**Direct Lanthanide–Transition Metal Interactions: Synthesis of (NH₃)₂YbFe(CO)₄ and Crystal Structures of \( [(CH₃CN)₃YbFe(CO)₄]⁺ \cdot CH₃CN \) and \( [(CH₃CN)₃YbFe(CO)₄]⁻ \)**

**Haibin Deng,† Sung-Ho Chun, Pierre Florian, Philip J. Grandinetti, and Sheldon G. Shore*\]**

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received November 22, 1995\(^b\)

The heterometal complex \((NH₃)₂YbFe(CO)₄\) was prepared from the reduction of \(Fe_3(CO)_{12}\) by Yb in liquid ammonia. Ammonia was displaced from \((NH₃)₂YbFe(CO)₄\) by acetonitrile in acetonitrile solution, and the crystalline compounds \([(CH₃CN)₃YbFe(CO)₄]⁺ \cdot CH₃CN \) and \([(CH₃CN)₃YbFe(CO)₄]⁻ \) were obtained. An earlier X-ray study of \([(CH₃CN)₃YbFe(CO)₄]⁺ \cdot CH₃CN \) showed that it is a ladder polymer with direct Yb–Fe bonds. In the present study, an X-ray crystal structure analysis also showed that \([(CH₃CN)₃YbFe(CO)₄]⁺ \) is a sheetlike array with direct Yb–Fe bonds. Crystal data for \([(CH₃CN)₃YbFe(CO)₄]⁺ \cdot CH₃CN \): monoclinic space group \(P2_1/c\), \(a = 21.515(8) \) Å, \(b = 7.838(2) \) Å, \(c = 19.866(6) \) Å, \(β = 105.47(2)°, Z = 4\). Crystal data for \([(CH₃CN)₃YbFe(CO)₄]⁻ \): monoclinic space group \(P2_h/n\), \(a = 8.364(3) \) Å, \(b = 9.605(5) \) Å, \(c = 17.240(6) \) Å, \(β = 92.22(3)°, Z = 4\). Electrical conductivity measurements in acetonitrile show that these acetonitrile complexes are partially dissociated into ionic species. IR and NMR spectra of the solutions reveal the presence of \([HFe(CO)₄]⁻\). However, upon recrystallization, the acetonitrile complexes show no evidence for the presence of \([HFe(CO)₄]^-\) on the basis of their IR spectra. The solid state MAS \(^{1}H\) NMR spectra of deuterated acetonitrile complexes give no evidence for \([HFe(CO)₄]^-\). It appears that rupture of the Yb–Fe bond could occur in solution to generate the ion pair \([L₂Yb]^{2+}[Fe(CO)₄]^{2−}\), but then the highly basic \([Fe(CO)₄]^{2−}\) anion could abstract a proton from a coordinated acetonitrile ligand to form \([HFe(CO)₄]^{−}\). However, upon crystallization, the proton could be transferred back to the ligand, which results in the neutral polymeric species.

**Introduction**

Metal–metal bonds are one of the principal themes of molecular organometallic and cluster chemistry. Bonding between transition metals are most common. However, metal–metal bonds between transition metals and electropositive elements, such as alkali,\(^2\) alkaline earth,\(^3\) lanthanide,\(^4,5\) and actinide elements\(^6\) are relatively rare. Direct transition metal–lanthanide bonds have been largely inferred from infrared and NMR spectroscopic data,\(^4,5\) while X-ray diffraction studies are scarce. A \(Lu^{3+}\) to Ru bond (2.955 Å) in \([Cp₂(THF)LuRu(CO)₂-\) would be shorter than the \(3.097 \) Å \([Cp₂Rh(CO)₂\) Ru(CO)] bond in \([Cp₂Rh(CO)₂Ru(CO)]\). A Lu–Fe bond in \((NH₃)₂YbFe(CO)₄\) would be much stronger than the \(3.51 \) Å \((NH₃)₂YbFe(CO)₄\) bond in \([NH₃]₂(YbFe(CO)₄)\). Our strategy for the synthesis of compounds containing direct transition metal–lanthanide bonds is to utilize divalent lanthanides and highly reduced transition metal centers, the former being softer Lewis acids than their trivalent counterparts\(^8\) and the latter being soft Lewis bases and excellent nucleophiles. In cases where transition metal centers are not sufficiently nucleophilic, the lanthanide ions either are surrounded by coordinating solvents, forming solvent-separated ion pairs with transition metal carbonylates,\(^9,10\) or are coordinated by carbonyl oxygens of the transition metal carbonylates, forming isocarbonyl linkages.\(^10\)

