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A Monometallic Iron(I) Organoferrate

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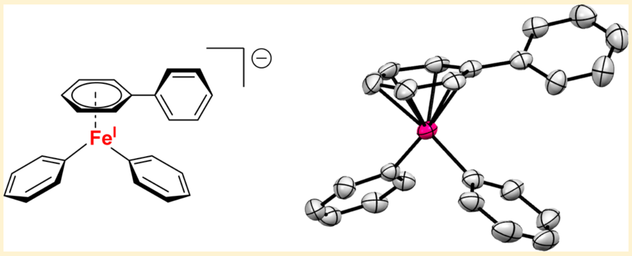
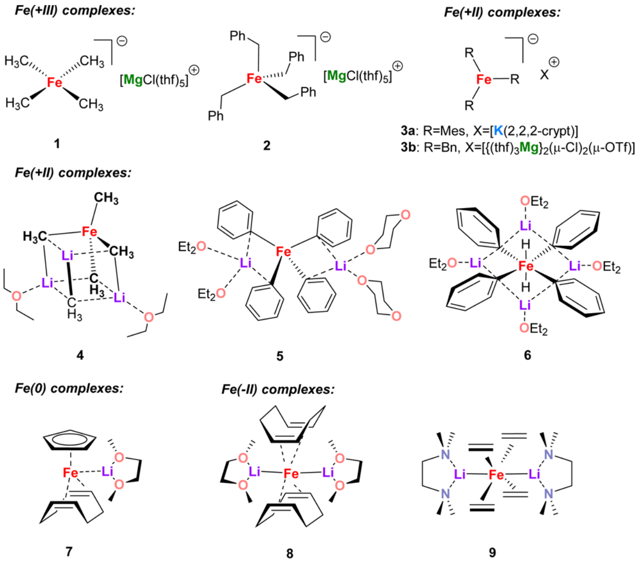
Ⓢ *Supporting Information*

ABSTRACT: Tetra-*n*-butylammonium (TBA) (η^6-biphenyl)-diphenylferrate was formed unexpectedly in the reaction of $(TBA)_2[Fe_4S_4Cl_4]$ with an excess of phenyllithium. This complex belongs to a novel type of organoferrate.



Organoferrates are anionic organometallic iron complexes.[1] They are invoked as important intermediates in many iron-catalyzed organic reactions.[1,2] Organoferrates devoid of stabilizing ligands (nonstabilized organoferrates) are scarce.[2] Reported examples include tetramethylferrate (**1**;[3] Scheme 1) and tetrabenzylferrate(III) (**2**),[4] $[Fe(Mes)_3]^-$ (**3a**)[5] and $[FeBn_3]^-$ (**3b**),[4] tetramethyl- and tetraphenyliron(II) complexes **4** and **5**,[2] the tetraphenyl dihydride complex **6**,[6] the Fe(0) complex **7**,[7] formally Fe(−II) complexes **8** and **9**,[8] and the octanuclear ferrate $[MgCl(thf)_5][Fe_8Me_{12}]$.[9]

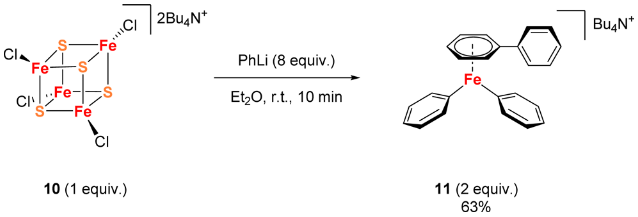
Scheme 1. Representative Examples of Nonstabilized Organoferrates



With the exception of **1**, **2**, and **3a**,**b**, these complexes often contain either direct Fe−metal (most often Fe−Li) interactions or solvated metal cation(s) (most often lithium) in the proximity of the iron center. The latter usually forms short contact with the ipso carbons of the organic ligands. Moreover, the oxidation states of iron in known organoferrates are limited to +III, +II, 0, and −II. Here we report a novel Fe(I) organoferrate which is unsupported by either another metal cation or a heteroatom-based ligand.

Inoue and co-workers studied the catalytic activity of the phenyllithium-treated cluster $[Fe_4S_4Cl_4]^{2-}$ in hydrogenation reactions. They prepared the catalyst by addition of $(TBA)_2[Fe_4S_4Cl_4]$ (**10**; TBA = tetra-*n*-butylammonium) to a solution of PhLi. This catalyst was active for hydrogenation of some olefins and carbonyl compounds.[10,11] In an attempt to isolate and characterize the active species in this system, we reacted $(TBA)_2[Fe_4S_4Cl_4]$ with 8 equiv of PhLi in ether under an inert atmosphere at room temperature (Scheme 2). In the first 1−2 min after PhLi addition, the liquid phase turned an intense orange-black. As the reaction proceeded, a black precipitate was formed (**11**) and the solution became nearly colorless. The precipitate could be dissolved in THF to yield a blood red solution. Slow diffusion of pentane into this solution yielded black needle-shaped crystals.

