (M = Mo or W).[12] The reaction of $[Fe_4N(CO)_{12}]^-$ with $[Mo(CO)_3(C_5H_5)]^-$ was performed in MeCN, with both reagents as their tetraethylammonium salts in a 2:1 molar ratio. Since the process of cluster growth cannot be described by a simple balanced chemical equation, the best conditions were empirically determined to obtain the maximum yield and the simplest way of purification. Indeed, when the tetranuclear iron cluster was completely consumed (after ca. 18 h) we detected formation of the new cluster species $[Fe_5MoN(CO)_{14}(C_5H_5)]^{2-}$ (**1**), together with the known compound $[Fe_6N(CO)_{15}]^{3-}$ [6] and a large amount of unreacted $[Mo(CO)_3(C_5H_5)]^-$. The anion **1** was separated by extraction with methanol and recovered by addition of a bulky cation. The reaction with $[W(CO)_3(C_5H_5)]^-$ proceeds exactly the same way, usually requiring more time to be completed, with lower yields. Frequently, the final products **1** and **2** are slightly contaminated by traces of the $[M(CO)_3(C_5H_5)]^-$ reagents.

$[Fe_3Mo_3N(CO)_{18}]^{3-}$ (3) and $[Fe_3W_3N(CO)_{18}]^{3-}$ (4)

The reaction of $[Fe_4N(CO)_{12}]^-$ with $[Mo_2(CO)_{10}]^{2-}$ or $[W_2(CO)_{10}]^{2-}$ (both as $[NEt_4]^+$ salts in a 1:1 molar ratio) is much more rapid and selective than above, yielding mainly $[Fe_3M_3N(CO)_{18}]^{3-}$. In this case the difference of reactivity between molybdenum and tungsten is relevant: the reaction with $[Mo_2(CO)_{10}]^{2-}$ in refluxing MeCN is completed within 1 h while the tungsten derivative requires more than 5 h, even in EtCN where the boiling temperature is ca. 15 °C higher. At the end, the soluble minor impurities can be extracted in methanol, leaving behind a residue which is analytically pure according to elemental analyses. Crystals of the salt $[NEt_4]_3$**3** were grown from acetonitrile/diisopropyl ether,[13] but, unfortunately, were unsuitable for an X-ray determination; we had to prepare many different salts by cation exchange with tetraalkylammonium halides. The same metathesis proved unsuccessful for tungsten, and therefore we could only obtain the parameters of the unit cell of $[NEt_4]_3$**4**, which was isomorphous with $[NEt_4]_3$**3**, thus confirming its formula. The infrared spectra of **3** and **4** are almost superimposable, suggesting that the two compounds are also isostructural in solution.

$[HFe_5MoN(CO)_{16}]^{2-}$ (5)

The trianion **3** can be also obtained in slightly lower yields from the reaction between $[Fe_4N(CO)_{12}]^-$ and a large excess of $[Mo(CO)_3(Me_3C_6H_3)]$ in refluxing THF. In this case, the new dianion **5** is formed as a by-product; it can be separated by selective extraction with methanol, and then precipitated in a microcrystalline form by the addition of bulky organic cations. Crystals of the $[PPh_4]^+$ and $[N(PPh_3)_2]^+$ salts, both unsuitable for X-ray analysis, were obtained by this method after crystallization from THF/2-propanol. The salt $[PPh_4]_2$**5** allowed a partial structural determination, which unambiguously showed an octahedral metallic framework with a Mo:Fe ratio of 1:5.[14] Several alternative procedures have been unsuccessfully tested to selectively obtain **5** or the hypothetical Fe−W−N analogue; they include the reaction between $[Fe_4N(CO)_{12}]^-$ and the neutral complexes $[M(CO)_3(NCEt)_3]$ or the reaction between the same iron cluster and the bimetallic anions $[HFeM(CO)_9]^-$.[15]