We describe here the reduction of the neutral transition metal carbonyl \(Fe_3(CO)_{12}\) by the lanthanide element ytterbium in liquid ammonia. Details of the synthesis and characterization of \((NH₃)₂YbFe(CO)₄\), \([(CH₃CN)₃YbFe(CO)₄]⁺ \cdot CH₃CN \), and \([(CH₃CN)₃YbFe(CO)₄]⁻ \) are given in the next section.

---

1. Deceased.


5. See, for example: *Organometallics*, 1995, 11, 5332.

6. (a) *Organometallics*, 1985, 8, 901.


---

1. Deceased.


5. See, for example: *Organometallics*, 1995, 11, 5332.

6. (a) *Organometallics*, 1985, 8, 901.


---

1. Deceased.


5. See, for example: *Organometallics*, 1995, 11, 5332.

6. (a) *Organometallics*, 1985, 8, 901.


[(CH₃CN)₃YbFe(CO)₄]∞ are described. Crystal structures of the acetonitrile complexes confirm the presence of direct metal–metal bonds between a divalent Yb²⁺ ion and a formal Fe(−II) atom.

Results and Discussion

Preparation of (NH₃)₂YbFe(CO)₄, [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN, and [(CH₃CN)₃YbFe(CO)₄]∞. Ytterbium is a strong reducing agent in liquid ammonia. It ionizes to give Yb²⁺ and solvated electrons. The ammonia solution reduces Fe(CO)₁₂ to form an iron carbonylate salt of ytterbium according to eq 1.

\[ 3\text{Yb} + \text{Fe}_3(\text{CO})_{12} \xrightarrow{\text{NH}_3(0)} 3(\text{NH}_3)_2\text{YbFe(CO)}_4 \] (1)

The solid compound isolated from this reaction after prolonged residence under dynamic vacuum contains approximately two NH₃ molecules per Yb atom, as determined by elemental analysis. It is an extremely air- and moisture-sensitive yellow solid which sometimes catches fire instantly upon exposure to air. It is not soluble in hydrocarbon or ether solvents. It is slightly soluble in acetonitrile, but the NH₃ ligands are displaced by CH₃CN molecules. Noticeable decomposition of the acetonitrile solutions is observed after several hours at room temperature.

While solutions of (NH₃)₂YbFe(CO)₄ in acetonitrile are unstable at room temperature, displacement of ammonia ligands by acetonitrile at low temperature produces discrete, isolable single crystals of [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN and [(CH₃CN)₃YbFe(CO)₄]∞. These acetonitrile complexes are orange and are also highly air sensitive.

Structures of [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN and [(CH₃CN)₃YbFe(CO)₄]∞. From single-crystal X-ray analyses, the molecular structures of [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN and [(CH₃CN)₃YbFe(CO)₄]∞ were determined. The structure of [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN was briefly described in a preliminary communication. It consists of "polymeric ladders" extending along the crystallographic b axis of the lattice. Figure 1 shows an ORTEP drawing of a portion of the lattice. Figure 2a displays the coordination geometries of the Fe and Yb atoms. The Fe(CO)₄ units have distorted trigonal-bipyramidal geometries, while those of the Yb²⁺ ions are distorted octahedra. In addition to three CH₃CN ligands, each Yb²⁺ ion is coordinated to two carbonyl oxygens from two different Fe(CO)₄ units; each Fe(CO)₄ unit is in turn connected to two different Yb²⁺ ions via isocarbonyl linkages, thus forming a zigzag ···Yb–O–C–Fe–C–O··· chain. Two such chains are coupled to form a ladder through Yb–Fe interactions. The Yb–Fe distance is 3.010(1) Å.

