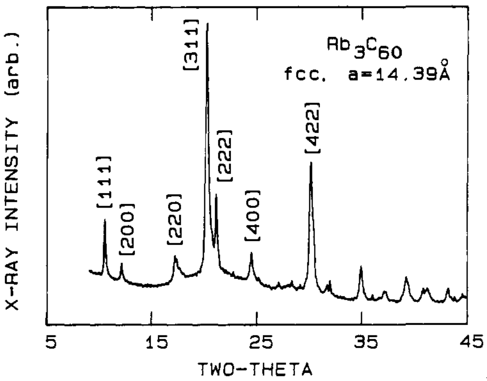

Figure 2. X-ray powder profile of Rb_3C_{60}, taken on beam line X10A at the National Synchrotron Light Source, Brookhaven National Laboratory; wavelength 1.5289 Å.

was also found necessary by the UCLA group to obtain large diamagnetic shielding fractions at nominal $x = 3$.[1]

We have successfully prepared single-phase K_3C_{60} and Rb_3C_{60} using this technique, the latter apparently for the first time.[10] Figure 1 shows SQUID (superconducting quantum interference device) magnetometer results for a typical Rb_3C_{60} sample [3.5 mg, crystallographic density 2.17 g/cm^3 (vide infra)]. The shielding diamagnetism (zero field cooled) is 60% of the ideal value ($1/4\pi$), and the transition onset (T_c = 29.8 K) is quite sharp. Previous susceptibility data for Rb_xC_{60} superconductors gave only 1% shielding and a broad transition,[11] or 7% shielding.[1] The limited Meissner fraction (field-cooled signal, 8% of ideal value) that we observe here would no doubt be improved by measurements on a compacted pellet.[12] Typical results for K_3C_{60} prepared via our dilution protocol are 38% shielding fraction and T_c = 19.6 K.

For Rb_3C_{60}, synchrotron X-ray powder diffraction reveals a structure analogous to that of K_3C_{60}.[3] Detailed analysis will be described elsewhere. Figure 2 shows the experimental profile. The face-centered-cubic lattice constant is 14.39 Å, slightly larger than the 14.24 Å found (and confirmed by us) for K_3C_{60}.[3] This would appear to support the conjecture that the higher T_c obtained with Rb doping is due to reduced molecular overlap relative to K_3C_{60}.[4] On the other hand, preliminary analysis of integrated intensities is equally consistent with complete molecular orientational disorder (as in pristine C_{60}[13]), or with a statistical distribution between two fixed orientations.[3] This leaves open the possibility that there may be important differences in the dynamics of K_3C_{60} and Rb_3C_{60} which could also contribute to different superconducting properties.

The dilution technique described here also permits the systematic preparation of varied, accurate stoichiometries other than $x = 3$, thus providing a convenient method to explore the phase boundaries between undoped and $x = 3$ fcc phases, and between $x = 3$ fcc and $x = 6$ body-centered cubic,[7] without sacrificing large amounts of C_{60}. The utility of this approach has already been demonstrated in the process of optimizing the synthesis of Rb_3C_{60}. For example, some of the reflections in Figure 2 exhibit high-Q shoulders which we attribute to the presence of a small amount of a dilute fcc phase resulting from a small error in stoichiometry (i.e., for this sample the actual $x = 3 - \epsilon$). The shoulder is particularly notable on the 220 reflection near $2\theta = 17°$; a similar shoulder is apparent in the K_3C_{60} data in ref 3. The implication is that the miscibility gap, implied by photoemission results,[14,15] does not cover the entire range $0 < x < 3$. Furthermore, these shoulders are absent in a slightly "overdoped" sample ($x = 3 + \epsilon$), which instead shows reflections of a second phase of symmetry lower than cubic. Increasing the design stoichiometry to $x = 4$ allowed us to isolate this new, body-centered-tetragonal, nonsuperconducting phase, which will be described in detail elsewhere.[10b] Extension of this new approach to the preparation of ternary compounds[16] will be straightforward.