Solid-State Structures

Molecular structures of $[Fe_5Mo(CO)_{14}(C_5H_5)]^{2-}$ and $[Fe_5W(CO)_{14}(C_5H_5)]^{2-}$

The solid-state structures of the two anions have been determined from their $[PPh_4]^+$ salts. $[PPh_4]_2$**1** and $[PPh_4]_2$**2**$\cdot C_4H_8O$ crystallize in different space groups, owing to the presence of one molecule of crystallization (THF) in the latter. However, the two clusters **1** and **2** have almost identical molecular geometries, with strikingly similar structural parameters. Relevant bond lengths and angles are presented in Table 1, and the structure of **1** is shown in Figure 1. The six metal atoms define an octahedron with an interstitial nitrogen atom. The cyclopentadienyl ligand is bound to molybdenum (or tungsten in **2**).

The clusters possess three edge-bridging ligands, the remainder being terminal. The disposition of the carbonyl groups strictly recalls that found in the heterometallic species $[Fe_5M'N(CO)_{15}]^{2-}$ (M′ = Rh or Ir).[7] This similarity is not unexpected considering that the "$M(C_5H_5)^-$" and the "$M'(CO)^-$" fragments are isoelectronic (12 valence electrons). As such, the four anions can be envisaged as adducts (from the stoichiometric and electronic point of view) between the well-known square pyramidal $[Fe_5N(CO)_{14}]^-$ cluster (74 valence electrons)[16] and the $[M-L]^-$ fragments, thus representing a nice example of the relationship between *nido* and *closo* cluster cages.[17]

The average bond lengths (Å) and angles (°) for the metal cage and the ligand environment are collected in Table 2. From the intermetallic distances in **1**, the covalent radii of iron and molybdenum can be estimated as r_{Fe} = 1.32 and r_{Mo} = 1.52 Å. The metal−nitrogen bond lengths also differ by 0.19 Å, suggesting that the interstitial ligand does not

Table 1. Selected interatomic distances (Å) and angles (°) for $[Fe_5MoN(CO)_{14}(C_5H_5)]^{2-}$ **(1)** and $[Fe_5WN(CO)_{14}(C_5H_5)]^{2-}$ **(2)**, with estimated standard deviations in parentheses

	(**1**, M = Mo)	(**2**, M = W)
M−Fe(1)	2.860(1)	2.839(1)
M−Fe(2)	2.847(1)	2.845(1)
M−Fe(3)	2.850(1)	2.825(1)
M−Fe(4)	2.800(1)	2.818(1)
Fe(1)−Fe(2)	2.566(1)	2.562(1)
Fe(1)−Fe(4)	2.701(1)	2.684(1)
Fe(1)−Fe(5)	2.634(1)	2.654(1)
Fe(2)−Fe(3)	2.663(1)	2.668(1)
Fe(2)−Fe(5)	2.675(1)	2.646(1)
Fe(3)−Fe(4)	2.687(1)	2.690(1)
Fe(3)−Fe(5)	2.608(1)	2.591(1)
Fe(4)−Fe(5)	2.637(1)	2.589(1)
M−N	2.075(3)	2.059(2)
Fe(1)−N	1.870(3)	1.874(2)
Fe(2)−N	1.888(2)	1.870(2)
Fe(3)−N	1.883(3)	1.882(2)
Fe(4)−N	1.871(3)	1.878(2)
Fe(5)−N	1.909(3)	1.893(2)
M−C(12)	2.060(5)	2.062(3)
M−C(13)	2.139(3)	2.069(3)
M−C(15)	2.279(5)	2.289(4)
M−C(16)	2.276(6)	2.277(3)
M−C(17)	2.306(6)	2.299(3)
M−C(18)	2.372(6)	2.343(3)
M−C(19)	2.328(5)	2.331(3)
Fe(1)−C(1)	1.750(5)	1.758(3)
Fe(1)−C(2)	1.734(5)	1.738(3)
Fe(1)−C(14)	1.928(4)	1.958(3)
Fe(2)−C(3)	1.756(4)	1.767(3)
Fe(2)−C(4)	1.752(4)	1.753(3)
Fe(2)−C(14)	1.994(5)	1.944(3)
Fe(3)−C(5)	1.769(4)	1.775(3)
Fe(3)−C(6)	1.753(5)	1.767(3)
Fe(3)−C(10)	2.252(5)	2.240(3)
Fe(3)−C(12)	2.123(5)	2.067(3)
Fe(4)−C(7)	1.754(4)	1.766(3)
Fe(4)−C(8)	1.766(4)	1.762(3)
Fe(4)−C(13)	1.948(4)	2.040(3)
Fe(5)−C(9)	1.717(5)	1.761(3)
Fe(5)−C(10)	1.856(5)	1.837(3)
Fe(5)−C(11)	1.782(4)	1.824(3)
M−C(12)−O(12)	144.8(4)	143.6(2)
M−C(13)−O(13)	138.2(3)	142.7(2)
Fe(3)−C(12)−O(12)	129.2(4)	129.9(2)
Fe(4)−C(13)−O(13)	135.3(3)	130.6(2)
Fe(5)−C(10)−O(10)	152.9(4)	153.3(3)
Fe(5)−C(11)−O(11)	168.1(5)	157.3(3)

