Crystal Structure of "[Li(Et₂O)]₄[FePh₄]": Corrigendum and Reformulation. A Remarkable Example of a False Solution in a Wrong Space Group

Jesse M. Jefferis and Gregory S. Girolami*

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Goodwin Avenue, Urbana, Illinois 61801

Summary: The crystal structure of the supposed tetra-phenylferrate(0) salt "[Li(Et₂O)]₄[FePh₄]" reported by Shilov et al. has been reinterpreted, and the unprecedented "flat rectangular" coordination geometry is proposed to be an artifact of a false solution in an incorrect space group. In the correct space group, the phenyl groups actually describe a regular square-planar geometry with cis C−Fe−C angles that are exactly 90°. In addition, the formulation of the compound as a derivative of zerovalent iron is almost certainly incorrect: we propose that the compound actually is an iron-(II) dihydride of stoichiometry [Li(Et₂O)]₄[trans-FeH₂-Ph₄].

The structures of binary metal alkyl and metal aryl complexes continue to be of interest, as shown, for example, by the finding that the zirconium centers in $[ZrMe_6]^{2-}$ and $[ZrPh_6]^{2-}$ both adopt trigonal-prismatic (rather than octahedral) geometries.[1,2] In 1983, Shilov et al. reported the synthesis and crystal structure of an organoiron compound of stoichiometry [Li(Et₂O)]₄-[FePh₄] (**1**).[3] Of particular interest was the claim that **1** reacted with N_2 to form a species that produced N_2H_4 when decomposed by HCl. According to the results of the crystallographic study (Figure 1), the iron center in **1** adopted an unprecedented coordination geometry described as "flat rectangular": the four ipso carbon atoms formed a planar array in which the cis C−Fe−C angles were either 61° or 119°. A remarkably short "nonbonded" C···C contact of 2.09 Å was said to exist between the ipso carbon atoms of the closely situated pairs of adjacent phenyl groups. The unusual structure of the complex was proposed to be related to its ability to activate N_2.

The structure of **1** has been discussed many times,[4] but none of these subsequent papers has reached what
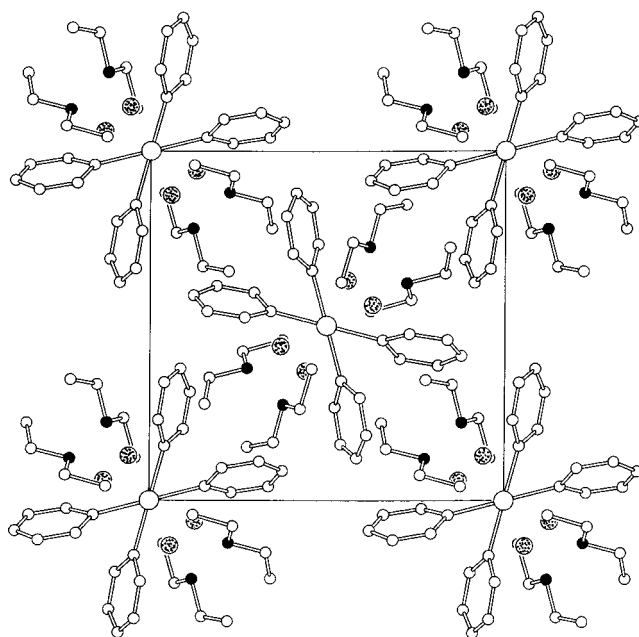
Figure 1. Projection of the $P4_22_12$ structure of "**1**" down the *c*-axis. Key: Fe (large open spheres), C (small open spheres), Li (large stippled spheres), O (small black spheres).

to us is an obvious conclusion: the structure is simply unbelievable. First, as formulated, the iron center is formally zerovalent and such a d^8 metal center should adopt a regular square-planar structure with 90° inter-ligand angles. Second, the 61° C−M−C angles are some 15° smaller than the smallest such angle seen between two phenyl groups in any other transition-metal complex. Third, the coordination geometries of the lithium centers are very unusual: most of the "surface" of each lithium atom points out toward "empty" space. Specifically, each lithium cation forms contacts with the oxygen atom of an ether molecule and with two carbon atoms of a phenyl ring, but all three of these contacts lie within a single hemisphere, i.e., on the same "side" of the lithium atom. In the present paper, we propose that the reported structure is a false solution in an incorrect space group and that the actual structure of the molecule differs significantly from that originally reported.

