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Heterobimetallic Complexes Containing Ca–Fe or Yb–Fe Bonds: Synthesis and Molecular and Electronic Structures of $[M\{CpFe(CO)_2\}_2(THF)_3]_2$ (M = Ca or Yb)

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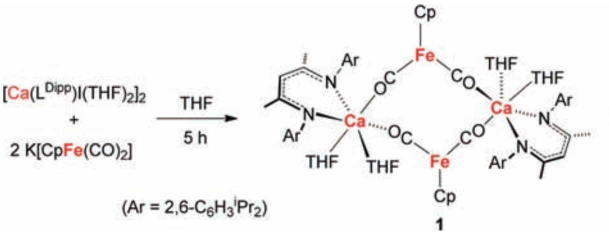
S *Supporting Information*

ABSTRACT: Reaction of calcium or ytterbium amalgam with $[CpFe(CO)_2]_2$ (Fp_2) gave the isostructural heavy alkaline earth or divalent rare earth compounds $[MFp_2(THF)_3]_2$ (M = Ca or Yb) containing two direct Ca–Fe (3.0185(6) Å) or Yb–Fe (2.9892(4) Å) bonds. Density functional theory supports experiment in finding shorter Yb–Fe than Ca–Fe distances, and Ziegler–Rauk, molecular orbital, and atoms-in-molecules analyses find the M–Fe bonding to be predominantly electrostatic in nature. The Yb–Fe interaction energy and bond critical point electron density are slightly larger than for Ca–Fe, in agreement with the shorter M–Fe bond in the former. The corresponding reaction for magnesium gave $MgFp_2(THF)_4$ with two O-bound Fp moieties and no Mg–Fe bond.

Metal–metal bonded molecular compounds have been an essential part of the development of inorganic chemistry for decades.[1] Very recently, this area has been re-energized by the discovery of the first chromium–chromium quintuple bond,[2] the first zinc–zinc[3] and magnesium–magnesium single bonds,[4] and a growing number of 4f element– and 5f element–main group[5,6] and transition metal[7,8] bond partners.[9] Within this rich and topical area, there nonetheless remains very little experimental or theoretical information regarding bonds between alkaline earth (Ae) elements and transition metals. In the past ca. 40 years there have been only three reports of structurally authenticated magnesium–transition metal bonds,[10] and the first (and only) beryllium–transition metal bond was found only 2 years ago.[11] While weak and long bonds between calcium and main group metals (Ga,[12] Sn[13]) have been reported, nothing is yet known about the structure or bonding of calcium with a transition metal. At the same time, interest in the heavier Ae metals is rapidly developing,[14] and the chemistry of the Ae elements has been compared to that of the lanthanides [e.g., Ca and Yb(II); Sr and Sm(II)].[15] Several examples are now known which contain lanthanide–transition metal bonds,[7] but the questions of whether analogous heavier alkaline earth–transition metal bonds can be prepared at all, and how they compare to rare earth–transition metal bonds, remain unanswered. Here we report synthetic, structural, and theoretical studies of the first Ca–Fe bonded compound and its isostructural Yb–Fe bonded analogue.

Marks has shown that the salt elimination reaction of Cp_3AnCl (An = Th, U) with $Na[CpFe(CO)_2]$ (NaFp) affords Cp_3AnFp containing An–Fe bonds.[8b] Likewise, Arnold recently reported that reaction of KFp with $[Nd(L^{NHC})I\{N(SiMe_3)_2\}]_2$ (L^{NHC} = $^tBuNCH_2CH_2\{C(NCSiMe_3CHN^tBu\}$) gave $Nd(L^{NHC})(Fp)\{N(SiMe_3)_2\}$, the first isolable 4f–3d bonded complex.[7d] Our initial attempts to prepare a compound with a transition metal–calcium bond took this synthetic approach (eq 1).



(1)

Reaction of KFp with $[Ca(L^{Dipp})I(THF)]_2$ (L^{Dipp} = $HC\{C(Me)N(2,6\text{-}C_6H_3{}^iPr_2)\}_2$) in THF afforded a product (**1**) of composition "$Ca(L^{Dipp})(Fp)(THF)_2$" according to NMR spectroscopy and elemental analysis. The solid-state IR spectrum of **1** showed two strong bands at 1823 and 1780 cm^{-1}, attributed to the symmetric and antisymmetric $\nu(CO)$ bands of a coordinated Fp ligand.[16,17] However, X-ray crystallography (Figure 1) showed that **1** is dimeric in the solid state, with two Fp anions bridging pairs of six-coordinate, formally cationic calcium centers through Fe–CO···Ca isocarbonyl interactions.