Table 2. Average interatomic distances (in Å) and angles in the nitride clusters **1−3**; (t = terminal, br = bridging, Cp = cyclopentadienyl)

	1 (M = Mo)	**2** (M = W)	**3** (M = Mo)
Fe−M	2.840	2.832	2.845
Mo−Mo			3.145
Fe−Fe	2.646	2.636	2.609
Fe−N	1.884	1.879	1.945
M−N	2.075	2.059	2.104
Fe−C_t	1.76	1.77	1.78
Mo−C_t			1.93
Fe−C_{br}	2.00	2.00	
M−C_{br}	2.10	2.07	
M−C_{Cp}	2.31	2.31	
C_t−O_t	1.16	1.15	1.16
C_{br}−O_{br}	1.18	1.17	
Fe−C_t−O_t	172°	172°	171°
Mo−C_t−O_t			176°
Fe−C_{br}−O_{br}	136°	135°	
M−C_{br}−O_{br}	142°	143°	

interact preferentially with iron or molybdenum. However, the $Fe(CO)_3$ vertex opposite to the MoCp group shows the longest Fe(5)−N separation (1.909 Å), which could be indicative of an excess of electron density on iron [contributed by the three terminal ligands CO(9), CO(10) and CO(11)]. In agreement with this, the CO(10) and CO(11) ligands show some deviation from linearity, and short nonbonding contacts with Fe(3) and Fe(4). CO(12) and CO(13), spanning Fe−Mo edges, are asymmetric; if the different dimensions of Mo and Fe, and the M−C−O angles are taken into account, the two carbonyl groups appears to interact more strongly with the molybdenum centres.

In the Fe−W cluster the cage undergoes a small, but significant, contraction and the distances are all shorter by about 0.01 Å. As a consequence, the apparent metallic radii in **2** are r_{Fe} = 1.32 and r_W = 1.51 Å. The difference between the W−N and the Fe−N bond lengths is only 0.18 Å, slightly smaller than expected, suggesting a negligible preference of nitrogen for tungsten.

Also, the parameters for the outer ligands are very similar in the two homologous clusters, and, indeed, the only relevant difference in their ligand architecture is a more marked tilting of CO(11) in **2** toward a bridging coordination.