Acknowledgment. This work was supported by the National Science Foundation through the MRL Program, Grant No. DMR88-19885 and by Grant No. DMR89-01219.

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Direct Yb-Fe Interaction in an Organometallic "Ladder Polymer": Synthesis and Structure of $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$

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Metal-metal interactions involving lanthanides and transition metals are rare in organometallic chemistry.[1-3] Although such interactions have been reported by several authors on the basis of infrared and ^1H NMR spectroscopic data,[2] confirmation through diffraction studies is scarce.[3] A direct Lu^{3+} to Ru bond of 2.955 (2) Å in $[Cp_2(THF)LuRu(CO)_2Cp]$ determined by an X-ray analysis was recently reported;[3a] however, neither an ORTEP drawing nor structural details were given. Divalent lanthanide to transition metal bonds have not been structurally characterized. Since divalent lanthanides are softer Lewis acids than trivalent lanthanides, they are expected to form more stable metal-metal bonds with low-valent transition metals that are soft bases.[4]

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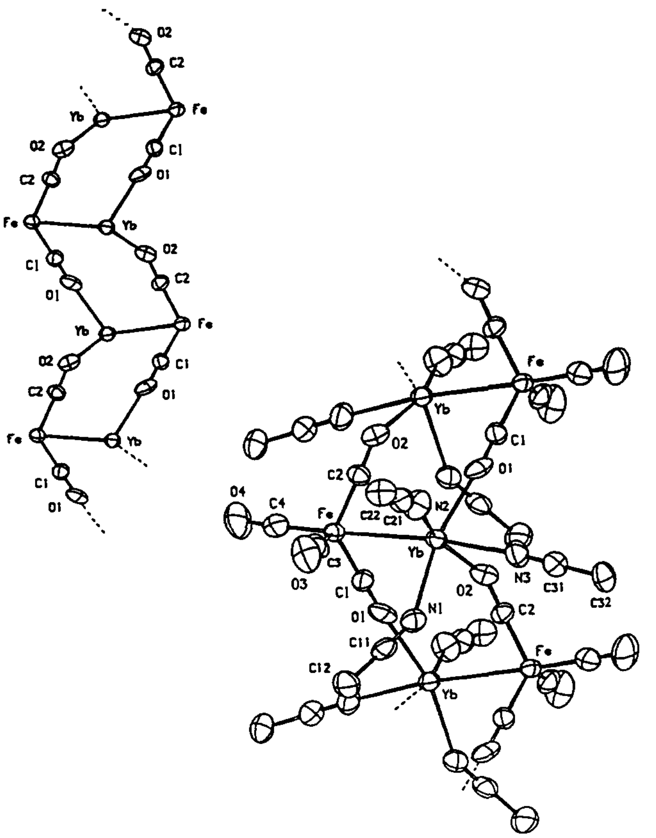

Figure 1. ORTEP drawing (50% probability ellipsoids) of a portion of one of the two independent "polymeric ladders" in $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$ (**2**). Acetonitrile hydrogens are omitted. Selected bond distances (Å):[20] Yb–Fe, 3.010 (1); Yb–O (av), 2.374 [7]; Yb–N (av), 2.515 [18]. Selected bond angles (deg): Fe–Yb–O1, 104.6 (1); Fe–Yb–O2, 103.0 (1); Fe–Yb–N1, 90.0 (1); Fe–Yb–N2, 101.1 (3); Fe–Yb–N3, 174.4 (3); O1–Yb–O2, 82.4 (3); O1–Yb–N1, 165.0 (3); O1–Yb–N2, 95.9 (3); O1–Yb–N3, 81.1 (3); O2–Yb–N1, 90.8 (3); O2–Yb–N2, 156.4 (3); O2–Yb–N3, 78.3 (3); N1–Yb–N2, 85.2 (3); N1–Yb–N3, 84.5 (3); N2–Yb–N3, 78.5 (3); Yb–Fe–C1, 73.9 (3); Yb–Fe–C2, 75.6 (3); Yb–Fe–C3, 79.5 (3); Yb–Fe–C4, 176.2 (4); C1–Fe–C2, 118.0 (4); C1–Fe–C3, 111.8 (4); C1–Fe–C4, 104.2 (4); C2–Fe–C3, 113.7 (4); C2–Fe–C4, 103.4 (4); C3–Fe–C4, 103.9 (4); Fe–C–O (av), 177.5 [1.5]; N–C–C (av), 178.5 [8].