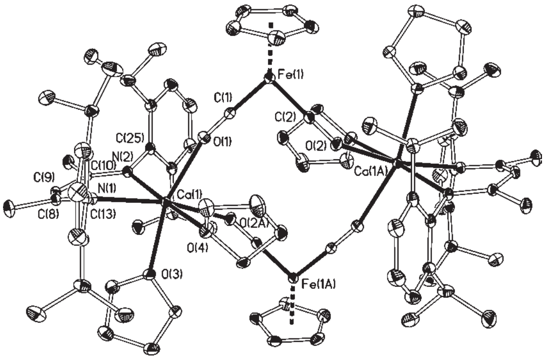


Figure 1. Displacement ellipsoid plot (20% probability) of $[Ca(L^{Dipp})Fp(THF)_2]_2$ (**1**). H atoms omitted. Atoms carrying the suffix "A" are related to their counterparts by the operator $-x$, $1-y$, $-z$.

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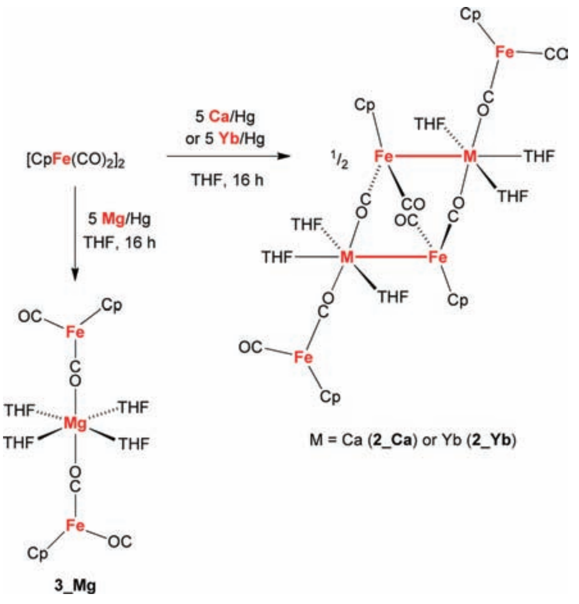
The absence of a Ca−Fe bond in **1** contrasts with the Mg−Mg bonded compounds $[Mg(L^{Dipp})(L)]_2$ (L = THF or none) and their homologues reported by Jones for the same diketiminate supporting ligand.[4] Since the number of heteroleptic starting compounds of the type Ca(L)X (X = halogen) is extremely limited for calcium (because of the Schlenk-type equilibria that accompany its chemistry),[14] we turned to an alternative synthetic approach.

Recalling Westerhausen's synthesis of $Ca(SnMe_3)_2(THF)_4$ from Sn_2Me_6 and calcium metal,[13] and Jones's preparation of $Ca\{Ga(NArCR)_2\}_2(THF)_4$ (Ar = 2,6-$C_6H_3{}^iPr_2$, R = H or Me) from $Ga\{(NArCR)_2\}I_2$ and calcium amalgam,[12a] we carried out the corresponding reaction of Fp_2 with Ca/Hg in THF (Scheme 1). After 16 h at room temperature, $[CaFp_2(THF)_3]_2$ (**2_Ca**) was isolated as large, red diffraction-quality crystals following recrystallization from THF. The molecular structure of **2_Ca** is shown in Figure 2, and selected distances and angles are given in Table 1. Attempts to form **2_Ca** by reaction of KFp with CaI_2 (2:1) in THF-d_8 gave mixtures of unknown Fp-containing species. In contrast, Kempe et al. have recently shown that the related Yb−Ru bonded compound $[Yb\{CpRu(CO)_2\}_2(THF)_2]_n$ could be formed from $Na[CpRu(CO)_2]$ and $YbI_2(THF)_4$.[18]

Scheme 1. Reactions of Metal Amalgams with $[CpFe(CO)_2]_2$



Compound **2_Ca** contains two symmetry-related $CaFp_2(THF)_3$ moieties joined by Fe−CO···Ca isocarbonyl linkages. Each octahedral calcium center is bonded to three THF molecules, one O−bound Fp (Fe(2)), and one further Fp moiety (Fe(1)) through an unprecedented, unsupported Ca−Fe bond (Ca(1)−Fe(1) = 3.0185(6) Å). The structure of **2_Ca** and other data are discussed further below.