Molecular structure of $[Fe_3Mo_3N(CO)_{18}]^{3-}$

The molecular structure of this trianion was determined on the mixed salt $[NMe_3(CH_2Ph)]_2[NEt_4]$**3**. The anion is depicted in Figure 2, and the relevant structural parameters are listed in Table 3. Compound **3** also has an octahedral metallic framework, with the three molybdenum atom in a *fac* arrangement. The architecture of the eighteen carbonyl ligands can be viewed as a perturbation of the idealized high symmetry system having three terminal ligands for each metal atom. In the real situation, many iron-bound CO groups are tilted toward molybdenum in order to compensate the different number of valence electrons. As a result, the average M−C−O angle is much smaller for Fe than Mo (171 vs. 176°). Nevertheless, only CO(18) can be classified as a bridging, though asymmetric, ligand. This description is also in keeping with the solution infrared spectrum, which shows a high-lying band at 1820 cm^{-1} indicative of semibridging ligands, overlapping a very weak band (at 1748 cm^{-1}) attributable to "true" bridging ligands.

The octahedral metal cage of **3** is heavily distorted, showing short Fe−Fe [2.609 Å] and very long Mo−Mo [3.145 Å] separations. The Mo−Mo bond lengths in **3** are quite unusual for octahedral clusters, but are well within the range observed for Mo−Mo single bonds.[18,19] The covalent radii of the metal atoms are, therefore, r_{Fe} = 1.30 and r_{Mo} = 1.57 Å, a difference of 0.27 Å. The average Fe−Mo interaction is 2.845 Å, which matches the sum of the apparent radii. However, when examining the metal−ligand bond

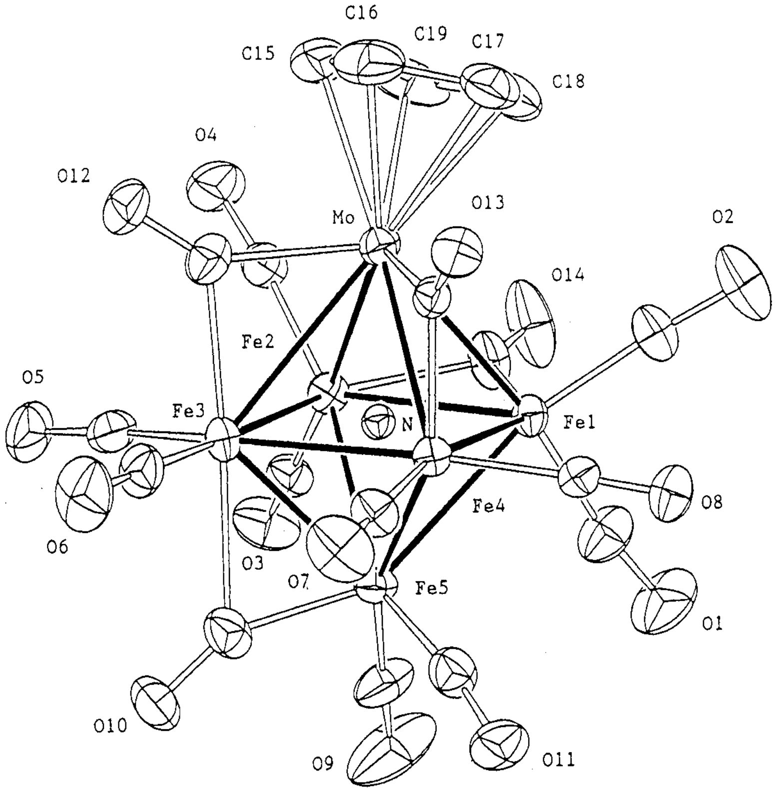

Figure 1. The solid state structure of $[Fe_5MoN(CO)_{14}(C_5H_5)]^{2-}$; ellipsoids are drawn at the 30% probability level; the carbon atoms of the carbonyl ligands are labelled as the oxygen to which they are attached