The X-ray structure of [(CH₃CN)₃YbFe(CO)₄]∞ consists of "polymeric sheets" stacked perpendicular to the crystallographic c axis. Figure 3 shows ORTEP drawings of a portion of the sheet. Figure 2b displays the coordination geometries of the Fe and Yb atoms. Crystal data and selected bond distances and angles for both structures are reported in Tables 1 and 2.


![Figure 1. Molecular structure of [(CH₃CN)₂YbFe(CO)₄]₂·CH₃CN.](attachment:image1)

![Figure 2. Coordination geometries of Yb and Fe in (a) [(CH₃CN)₃YbFe(CO)₄]∞ and (b) [(CH₃CN)₃YbFe(CO)₄]∞.](attachment:image2)
to the higher coordination number of Yb$^{2+}$ in [(CH$_3$CN)$_3$YbFe(CO)$_4$].

The most salient features of these two structures are the direct Yb–Fe interactions and the distorted trigonal bipyramidal geometry of the Fe coordination sphere. The Yb–Fe distances of 3.010(1) Å in [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$ and 3.046(1) Å in [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$ are comparable to a Yb–Fe distance of 3.00 Å in YbFe$_2$ alloy.\footnote{Wells, A. F. Structural Inorganic Chemistry, 5th ed.; Oxford University Press: New York, 1984; p 1288.} They are 0.19 and 0.15 Å shorter than the sum of Yb and Fe metallic radii (3.2 Å),\footnote{Cannon, J. F.; Robertson, D. L.; Hall, H. T. Mater. Res. Bull. 1972, 7, 5.} respectively. This indicates a significant bonding interaction between Yb and Fe in both structures. Similarly, in [C$_2$(THF)LuRu(CO)$_3$Cp] the direct Lu–Ru bond distance of 2.955 Å$^{2a}$ is 0.10 Å shorter than the sum of the Lu and Ru metallic radii (3.06 Å),\footnote{Wells, F. M. Inorganic Chemistry, Vol. 35, No. 13, 1996 3893} and in [(C$_5$Me$_5$)$_2$Ti(THu(CO)$_3$)Cp] the direct Th–Ru bond distance (3.028 Å$^2$) is 0.11 Å shorter than the sum of Th and Ru metallic radii (3.14 Å).\footnote{Two crystallographically independent but stereochemically similar molecules were found in the crystal structure of [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$·CH$_3$CN. Only one set of bond distances and angles are listed here. See the supplementary material of ref 7 for full listings of bond distances and angles.}
through the application of quasi-relativistic X-ray symmetry, probably due to the predominantly ionic nature of acceptor in \( [(C5 Me 5)2(I)ThRu(CO)2Cp] \) has been developed of this type of dative bond between a low-valent transition metal acceptor interaction between the Fe center in \( [Fe(CO)4]2 \) -site. The Yb \( ^{2+} \) dianion should have an electron pair directed toward an axial angles in proceeding from the Fe coordination sphere of a Yb \( ^{2+} \) in \( [(CH3CN)3YbFe(CO)4]2 \) \( \{CH3CN\}_n \) and \( [(CH3CN)2YbFe(CO)4]_n \) are closer to tetrahedral symmetry, probably due to the predominantly ionic nature of the Yb-Fe bond.

Under \( C3v \) symmetry, the \( ^{10} \)Fe atom in the \( [Fe(CO)4]^{2-} \) dianion should have an electron pair directed toward an axial site. The Yb-Fe bond can thus be described as a donor-acceptor interaction between the Fe center in \( [Fe(CO)4]^{2-} \) and Yb \( ^{2+} \), in spite of its high ionic character (Chart 2a). The concept of this type of dative bond between a low-valent transition metal center as the donor and an electropositive element as the acceptor in \( [(CsMe3)2(I)ThRu(CO)2Cp] \) has been developed through the application of quasi-relativistic X\( \alpha \)-SW calculations.