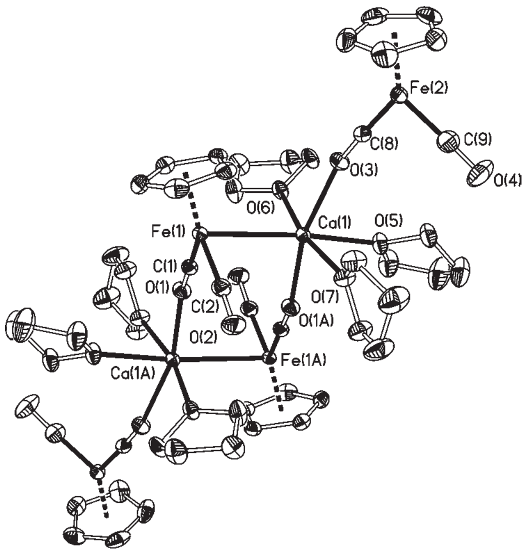


Figure 2. Displacement ellipsoid plot (25% probability) of $[CaFp_2(THF)_3]_2$ (**2_Ca**). H atoms and THF of crystallization omitted. Atoms carrying the suffix "A" are related to their counterparts by the operator $-x$, $1-y$, $1-z$. $[YbFp_2(THF)_3]_2$ (**2_Yb**) follows an identical numbering scheme (see the SI).

Table 1. Selected Bond Distances (Å) and Angles (°) for $[MFp_2(THF)_3]_2$ [M = Ca (2_Ca) or Yb (2_Yb)]

	2_Ca	2_Yb
M−Fe	3.0185(6)	2.9892(4)
M−O_{Fp} [Fe1(A)]	2.3597(18)	2.4069(19)
M−O_{Fp} [Fe(2)]	2.3100(19)	2.356(2)
M−O_{THF} [*trans* to M−Fe]	2.3968(18)	2.451(2)
M−O_{THF} [*cis* to M−Fe]	2.3527(19)	2.408(2)
	2.3397(19)	2.396(2)
Fe(1)−CO (bridging)	1.705(2)	1.699(3)
Fe(1)−CO (terminal)	1.732(3)	1.735(3)
Fe(2)−CO (bridging)	1.689(3)	1.689(3)
Fe(2)−CO (terminal)	1.724(3)	1.718(4)
OC−Fe(1)−CO	92.07(13)	91.66(14)
OC−Fe(2)−CO	88.43(13)	88.07(15)

To gain additional experimental insight into the bonding situation in **2_Ca** and factors influencing its formation, we carried out the corresponding reactions of Fp_2 with ytterbium or magnesium amalgams (Scheme 1). Reaction of Fp_2 with Yb/Hg followed by recrystallization from THF gave red diffraction-quality crystals of $[YbFp_2(THF)_3]_2$ (**2_Yb**). Crystals of **2_Yb** are isomorphic with those of **2_Ca**, and the coordination geometries of the metal centers in **2_Ca** and **2_Yb** are identical. The Yb(1)−Fe(1) bond distance in **2_Yb** is 2.9892(4) Å. Other selected metric data are listed in Table 1, and a view of the molecular structure is given in the SI. Compound **2_Yb** is somewhat different from Kempe's related polymeric $[Yb\{CpRu(CO)_2\}_2(THF)_2]_n$, which possesses two Yb−Ru bonds per lanthanide metal center.[18]

In contrast, the analogous reaction of Fp_2 with Mg/Hg followed by recrystallization from THF gave yellow diffraction-quality crystals of monomeric $MgFp_2(THF)_4$ (**3_Mg**, Scheme 1). Unlike **2_Ca** and **2_Yb**, compound **3_Mg** contains a six-coordinate Mg center ligated by two O-bound Fp moieties and four THF ligands; there is no Fe−Mg bond in **3_Mg**. Further details of the structure are given in the SI. Transition metal−alkaline earth isocarbonyl-bridged compounds have been structurally authenticated previously.[19]

The Ca−O_{THF} and Ca−O_{Fp} distances in **2_Ca** are within the expected ranges, as are those for the Fp moieties.[19b] The main

Table 2. Selected Computational Results for 2_Ca, 2_Yb, and 2_Mg[a]