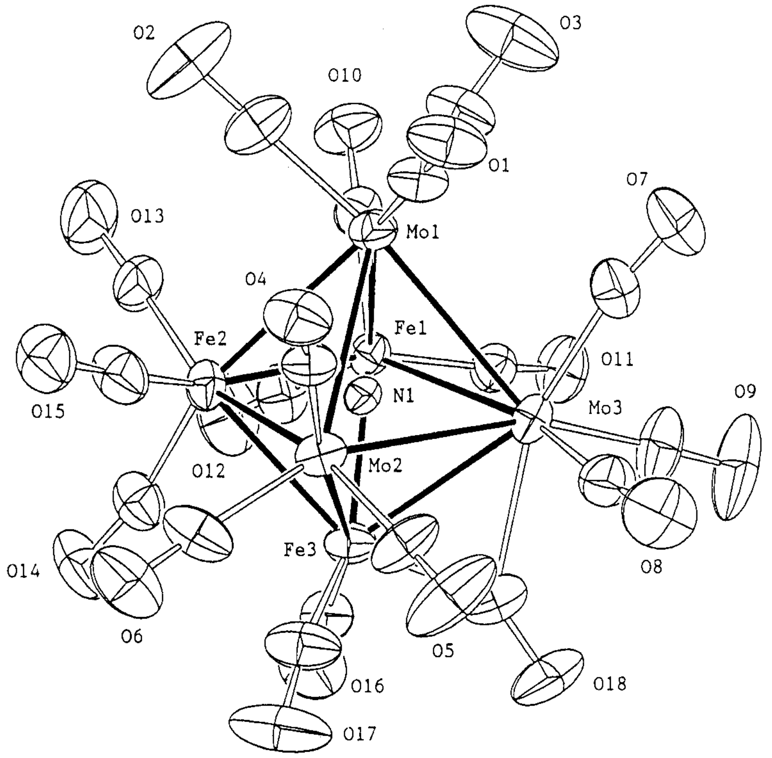

Figure 2. The solid state structure of $[Fe_3Mo_3N(CO)_{18}]^{3-}$

lengths, the difference between Mo and Fe appears much smaller: 0.14 Å for the metal−CO distances, and 0.16 Å for the metal−nitrogen separations. For example, the Mo−N bond lengths average 2.104 Å and the Fe−N 1.945 Å. On that basis, it appears that the three molybdenum atoms bind much more efficiently with the ligands (both external and interstitial), whereas iron would rather reinforce the bonds within the metal cages.

Table 3. Selected interatomic distances (Å) and angles (°) for $[Fe_3Mo_3N(CO)_{18}]^-$ **(3)** with estimated standard deviations in parentheses

Mo(1)−Mo(2)	3.143(1)
Mo(1)−Mo(3)	
Mo(1)−Fe(1)	2.852(1)
Mo(1)−Fe(2)	2.921(1)
Mo(2)−Mo(3)	3.212(1)
Mo(2)−Fe(2)	2.801(1)
Mo(2)−Fe(3)	2.825(1)
Mo(3)−Fe(1)	2.892(1)
Mo(3)−Fe(3)	2.779(1)
Fe(1)−Fe(2)	2.557(1)
Fe(1)−Fe(3)	2.620(1)
Fe(2)−Fe(3)	2.649(1)
Mo(1)−N	2.102(4)
Mo(2)−N	2.109(4)
Mo(3)−N	2.101(3)
Fe(1)−N	1.950(4)
Fe(2)−N	1.956(3)
Fe(3)−N	1.928(4)
Mo(1)−C(1)	1.915(6)
Mo(1)−C(2)	1.921(7)
Mo(1)−C(3)	1.910(8)
Mo(2)−C(4)	1.900(6)
Mo(2)−C(5)	1.895(6)
Mo(2)−C(6)	1.943(7)
Mo(3)−C(7)	1.973(7)
Mo(3)−C(8)	1.925(7)
Mo(3)−C(9)	1.944(7)
Mo(3)−C(18)	2.333(8)
Fe(1)−C(10)	1.804(7)
Fe(1)−C(11)	1.764(6)
Fe(1)−C(12)	1.769(6)
Fe(2)−C(13)	1.750(8)
Fe(2)−C(14)	1.801(7)
Fe(2)−C(15)	1.735(7)
Fe(3)−C(16)	1.769(6)
Fe(3)−C(17)	1.759(8)
Fe(3)−C(18)	1.893(6)
Mo(3)−C(18)−O(18)	133.3(5)°
Fe(3)−C(18)−O(18)	145.2(6)°