Contacts between Yb \( ^{2+} \) and carbonyl carbons of \( [Fe(CO)4]^{2-} \) are also observed in \( [(CH3CN)2YbFe(CO)4]_n \) and \( [(CH3CN)YbFe(CO)4]_n \). The three Yb-C distances are 3.026(9), 3.073(8), and 3.201(9) \( \text{Å} \) in the former and 3.12(1), 3.13(1), and 3.17(1) \( \text{Å} \) in the latter. These distances are longer than the respective Yb-Fe bond distances, and the carbonyl groups involved are nearly linear, suggesting that there are only weak interactions between the Yb \( ^{2+} \) ion and the three carbonyl carbons. Therefore, any contribution due to the trimethylamine-like coordination of the FeC\( _3 \) region of \( [Fe(CO)4]^{2-} \) to Yb \( ^{2+} \) (Chart 2b) should be negligible compared to the direct Yb-Fe bonding, unlike that observed by Bau and co-workers in their study of Na\( _2Fe(CO)4\cdot1.5\)(dioxane)\( ^{17a} \) and K\( _2Fe(CO)4\)\( ^{17b} \). They showed that interactions between the alkali metal cation and the C-Fe-C regions may be described as that of a metal-allyl type.

Other bond distances are in the normal range. Due to the high ionic character of the Yb \( ^{2+} \)-ligand bonds, the bond distances increase as the coordination numbers increase. Thus the average Yb-N bond distance of 2.52(2) \( \text{Å} \) in \( [(CH3CN)YbFe(CO)4]_n \) is comparable to that in \( [(CH3CN)2Yb(μ-H)2BH3]_2 \). The average Yb-N bond distance of 2.55(1) \( \text{Å} \) in \( [(CH3CN)2YbFe(CO)4]_n \) is comparable with or shorter than those in \( [(CH3CN)6Yb(μ-H)2B10H12\cdot2CH3CN \) \( (2.55[3] \text{Å}), \) \( (C5Me5)2Yb(C5H5N)2 \) \( (2.57[3] \text{Å}), \) and \( (CH3)2Yb(C2H5N)\( _2 \) \( (2.58[2] \text{Å}) \). The average Yb-O bond distances for the Yb-isocarbonyl linkages in \( [(CH3CN)2YbFe(CO)4]_n \) and \( [(CH3CN)YbFe(CO)4]_n \) are 2.374[7] and 2.48[5] \( \text{Å} \), respectively. The latter is comparable to those involving eight-coordinate trivalent Yb ions\(^{11a-d} \) due to the competing effects of coordination numbers and ionic radii on bond distances.

Interestingly, some of the Yb-N-C bond angles and Yb-O-C bond angles deviate substantially from linearity. The Yb-N-C bond angles range from 135 to 171°, and the Yb-O-C bond angles range from 135 to 168°. This phenomenon is also observed in a variety of compounds in which M-NCCCH coordination or M-isocarbonyl linkages are involved. It has been proposed that the angular position of the metal cation may allow interaction with electron density in both lone pairs and \( π \) orbitals on CH3CN or isocarbonyls.\(^{22} \) On the other hand, the energy gain or loss involved in the bending of the ligands might be sufficiently small that the crystal packing forces would suffice to cause the deviation of the M-N-C and M-O-C bonds from linearity. The Fe-C-O and N-C-C bond angles are close to 180°.

**Proposed Structural Features of (NH\(_3\))\(_2\)YbFe(CO)\(_4\).** Suitable crystals of (NH\(_3\))\(_2\)YbFe(CO)\(_4\) for X-ray analysis could not be produced. However, its essential structural features are likely to be similar to the main structural features of \( [(CH3CN)2YbFe(CO)4]_n \) and \( [(CH3CN)YbFe(CO)4]_n \), on the basis of similarities in their IR spectra and their limited solubilities in acetonitrile. The Nujol mull IR spectrum of (NH\(_3\))\(_2\)YbFe(CO)\(_4\) in the carbonyl stretching region consists of three broad bands (1898 w, br, 1826 m, br, 1758 s, br cm\(^{-1}\)). This spectrum resembles the Nujol IR spectra of \( [(CH3CN)2YbFe(CO)4]_n \) and \( [(CH3CN)YbFe(CO)4]_n \). Thus the Fe(CO)\(_4\) units in (NH\(_3\))\(_2\)YbFe(CO)\(_4\) are believed to be distorted tetrahedra of pseudo-\( C3v \) symmetry (Chart 1), similar to the Fe(CO)\(_4\) units in the acetonitrile complexes (Figure 2). A three-band pattern in the carbonyl stretching region of the