Furthermore, strong nucleophilicity is necessary for transition metals to interact with lanthanide ions; otherwise the available coordination sites of the lanthanide ions will be occupied by coordinating solvents[5] or carbonyl oxygens from transition-metal carbonyl complexes (i.e., isocarbonyl linkages).[6] With these two considerations in mind, we investigated the interaction between Yb^{2+} and the "supernucleophile"[7] $[Fe(CO)_4]^{2-}$. Reported herein are the syntheses of $(NH_3)_xYbFe(CO)_4$ (**1**) and $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$ (**2**) and the X-ray single-crystal structure of **2**. This study presents the first structural evidence for significant metal–metal interaction involving a divalent lanthanide and a transition metal.

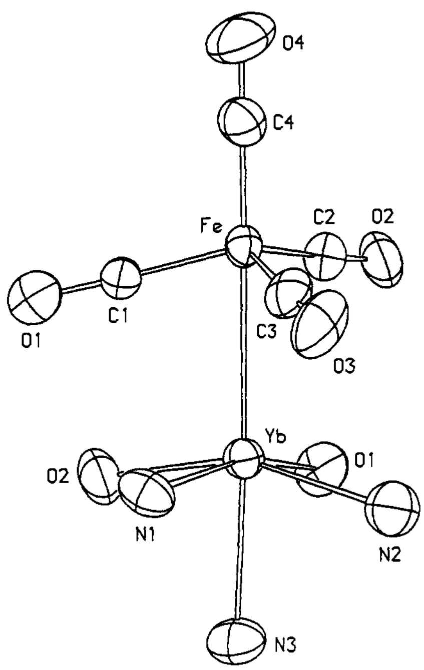

Figure 2. ORTEP drawing (50% probability ellipsoids) showing the coordination geometries of Fe and Yb in $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$ (**2**).

Reduction of $Fe_3(CO)_{12}$ by 3 equiv of Yb metal in liquid NH_3 results in the formation of $(NH_3)_xYbFe(CO)_4$ (**1**) (eq 1), an extremely air sensitive yellow solid.[8] Crystals of $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_2$ (**2**) were obtained by keeping a saturated CH_3CN solution of **1** at −40 °C for more than 2 weeks (eq 2). The infrared spectrum of **2** in Nujol mull displays three ν_{CO} absorptions at 1890 (w), 1781 (m, sh), and 1720 (s) cm^{-1}; this spectrum suggests that the $[Fe(CO)_4]^{2-}$ dianions[9] in **2** are distorted from ideal tetrahedral geometries and may have local C_{3v} symmetry.

$$3\,Yb + Fe_3(CO)_{12} \xrightarrow{NH_3} \underset{\mathbf{1}}{(NH_3)_xYbFe(CO)_4} \qquad (1)$$

$$\underset{\mathbf{1}}{(NH_3)_xYbFe(CO)_4} \xrightarrow{CH_3CN} \underset{\mathbf{2}}{\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty} \qquad (2)$$

The crystal structure of **2**, determined by the X-ray analysis,[10]