Experimental Section

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques.[20] $[NEt_4][Fe_4N(CO)_{12}]$,[21] $[NEt_4][M(CO)_3(C_5H_5)]$,[22] $[NEt_4]_2[M_2(CO)_{10}]$[23] and $[Mo(CO)_3(Me_3C_6H_3)]$[24] were prepared by literature methods. Infrared spectra in solution were recorded on a Perkin−Elmer 16 PC FT-IR spectrophotometer, using calcium fluoride cells previously purged with N_2. Elemental analyses were carried out by the staff of Laboratorio di Analisi of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica. ^{1}H NMR spectra were recorded on a Bruker AC200 spectrometer. Yields refer to the starting iron nitride.

Synthesis of $[PPh_4]_2[Fe_5MoN(CO)_{14}(C_5H_5)]$: $[NEt_4][Fe_4N(CO)_{12}]$ (0.32 g, 0.45 mmol) and $[NEt_4][Mo(CO)_3(C_5H_5)]$ (0.08 g, 0.22 mmol) were dissolved in MeCN (20 mL) and refluxed for 18 h. The solvent was evaporated in vacuum, and the residue suspended in MeOH (20 mL). The solid left undissolved (which consisted of $[NEt_4]_3[Fe_6N(CO)_{15}]$ and decomposition products) was removed by filtration, and solid $[PPh_4]$Br (1 g) was added. The precipitate was collected by filtration, washed with 2-propanol and dried. The dark red solid was extracted from the frit with the minimum amount of THF and layered with 2-propanol to give dark crystals of $[PPh_4]_2[Fe_5MoN(CO)_{14}(C_5H_5)]$. Elemental analyses of the product material are satisfactory. Yield 0.14 g; 20%.

The salt $[PPh_4]_2$**1** is insoluble in MeOH or 2-propanol, sparingly soluble in THF, and very soluble in acetone or MeCN. − IR (MeCN): ν(CO) = 2002m, 1943vs, 1745mw cm^{-1}. − ^{1}H NMR (CD_3CN): δ = 4.59 (s, 5 H, C_5H_5), 7.9 (m, 40 H, $[PPh_4]^+$).

Synthesis of $[PPh_4]_2[Fe_5WN(CO)_{14}(C_5H_5)]$THF: $[NEt_4][Fe_4N(CO)_{12}]$ (0.51 g, 0.72 mmol) and $[NEt_4][W(CO)_3(C_5H_5)]$ (0.16 g, 0.35 mmol) were dissolved in MeCN (30 mL) and refluxed for 24 h. The mixture was worked-up as above. Typical yields are as low as 5−10%. − $C_{71}H_{53}Fe_5NO_{15}P_2W$ (1685.2): calcd. C 50.60, H 3.17, N 0.83; found C 51.4, H 3.0, N 0.6. Elemental analysis confirms the presence of one molecule of clathrated THF. − IR (MeCN): ν(CO) = 2020w, 2000w, 1958vs, 1946sh, 1811m, 1784mw, 1725mw cm^{-1}. − ^{1}H NMR (CD_3CN): δ = 4.73 (s, 5 H, C_5H_5), 7.9 (m, 40 H, $[PPh_4]^+$).

Synthesis of $[NEt_4]_3[Fe_3Mo_3N(CO)_{18}]$: $[NEt_4][Fe_4N(CO)_{12}]$ (0.24 g, 0.34 mmol) and $[NEt_4]_2[Mo_2(CO)_{10}]$ (0.22 g, 0.30 mmol) were dissolved in MeCN (20 mL) and refluxed for 1 h. The solvent was then evaporated in vacuum, and the residue suspended in MeOH (20 mL). The solid residue was collected by filtration, washed with 2-propanol and then dried. The black solid was extracted from the frit with the minimum amount of MeCN and layered with diisopropyl ether to give black crystals of $[NEt_4]_3[Fe_3Mo_3N(CO)_{18}]$]. Yield 0.12 g, 26%.