**Chart 1**

![](chart1.png)

<table>
<thead>
<tr>
<th>Avg. Angles C(eq)-Fe-C(eq)</th>
<th>103.8°</th>
<th>99.1°</th>
<th>98.1°</th>
<th>90°</th>
</tr>
</thead>
</table>

**Chart 2**

![](chart2.png)


IR spectrum of an Fe(CO)₄ unit is indicative of C₄v symmetry, while a single band is indicative of tetrahedral symmetry. Local C₄v geometry of Fe(CO)₄ would result from the occupation of an axial site by a Yb⁺⁺ ion in a trigonal-bipyramidal YbFe(CO)₄ coordination sphere, similar to that of the Fe(CO)₄ unit in \( [\text{L} \text{Fe(CO)}_4]_2 \) and \( [\text{L} \text{Fe(CO)}_4] \).

The \([\text{HFe(CO)}_4]^-\) anion has C₃ symmetry. Its IR spectrum contains three bands in the carbonyl stretching region (Nujol mull of K[Fe(CO)₄]; 2017 w, 1928 m, 1835 s, br, cm⁻¹). They are ca. 100 cm⁻¹ higher than those observed in the spectra of \((\text{NH}_3)_2 \text{YbFe(CO)}_4\) and the acetonitrile complexes. It is unlikely that \([\text{HFe(CO)}_4]^-\) is responsible for the Nujol null IR spectra produced by the ammonia and acetonitrile complexes of YbFe(CO)₄, since the MAS solid state ¹H NMR spectra of \((\text{NH}_3)_2 \text{YbFe(CO)}_4\) give no evidence for the presence of \([\text{HFe(CO)}_4]^-\) (δ = 1.05 ppm) or any indication of the presence of \([\text{HFe(CO)}_4]^-\) (δ = -11.2 ppm). Only the deuterium in the coordinated acetonitrile is observed. However, when single crystals of the acetonitrile complexes are dissolved in acetonitrile, the presence of \([\text{HFe(CO)}_4]^-\) is detected in both infrared and NMR spectra. These observations imply that an equilibrium exists between ionic species in solution and polymeric covalent species in the solid state identified by the X-ray structural studies. Electrical conductance measurements of \(\{\text{ICD}_3 \text{CN)}_3 \text{YbFe(CO)}_4\} \text{CD}_3 \text{CN}\) in acetonitrile solution over the concentration range 8.8 × 10⁻⁴ to 9.6 × 10⁻⁴ M gives \(\Lambda_m = 86.2 \text{ cm}^2 \text{ mol}^{-1} \text{ cm}^{-1}\), which falls below the range usually observed for 1:1 electrolytes in CH₃CN solution (\(\Lambda_m = 120 – 160 \text{ cm}^2 \text{ mol}^{-1} \text{ cm}^{-1}\).²³ Thus it appears that \(\{\text{ICD}_3 \text{CN)}_3 \text{YbFe(CO)}_4\} \text{CD}_3 \text{CN}\) is not completely dissociated in CH₃CN solution. In solution, rupture of the Yb–Fe bond could occur to generate the ion pair \(\text{[Yb]} [\text{Fe(CO)}_4]^2-\), but then the highly basic \([\text{Fe(CO)}_4]^2-\) anion could abstract a proton from a coordinated acetonitrile ligand to form \([\text{HFe(CO)}_4]^-\). However, upon crystallization, the proton could be transferred back to the ligand, which would result in the neutral polymeric species. We have not been able to identify CH₃CN⁻ either in solution or as a coordinated ligand. However, we have shown that \([\text{Fe(CO)}_4]^2-\) induces catalytic exchange of deuterium and protium in CH₂CN–CH₃CN mixtures. The exchange process undoubtedly occurs through the initial deprotonation of the acetonitrile to form the \([\text{HFe(CO)}_4]^-\) intermediate.²⁴