	2_Ca	**2_Yb**	**2_Mg**
r(M−Fe) (Å)	2.984, 2.978	2.965, 2.956	2.815, 2.815
M−Fe interaction energy (per M−Fe bond)	−134.9	−143.3	−150.5
orbital mixing energy	−91.1	−107.4	−117.9
electrostatic interaction energy	−191.2	−249.5	−207.6
Pauli repulsion energy	147.4	213.5	175.0
charge M ([$MFp_2(THF)_3$] fragment)	1.51	1.32	1.20
charge Fe(1) ([$MFp_2(THF)_3$] fragment)	0.14	0.15	0.14
charge M	1.38	1.01	1.10
charge Fe(1)	−0.05	−0.01	−0.05
ρ (electron density)	0.022	0.029	0.021
$\nabla^2\rho$ (electron density Laplacian)	0.041	0.040	0.039
H (energy density)	−0.002	−0.006	−0.003

[a] All energies in kJ mol^{-1}. Orbital mixing (and hence total interaction) energies corrected for basis set superposition error (**2_Mg**, 9.1; **2_Ca**, 7.2; **2_Yb**, 10.2). AIM data (atomic units) obtained at the bond critical point. Charges obtained from Mulliken analyses.

features of interest are the Ca−Fe bonds, the symmetry-equivalent distances of which (3.0185(6) Å) are somewhat shorter than the sum of the respective covalent radii (3.08 Å).[20] This contrasts to the calcium−main group metal bonded complexes $Ca(SnMe_3)_2(THF)_4$ (Ca−Sn = 3.2721(3) Å; r_{cov}(Ca) + r_{cov}(Sn) = 3.15 Å)[13] and $Ca\{Ga(NArCH)_2\}_2(THF)_4$ and $Cp^*_2Ca(Cp^*Ga)$ (Ca−Ga = 3.1587(6) and 3.183(2) Å; r_{cov}(Ca) + r_{cov}(Ga) = 2.98 Å),[12] where the metal−metal bonds were *longer* than expected on this basis.

The isomorphic structures of **2_Ca** and **2_Yb** allow the first experimental comparison of any alkaline earth−transition metal bond with that of a divalent rare earth analogue (Table 1). The Yb−O distances in **2_Yb** are ca. 0.05 Å longer on average than their counterparts in **2_Ca**, which is consistent with the larger covalent radius of Yb (r_{cov} = 1.76(10) (Ca) and 1.87(8) (Yb) Å).[20] The distances and angles for the Fp moieties in **2_Yb** are identical within error to those in **2_Ca**. However, the Yb−Fe distance of 2.9892(4) Å is 0.0293(1) Å *shorter* than in **2_Ca**, despite the larger r_{cov} of Yb. The Yb−Fe interaction in **2_Yb** therefore appears to be somewhat stronger than in **2_Ca**. Both complexes react immediately in THF-d_8 with MeI to form FpMe, consistent with them being Fp^- anion sources.[16]

Gradient-corrected density functional theory was employed to study **2_Ca** and **2_Yb** (full models without symmetry constraints), and selected results are collected in Table 2; further details are given in the SI. Calculations were also carried out on the hypothetical compound $[MgFp_2(THF)_3]_2$ (**2_Mg**), having a structure analogous to those of **2_Ca** and **2_Yb**. For **2_Ca** and **2_Yb**, the agreement between the experimental and computed structures is very good. In particular, the calculated Yb−Fe distances are ca. 0.021 Å shorter than those for Ca−Fe, consistent with the solid-state structures.

The Ziegler−Rauk energy decomposition scheme[21] has been employed to probe the interaction between the two $[MFp_2(THF)_3]$ fragments at the converged geometries of **2_M** (Table 2). These data indicate a significant interaction energy between the two fragments (effectively a measure of the M−Fe interaction), which is 8.4 kJ mol^{-1} larger per M−Fe bond in **2_Yb** than in **2_Ca**, in agreement with the slightly shorter M−Fe distance in the former. Of particular interest are the relative contributions of the pre-relaxation electrostatic term and the post-relaxation orbital mixing term; it is unusual that the electrostatic term is the largest in the energy decomposition of interactions between neutral fragments. This suggests that the M−Fe bonds are predominantly ionic, and population analysis of the valence molecular orbitals supports this conclusion in finding no contributions from M larger than 1%. Table 2 shows that the difference in the Mulliken charges of the M and Fe(1) atoms in each $[MFp_2(THF)_3]$ fragment is large, in keeping with the large electrostatic terms in the energy decomposition. Table 2 also reveals that the difference in the Mulliken charges of the M and Fe(1) atoms in **2_M** is large in each case, as expected for an ionic interaction, and also that the charges of M and Fe(1) are significantly different in **2_M** than in the $[MFp_2(THF)_3]$ fragments. This indicates that, on relaxation to self-consistency, there is a significant redistribution of charge within each fragment. This accounts for the favorable orbital mixing contributions to the M−Fe interaction energy, despite there being very little M character in the valence molecular orbitals.[22]