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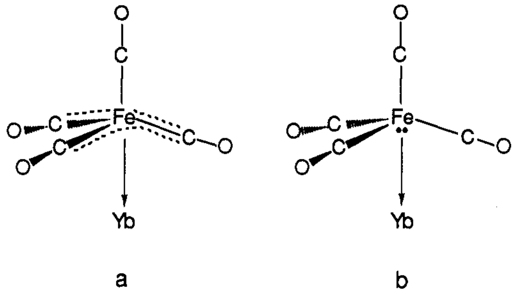
(10) Crystal data for $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$ (**2**) (−60 °C): space group $P2_1/c$ (No. 14), a = 21.515 (8) Å, b = 7.838 (2) Å, c = 19.866 (6) Å, β = 105.47 (2)°, V = 3228.7 $Å^3$, FW = 969.23, ρ (calcd) = 1.994 g/cm^3, Z = 4, μ = 66.553 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. All data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scans) was applied. Crystallographic computations were carried out on a DEC Vax station 3100 computer, using the Structure Determination Package (SDP). The structure was solved by the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed, and all non-hydrogen atoms were refined anisotropically. R_F = 0.031, R_{wF} = 0.040, GOF = 1.44 with 371 variables (including secondary extinction coefficient refined to 1.86×10^{-8}) refined for 3760 unique observations $[I \geq 3.0\sigma(I)]$ of 5848 reflections collected over the 2θ range $4° \leq 2\theta \leq 50°$. The highest residual electron density on the final difference Fourier map is 0.63 e/$Å^3$ except those (maximum 1.46 e/$Å^3$) within 1.2 Å of the Yb atoms.

Chart I



consists of "polymeric ladders" extending along the crystallographic *b* axis of the lattice. There are two crystallographically independent ladders, and they are stereochemically similar. Figure 1 shows a portion of one ladder. The local coordination geometries for the Fe and Yb atoms are shown in Figure 2. The geometries of the $[Fe(CO)_4]^{2-}$ units in **2** are intermediate between a tetrahedron and a trigonal bipyramid, while those of the Yb^{2+} ions are distorted octahedrons. In addition to three CH_3CN ligands, each Yb^{2+} ion is coordinated by two carbonyl oxygens from two different $Fe(CO)_4$ units; and each $Fe(CO)_4$ unit is in turn connected to two different Yb^{2+} ions via isocarbonyl linkages, thus forming a zigzag ···Yb-O-C-Fe-C-O-Yb··· chain. Two such chains are coupled to form a ladder through Yb-Fe interactions.[11] Two independent Yb-Fe distances are 3.012 (1) Å and 3.009 (1) Å. These distances are comparable to a Yb-Fe distance of 3.00 Å in $YbFe_2$ alloy,[12] and shorter than the sum of Yb and Fe metallic radii (3.2 Å).[13] Long Yb···C contacts are observed at 3.026 (9), 3.073 (8), and 3.201 (9) Å for Yb···C1, Yb···C2, and Yb···C3, respectively (Figure 2). Metal-metal distances in several oligomeric $Fe(CO)_4$-containing complexes are cited here for comparison. The average bond distances of 2.56 (4) Å for Zn-Fe in $[(bpy)ZnFe(CO)_4]_2$,[14] 2.562 (3) Å for Cd-Fe in $[CdFe(CO)_4]_4{\cdot}2C_3H_6O$,[15] and 2.640 (7) Å for Cd-Fe in $[(bpy)CdFe(CO)_4]_3{\cdot}{}^3/_4C_6H_3Cl_3$[16] are 0.07, 0.22, and 0.14 Å shorter than the sums of their respective metallic radii.[13]