Salts of **3** are usually insoluble in alcohols or THF, sparingly soluble in acetone and very soluble in MeCN. − IR (MeCN): ν(CO) = 2006 vw, 1931 vs, 1822 w,br 1748 w cm^{-1}. − $C_{42}H_{60}Fe_3Mo_3N_4O_{18}$ (1364.3): calcd. C 36.98, H 4.43, N 4.11; found C 37.2, H 4.5, N 4.3.

Crystals of the mixed salt used for X-ray analysis were obtained from an incomplete metathesis reaction between $[NEt_4]_3$**3** and $[NMe_3(CH_2Ph)]$Cl in MeCN.

Synthesis of $[NEt_4]_3[Fe_3W_3N(CO)_{18}]$: $[NEt_4][Fe_4N(CO)_{12}]$ (0.24 g, 0.34 mmol) and $[NEt_4]_2[W_2(CO)_{10}]$ (0.31 g, 0.34 mmol) were dissolved in EtCN (20 mL) and refluxed for 4 h. The solvent was then evaporated in vacuo and the black residue treated as above. − IR (MeCN): ν(CO) = 2007 vw, 1933 vs, 1821 w,br 1759 w cm^{-1}.

Synthesis of $[PPh_4]_2[HFe_5MoN(CO)_{16}]$: $[NEt_4][Fe_4N(CO)_{12}]$ (0.55 g, 0.78 mmol) and $[Mo(CO)_3(Me_3C_6H_3)]$ (1.04 g, 3.47 mmol) were dissolved in THF (20 mL) and refluxed for 5 h. The solvent was evaporated in vacuum, and the residue washed repeatedly with toluene (4 × 10 mL). It was than suspended in MeOH (20 mL). Solid $[NEt_4]$Br was added and the mixture was stirred for 0.5 h. Addition of water induced complete precipitation. The solid was collected by filtration, washed with water and dried. Impure $[NEt_4]_2[HFe_5MoN(CO)_{16}]$ was extracted from the frit with THF leaving the insoluble $[NEt_4]_3$**3** behind (yield 18%).

Pure $[PPh_4]_2$**5** was obtained by metathesis. The THF was evaporated in vacuo, the residue was dissolved in MeOH and $[PPh_4]$Br was added. The microcrystalline solid was collected by filtration, washed with 2-propanol, dried and dissolved in the minimum amount of THF. Crystals were obtained by layering with 2-propanol. Yield 21%. − IR (THF): ν(CO) = 1959 vs, 1880m,br 1799 m cm^{-1}. − ^{1}H NMR (CD_3CN): δ = −19.77. − $C_{64}H_{41}Fe_5MoNO_{16}P_2$ (1517.2): C 50.67, H 2.72, N 0.92; found C 50.3, H 2.7, N 0.9.

X-ray Data Collection and Structure Determination: Crystal data and other experimental details are summarized in Table 4. The dif-

Table 4. Crystallographic data and collection parameters for compounds $[PPh_4]_2\mathbf{1}$, $[PPh_4]_2\mathbf{2}\cdot OC_4H_8$ and $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$