Experimental Section

General Data. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of dry, pure N₂. CH₃CN was dried over P₂O₅ with continuous stirring for 5 days, followed by distillation into storage bulbs. CD₃CN (99.96% atomic deuterium, Isotec Inc.) was used as received. NH₃ (Matheson) was used as received. ND₃ was prepared similarly in liquid ND₃. IR (Nujol mull, cm⁻¹): 3345 (w), 3265 (w) (ν₁N=H), 1988 (w), 1826 (m), 1758 (s) (ν₁C=O). Anal. Caled for Cd₃Fe₁₂O₂_y: C, 12.99; H, 1.42; N, 6.94. Found: C, 12.99; H, 1.42; N, 6.94. (ND₃)₂Yb(CO)₄ was prepared similarly in liquid ND₃. IR (Nujol mull, cm⁻¹): 2496 (w) (ν₁N=H), 1898 (w), 1812 (m, sh), 1746 (s) (ν₁C=O). ¹H MAS NMR: ~1.05 ppm.

NMR Spectra in Acetonitrile. \((\text{NH}_3)_3 \text{YbFe(CO)}_4\) in CD₃CN (99.96% atomic deuterium) ¹H NMR: δ 1.96 (q, J = D-D = 2.5 Hz, residual CHD-CN), ~8.96 (s, [HFe(CO)₄⁻]).

Preparation of \([\text{ICD}_3 \text{CN)}_3 \text{YbFe(CO)}_4\] \text{CD}_3 \text{CN}. 10 mL portion of CD₃CN was added to a freshly prepared sample of \((\text{NH}_3)_3 \text{YbFe(CO)}_4\). The mixture was stirred for 10 min and filtered. The volume of the orange filtrate was reduced until small crystals could be seen. The filtrate was then placed in a −40 °C refrigerator for about 2 weeks. About a dozen orange needle-like crystals were obtained. IR (Nujol mull, cm⁻¹): 1890 (m), 1781 (m, sh), 1720 (s). Anal. Caled for Cd₃H₂Fe₂N₁O₁₂Yb: C, 26.80; H, 2.08; N, 10.22. \(\{\text{ICD}_3 \text{CN)}_3 \text{YbFe(CO)}_4\} \text{CD}_3 \text{CN}\) was prepared similarly in CD₃CN from fresh (ND₃)₂Yb(CO)₄. ²H MAS NMR: ~0.65 ppm.

Preparation of \([\text{ICD}_3 \text{CN)}_3 \text{YbFe(CO)}_4\]. A freshly prepared sample of \((\text{NH}_3)_3 \text{YbFe(CO)}_4\) in a minimal amount of liquid NH₃ was quenched by 15 mL of CH₃CN (distilled into the flask at −78 °C), and the mixture was stirred for 10 min at room temperature. All volatiles were then removed under vacuum. A 10 mL portion of fresh CH₃CN was distilled into the flask, and the mixture was filtered. The volume of the orange filtrate was reduced until small crystals could be seen. The filtrate was then placed in a −40 °C refrigerator for about

(²⁴) Deng, H. Unpublished observation.
2 weeks, and about a dozen orange single crystals of [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$ were obtained. IR (Nujol mull, $v_{CO}$, cm$^{-1}$): 1890 (m), 1794 (m), 1715 (s). Anal. Calc’d for C$_{39}$H$_{39}$Fe$_{6}$O$_{26}$Yb: C, 25.81; H, 1.95; N, 9.04. Found: C, 24.97; H, 2.08; N, 8.88.

X-ray Structure Determination of [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$: CH$_3$CN. The structure of [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$: CH$_3$CN was reported in our preliminary study. Crystal data and important bond distances and angles are listed in Tables 1 and 2, respectively.