Atoms-in-molecules (AIM) analysis[23] supports the existence of Ca−Fe and Yb−Fe bonds in finding M−Fe bond paths, and selected data at the M−Fe bond critical points (BCPs) are given in Table 2. The electron density ρ is slightly larger at the Yb−Fe BCP than the Ca−Fe BCP, in agreement with the shorter Yb−Fe bond and larger interaction energy. The small positive values of both ρ and its Laplacian $\nabla^2\rho$ reinforce the molecular orbital and Ziegler−Rauk analyses in finding little covalency in the bonding. Following the approach of Vlaisavljevich et al.[24] and Bianchi et al.,[25] the value of H may be used to further classify the M−Fe interactions. Vlaisavljevich et al. used AIM to study a range of heterobimetallic lanthanide−M and actinide−M bonds and found H values at the BCPs to be similar in magnitude to the present results, but very slightly positive. H values close to zero indicate metallic bonding in the Bianchi approach, and we therefore place, as do Vlaisavljevich et al., the metal−metal interactions into this category.

Table 2 indicates that the calculated Mg−Fe interaction energy in hypothetical **2_Mg** is larger than in either **2_Ca** or **2_Yb**, but yet, experimentally, monomeric $MgFp_2(THF)_4$ (**3_Mg**) forms when crystallized from THF solution. To probe this further, the reactions summarized in eq 2 were assessed computationally for M = Mg, Ca, and Yb. Since the (favorable) entropic contribution associated with the formation of **2_M** may be considered to be approximately constant for all three metals, we focus only on the enthalpy of the processes. DFT finds that formation of **2_Mg** from

$$2\ \mathrm{MFp_2(THF)_4} \rightleftharpoons [\mathrm{MFp_2(THF)_3}]_2 + 2\ \mathrm{THF} \qquad (2)$$

M = Mg, Ca, or Yb (**3_M**) M = Mg, Ca, or Yb (**2_M**)

3_Mg is disfavored by $\Delta_r H = +48.9$ kJ mol^{-1}, in agreement with experiment. However, formation of **2_Ca** and **2_Yb** has favorable $\Delta_r H$ values of -11.9 and -33.5 kJ mol^{-1}, respectively, again in agreement with experiment.

The results in Scheme 1 and eq 2 illustrate the delicate balance between metal−solvent and metal−metal interactions in these predominantly ionic systems. Furthermore, the modest computed $\Delta_r H$ values for **3_Ca** or **3_Yb** → **2_Ca** or **2_Yb** suggest that these equilibria might lie in favor of the monomeric **3_M** in the presence of an excess of THF. Consistent with this, comparison of the solid-state (Nujol mull) and solution (THF) IR spectra of **2_Ca** and **2_Yb** shows that different structures are formed in each case. The solid-state IR spectra show four ν(CO) bands (two overlapping) for the symmetry-inequivalent Fp groups of dimeric $[\mathrm{MFp_2(CO)_3}]_2$, whereas in THF solution only two bands are observed, as in the case of **3_Mg** in both the solution and solid states.

In summary, we have reported the first example of a complex containing a calcium−transition metal bond, along with a study of its molecular and electronic structures. Through corresponding studies of its ytterbium counterpart, we have also made the first comparison of the bonding for an alkaline earth element and a rare earth element with a transition metal. The nature of the bonding is the same in each case (predominantly electrostatic), but the Yb−Fe interaction is stronger than the Ca−Fe one. Work toward other alkaline earth−transition metal complexes is under way in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information. Synthesis and computational details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Recall that, in the Ziegler−Rauk scheme, charge redistributions within a fragment as a result of interaction with the charge of neighboring fragments can yield stabilizing contributions to the orbital mixing term without there necessarily being significant interfragment charge transfer.

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