Compound	$[PPh_4]_2\mathbf{1}$	$[PPh_4]_2\mathbf{2}\cdot OC_4H_8$	$[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$
Empirical formula	$C_{67}H_{45}Fe_5MoNP_2O_{14}$	$C_{71}H_{53}Fe_5NO_{15}P_2W$	$C_{46}H_{52}Fe_3Mo_3N_4O_{18}$
Mass	1525.2	1685.2	1404.3
Space group	*P*1(bar) (no.2)	*C*2/*c* (no.15)	*P*1(bar) (no.2)
a/Å	11.297(2)	41.244(4)	12.018(2)
b/Å	12.712(2)	15.135(1)	13.164(2)
c/Å	23.993(4)	21.907(2)	18.270(2)
α/°	99.70(1)		77.87(1)
β/°	99.89(1)	97.32(1)	89.73(1)
γ/°	106.87(1)		75.80(1)
V/Å^3	3160(1)	13563(2)	2751(1)
Z	2	8	2
D_c/g cm^{-3}	1.603	1.650	1.696
μ (Mo-K_α)/cm^{-1}	14.2	28.8	14.9
Final R and R_w indices[a]	0.037, 0.047	0.023, 0.030	0.044, 0.052

[a] $R = [\Sigma(\,|F_o - k\,|F_c\,|\,|)/\Sigma F_o]$, $R_w = [\Sigma w(F_o - k\,|F_c\,|)^2/\Sigma w F_o{}^2]^{1/2}$, $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(F_o{}^2) + (0.04F_o{}^2)^2]^{1/2}/2F_o$.

fraction experiments were carried out on a Siemens SMART CCD area-detector diffractometer at room temperature using Mo-K_α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrices were obtained from the least-squares refinement of 150 (for $[PPh_4]_2\mathbf{1}$), 278 (for $[PPh_4]_2\mathbf{2}\cdot OC_4H_8$), and 100 {for $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$} reflections measured in three different sets of 15 frames each, in the range $3 < \theta < 23°$. At the end of the data collection the first 50 frames, containing 416 reflections (for $[PPh_4]_2\mathbf{1}$), 894 reflections (for $[PPh_4]_2\mathbf{2}C_4H_8O$), and 249 reflections (for $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$) were recollected to monitor crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[25] and an absorption correction was applied (SADABS)[26] to the 34144 collected reflections of $[PPh_4]_2\mathbf{1}$ {13768 of which are unique with $R_{int} = 0.0224$ [$R_{int} = \Sigma|F_o^2 - F_{mean}^2|/\Sigma F_o^2$]}, the 76667 collected reflections of $[PPh_4]_2\mathbf{2}\cdot C_4H_8O$ (16514 of which are unique with $R_{int} = 0.0263$), and the 29939 collected reflections of $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$ (11983 of which are unique with $R_{int} = 0.0436$).

The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package[27] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref.[28] The structures were solved by SHELXS direct methods (contained in the Personal SDP)[27] and refined by full-matrix least-squares minimizing the function $\Sigma w(F_o - kF_c)^2$ (refinement on F).

In $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$ one of the two $[NMe_3(CH_2Ph)]^+$ cations is partially disordered, with four phenylic carbon atoms split into eight peaks, four with occupancy factors of 0.60, and four with occupancy factors of 0.40. These eight atoms were refined with isotropic thermal parameters. All the other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to the eight disordered carbon atoms were ignored. All the other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å, B = 1.15 times that of the carbon atom to which they are attached) and not refined. In the final difference Fourier maps, maximum residuals were 0.82(7) e Å^{-3} at 0.84 Å from Fe(2) in $[PPh_4]_2\mathbf{1}$, 0.57(6) e Å^{-3} at 1.04 Å from C(222) (a carbon atom of a $[PPh_4]^+$ cation) in $[PPh_4]_2\mathbf{2}\cdot C_4H_8O$, and 1.36(9) e Å^{-3} at 1.08 Å from Fe(2) in $[NMe_3(CH_2Ph)]_2[NEt_4]\mathbf{3}$.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-135691 (**1**), CCDC-135692 (**2**), and CCDC-135693 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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[14] Monoclinic, space group $P2_1/n$ (n. 14) $a = 11.492(2)$ $b = 14.845(3)$ $c = 19.149(3)$ Å $\beta = 100.78(2)°$, $V = 3209$ Å^3, $Z = 2$. The structure solution was incomplete, because of ligand disorder.

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