X-ray Structure Determination of [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$: CH$_3$CN. Crystals of suitable size were coated with epoxy resin in the drybox and glued to the tips of glass fiber. All crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K$_\alpha$ radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings of 25 reflections, well distributed in reciprocal space and lying in a 2 $\theta$ range of 24–30°. The diffraction symmetry (C$_{2h}$, 2/m) and the systematic absences ($h0l$ for $h + l = 2n + 1$; $0k0$ for $k = 2n + 1$) uniquely determine the space group P2$_1$/n (No. 14). Crystallographic data are given in Table 1, and bond distances and angles are given in Table 2. Positional and equivalent isotropic thermal parameters are given in Table 3.

The diffraction data were corrected for Lorentz and polarization effects, decay, and absorption (empirically from $\psi$-scan data). The structure was solved by employing a combination of MULTAN 11/82 and difference Fourier techniques with analytical scattering factors used throughout the structure refinement and both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. All crystallographic computations were carried out on a DEC Vax station 3100 computer, using the Structure Determination Package (SDP). After all of the non-hydrogen atoms were located and refined, one hydrogen atom for every acetonitrile methyl group was located from difference Fourier maps and the remaining hydrogen atoms on the CH$_3$CN ligands were placed at calculated positions by assuming ideal geometries with $d(C-H) = 0.95$ Å and $B(H) = 1.3B(C)$ Å$^2$. Then with the positional and thermal parameters of all of the hydrogens fixed, the non-hydrogen atoms were refined anisotropically (atoms O1, C3, and C4 were refined isotropically as they became non-positive definite throughout the structure refinement and both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms). After anisotropic refinement; crystal decomposition during data collection. The highest residual peak on the final map is 1.52 e/Å$^3$ except those within 1.3 Å of Yb and Fe atoms (with maximum density of 5.21 e/Å$^3$).