The Yb-Fe interaction in **2** can be described as a dative bond formed by electron-pair donation from the Fe center in $[Fe(CO)_4]^{2-}$ to Yb^{2+}, similar to a Ru-Th dative bond in $Cp^*_2(I)ThRuCp(CO)_2$.[1f] The Yb···C contact distances of over 3 Å and the fact that the carbonyl groups are nearly linear (the Fe-C-O angles average 177.0 [1.4]°[20b]) suggest that there are only weak interactions between the Yb^{2+} ions and three carbonyl carbons. Therefore, any contribution due to the trimethylenemethane-like coordination of the FeC_3 region of $[Fe(CO)_4]^{2-}$ to Yb^{2+} (Chart Ia) is less significant than that of the direct Yb-Fe bonding (Chart Ib). This conclusion is further supported by comparison of the structural data of **2** with that of $Na_2[Fe(CO)_4]{\cdot}1.5(C_4H_8O_2)$.[17] In the latter, an allyl-like interaction between the Na^+ ions and the C-Fe-C regions of $[Fe(CO)_4]^{2-}$ was proposed. Note that six-coordinate Na^+ and Yb^{2+} have the same ionic radii of 1.02 Å.[18] In $Na_2[Fe(CO)_4]{\cdot}1.5(C_4H_8O_2)$ the Na···Fe distance of 3.086 (2) is longer than two Na···C distances of 2.860 (5) and 3.050 (5) Å, while in **2** the Yb-Fe distances are shorter than the Yb···C distances.

The average Yb-N bond distance of 2.515 [18] Å in **2** is comparable to the Yb-N bond distances in $(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$[19b] and $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}$[19a] (2.525 [6] and 2.55 [3] Å, respectively). The average Yb-O bond distance for the Yb-isocarbonyl linkages in **2** is 2.374 [7] Å, ca. 0.1 Å longer than those involving eight-coordinate trivalent Yb ions.[6] For the carbonyls involved in the isocarbonyl linkages, the average C-O bond distance of 1.195 [7] Å and the average Fe-C bond distance of 1.726 [9] Å suggest the weakening of the C-O bonds and the strengthening of the Fe-C bonds upon isocarbonyl coordination to Yb^{2+}.[6] The average C-O and Fe-C bond distances for the terminal carbonyls are 1.154 [9] and 1.768 [11] Å, respectively. The Yb-N-C angles vary from 140.0 (7) to 170.8 (7)°, and the Yb-O-C angles vary from 134.8 (5) to 168.4 (5)°. The angularity of the Yb-O-C and $Yb\text{-}N\text{-}CCH_3$ interactions in **2** is probably controlled by steric effects.

Presently we are developing the chemistry of this system and extending our procedures to additional examples of metal-metal interactions involving lanthanides and transition metals.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE88-00515.

Supplementary Material Available: Listings of positional parameters, anisotropic thermal parameters, bond distances, and bond angles of **2**, a brief description of the crystal structure of **2**, and a stereoview of the crystal packing diagram of the unit cell of **2** (11 pages); listing of calculated and observed structure factor amplitudes for **2** (19 pages). Ordering information is given on any current masthead page.

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[11] The difference Fourier map gives no evidence of residual electron density that can be assigned to a hydrogen bridging Yb and Fe. This is consistent with the infrared spectrum of **2**, which suggests the presence of distorted $[Fe(CO)_4]^{2-}$ instead of $[HFe(CO)_4]^-$. For infrared spectra of $[Fe(CO)_4]^{2-}$ and $[HFe(CO)_4]^-$, see ref 9 and the following: Mitsudo, T.; Watanabe, Y.; Yamashita, M.; Takegami, Y. *Chem. Lett.* **1974**, 1385.

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[20] (a) The specific distance or angle given for **2** is the average of two crystallographically independent values, with estimated standard deviation $s = (s_1 + s_2)^{1/2}$ shown in parentheses. (b) The average distance or angle is the mean of several values, and the esd shown in brackets is calculated from $[\sum_{i=1}^{N}(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the *i*th value and $\bar{d}$ is the mean of N values.

Photoinduced Electron Transfer in Redox-Active Lysines

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Intramolecular photoinduced redox separation in molecules incorporating both an electron transfer donor and an acceptor as well as a chromophore has previously been achieved in carotenoid porphyrin-quinones,[1] aniline porphyrin-quinones,[2] and ruthenium

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