Scheme 2. Synthesis of Complex 11



X-ray crystallography revealed the molecular structure of **11** (Figure 1). The compound is a TBA salt of an iron(I) complex anion, which is coordinated by a π-bound η^6-biphenyl ligand and two σ-bound phenyl ligands. The Fe−C(η^1-Ph) distance (1.971−1.977 Å; see the Supporting Information) in complex

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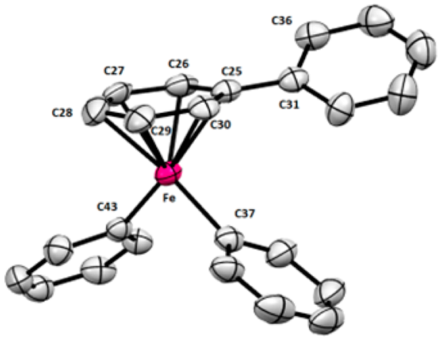

Figure 1. X-ray crystal structure of the (η^6-biphenyl)diphenylferrate anion in complex **11**. Two molecules were found in one asymmetric unit of **11**; only one of them is shown. The TBA cation and hydrogen atoms are omitted for clarity. The ellipsoids are drawn at the 50% probability level.

11 is slightly shorter than its counterpart in **5** (2.084−2.216 Å)[2] and **6** (2.056 Å).[6] The distance between the Fe(I) center and the η^6-phenyl ring (1.578 Å) is in line with the values reported for (η-arene)(Cp)Fe^{II} complexes.[12,13] It is remarkable that, despite the presence of lithium ion and diethyl ether in the reaction mixture, neither is present in complex **11**. Formation of a η^6-biphenyl iron(0) complex upon reaction of an iron(II) bisphosphine complex with phenyl nucleophiles, which proceeds through reductive elimination, has been reported.[14] Complex **11** might be formed in a similar process via an Fe(III) tetraphenyl intermediate.

Complex **11** is paramagnetic. The solution magnetic moment in THF is 1.75 μ_B, determined by the Evans method after diamagnetic corrections. This value is consistent with a low-spin Fe(I) center ($S = 1/2$). DFT computations at the OPBE/def2-TZVPP levels confirmed the doublet spin multiplicity for the ground state of **11**. The quartet state was found to be 19.8 kcal/mol higher in energy. Moreover, the optimized geometry of the quartet spin multiplicity deviates significantly from the crystal structure in Figure 1. An Fe(I) $S = 1/2$ species was previously observed by electron paramagnetic resonance (EPR), but not isolated, in the reaction of $FeCl_3$ with (4-tolyl)MgBr at −30 °C.[4] The N and H contents determined by elemental analysis agree with the formula of **11**; however, the C content is lower than that predicted, despite repetitive measurements, including on single crystals. This discrepancy might be due to decomposition of the complex during elemental analysis. The Fe content, determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), also agrees with the theoretical formula.

Attempts were made to look for alternative conditions for the synthesis of complex **11**. The reaction solvent could be changed to benzene. However, the iron precursor was limited to **10**. Replacing **10** with simpler iron salts such as $FeCl_3$, $FeCl_2$, and TBA[$FeCl_4$] failed to yield complex **11**. In fact, reactions of iron salts with PhLi were previously widely studied,[2,6,15] but the formation of complex **11** in these systems is hitherto unknown.

Complex **11** is insoluble in hydrocarbon solvents and 1,4-dioxane but shows good solubility in THF and acetonitrile. It does not react with H_2 or catalyze hydrogenation of *cis*-stilbene, ruling out its role as the active species in the hydrogenation system of Inoue.[10] Reactions of **11** with CO, CO_2, or air led to its decomposition, with concomitant formation of free biphenyl. No reaction occurred with chlorobenzene. However, **11** reacted with 2-bromopyridine, *p*-bromoanisole, and 1-bromobutane (see the Supporting Information) to give the corresponding C−C coupling products (eq 1), albeit in low yields. Biphenyl was also formed.

11

R = 2-py, *p*-MeOC$_6$H$_4$ or *n*-C$_4$H$_9$

In summary, a novel ferrate complex, (η^6-biphenyl)-diphenylferrate, was isolated. This complex is neither supported by an alkali-metal ion nor supported by a heteroatom ligand, making it a unique Fe(I) ferrate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00841.

Experimental procedures and characterization of complex **11** and computational details (PDF)
Crystallographic data for complex **11** (CIF)
Cartesian coordinates for the calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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