### Table 3. Positional and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$.

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>0.64132(7)</td>
<td>0.23814(5)</td>
<td>0.80763(3)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0045(2)</td>
<td>0.2440(2)</td>
<td>0.7999(1)</td>
<td>1.22(3)</td>
</tr>
<tr>
<td>O1</td>
<td>0.350(1)</td>
<td>0.2432(9)</td>
<td>0.8153(6)</td>
<td>2.8(2)$^a$</td>
</tr>
<tr>
<td>O2</td>
<td>-0.084(1)</td>
<td>0.478(1)</td>
<td>0.6987(6)</td>
<td>3.1(2)</td>
</tr>
<tr>
<td>O3</td>
<td>-0.071(2)</td>
<td>-0.046(1)</td>
<td>0.7622(7)</td>
<td>3.4(3)</td>
</tr>
<tr>
<td>O4</td>
<td>-0.032(2)</td>
<td>0.300(2)</td>
<td>0.9645(7)</td>
<td>5.0(3)</td>
</tr>
<tr>
<td>N1</td>
<td>0.625(2)</td>
<td>0.442(1)</td>
<td>0.9022(7)</td>
<td>3.0(3)</td>
</tr>
<tr>
<td>N2</td>
<td>0.642(2)</td>
<td>0.127(1)</td>
<td>0.9431(8)</td>
<td>3.1(3)</td>
</tr>
<tr>
<td>N3</td>
<td>0.546(2)</td>
<td>0.173(1)</td>
<td>0.6694(8)</td>
<td>3.3(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.211(2)</td>
<td>0.242(1)</td>
<td>0.8041(8)</td>
<td>1.5(2)</td>
</tr>
<tr>
<td>C2</td>
<td>-0.057(2)</td>
<td>0.380(1)</td>
<td>0.7403(9)</td>
<td>2.5(3)</td>
</tr>
<tr>
<td>C3</td>
<td>-0.046(2)</td>
<td>0.074(1)</td>
<td>0.7753(9)</td>
<td>2.4(3)$^a$</td>
</tr>
<tr>
<td>C4</td>
<td>-0.025(2)</td>
<td>0.276(1)</td>
<td>0.8980(9)</td>
<td>2.8(3)$^a$</td>
</tr>
<tr>
<td>C11</td>
<td>0.639(2)</td>
<td>0.551(2)</td>
<td>0.9234(9)</td>
<td>2.7(3)</td>
</tr>
<tr>
<td>C12</td>
<td>0.659(2)</td>
<td>0.695(2)</td>
<td>0.951(1)</td>
<td>3.8(4)</td>
</tr>
<tr>
<td>C21</td>
<td>0.694(2)</td>
<td>0.087(2)</td>
<td>1.0002(9)</td>
<td>2.9(4)</td>
</tr>
<tr>
<td>C22</td>
<td>0.759(3)</td>
<td>0.037(2)</td>
<td>1.076(1)</td>
<td>5.5(5)</td>
</tr>
<tr>
<td>C31</td>
<td>0.428(2)</td>
<td>0.131(2)</td>
<td>0.6405(9)</td>
<td>2.9(3)</td>
</tr>
<tr>
<td>C32</td>
<td>0.270(2)</td>
<td>0.081(2)</td>
<td>0.610(1)</td>
<td>3.9(4)</td>
</tr>
<tr>
<td>H1</td>
<td>0.7929</td>
<td>0.7207</td>
<td>0.9570</td>
<td>5$^c$</td>
</tr>
<tr>
<td>H2</td>
<td>0.8339</td>
<td>-0.0566</td>
<td>1.0742</td>
<td>7$^c$</td>
</tr>
<tr>
<td>H3</td>
<td>0.2500</td>
<td>-0.0293</td>
<td>0.6035</td>
<td>5$^c$</td>
</tr>
<tr>
<td>H4</td>
<td>0.6123</td>
<td>0.7040</td>
<td>1.0005</td>
<td>4$^c$</td>
</tr>
<tr>
<td>H5</td>
<td>0.6072</td>
<td>0.7569</td>
<td>0.9155</td>
<td>4$^c$</td>
</tr>
<tr>
<td>H6</td>
<td>0.6707</td>
<td>0.0167</td>
<td>1.1072</td>
<td>7$^c$</td>
</tr>
<tr>
<td>H7</td>
<td>0.8207</td>
<td>0.1096</td>
<td>0.1987</td>
<td>9$^c$</td>
</tr>
<tr>
<td>H8</td>
<td>0.2622</td>
<td>0.1199</td>
<td>0.5591</td>
<td>5$^c$</td>
</tr>
<tr>
<td>H9</td>
<td>0.1972</td>
<td>0.1176</td>
<td>0.6422</td>
<td>5$^c$</td>
</tr>
</tbody>
</table>

$^a$ Anisotropically refined atoms are given in the form of the isotopic equivalent displacement parameter defined as $(4/3)[a^2(b^2+2c^2)+b^2(c^2+2a^2)+c^2(a^2+2b^2)]$. For the direction cosines $\alpha, \beta, \gamma$ of the $a, b, c$ axis, respectively.

$^b$ Refined isotropically. $^c$ Hydrogen atoms H1, H2, and H3 were located from difference Fourier maps, and the remaining ones were calculated at $d(C-H) = 0.95$ Å; their thermal parameters were assigned to $B(H) = 1.3B(C)$ Å$^2$.

**Acknowledgment.** This work was supported by the National Science Foundation through Grant CHE 94-01213.

**Supporting Information Available:** Listings of additional X-ray experimental details and anisotropic thermal parameters for [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$: CH$_3$CN were obtained. Analogous Supporting Information for [(CH$_3$CN)$_3$YbFe(CO)$_4$]$_2$: CH$_3$CN is given elsewhere. 

IC951513

---

27 To obtain the average of several values, and the standard deviation, the value is calculated from $\sqrt{\sum_{i=1}^{N} (d_i - \bar{d})^2/(N - 1)}$, where $d_i$ is the $i$th value and $\bar{d}$ is the mean of $N$ values.

28 SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, to apply corrections, and to solve and refine structures.