The crystal studied by Shilov et al. was tetragonal, with *a* = *b* = 12.624(4) Å and *c* = 13.250(8) Å. The structure was solved in the space group $P4_22_12$ and refined anisotropically to a final residual of $R_1 = 0.078$ for 502 independent reflections with $I > 2\sigma(I)$. Although

(1) Morse, P. M.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114−4116.

(2) Nelsen, M. J. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1996.

(3) Bazhenova, T. A.; Lobkovskaya, R. M.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K.; Gruselle, M.; Leny, G.; Tchoubar, B. *J. Organomet. Chem.* **1983**, *244*, 265−272.

(4) Kerber, R. C. *J. Organomet. Chem.* **1984**, *278*, 205−254. Hubberstey, P. *Coord. Chem. Rev.* **1985**, *66*, 1−92. Bartlett, R. A.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1966−1968. Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Organometallics* **1988**, *7*, 1380−1385. Taube, R.; Steinborn, D.; Drevs, H.; Chuong, P. N.; Stransky, N.; Langlotz, J. *Z. Chem.* **1988**, *28*, 381−396. Koschmieder, S. U.; Wilkinson, G. *Polyhedron* **1991**, *10*, 135−173. Shilov, A. E. *New J. Chem.* **1992**, *16*, 213-218. Müller, H.; Seidel, W.; Görls, H. *J. Organomet. Chem.* **1993**, *445*, 133−136. Poli, R. *Chem. Rev.* **1996**, *96*, 2135−2204. Kerber, R. C. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 7, Chapter 2.
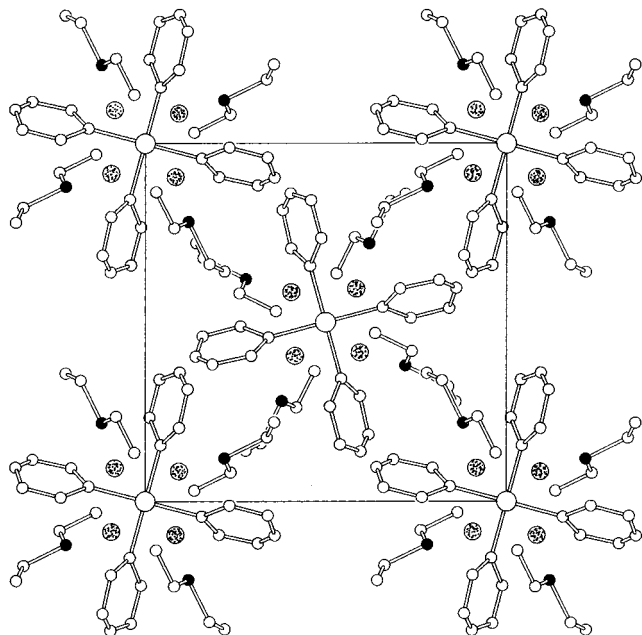
Figure 2. Projection of the $P\bar{4}2_1c$ structure of "**1**" down the *c*-axis. Key: Fe (large open spheres), C (small open spheres), Li (large stippled spheres), O (small black spheres).

the residual is reasonably low, a clue to the correct structure can be drawn from an examination of Figure 1. The unit cell of [Li(Et$_2$O)]$_4$[FePh$_4$] contains two symmetry-related molecules: one centered on the position 0,0,0 and one centered on the position $^1/_2$,$^1/_2$,$^1/_2$. Consider any C$_{ipso}$–C$_{ipso}$ vector between two mutually trans phenyl groups on an iron center. This vector forms an angle of 60° with respect to the C$_{ipso}$–C$_{ipso}$ vector described by the other two phenyl groups on the same iron center *but forms an angle of 90°* with respect to one of the C$_{ipso}$–C$_{ipso}$ vectors on the other iron center in the unit cell. This observation suggests that two of the phenyl groups on each iron center are mispositioned in the unit cell and, instead, should be moved so that they are bound to the *other* iron center. Therefore, we generated positions for all of the atoms in the unit cell from the published coordinates under the group $P4_22_12$ and then shifted the coordinates of *one-half* of the phenyl groups in the cell (and their associated Li–Et$_2$O units) by the operation $^1/_2 - x$, $^1/_2 - y$, $^1/_2 - z$. This transformation produces a unit cell that still contains two [Li(Et$_2$O)]$_4$[FePh$_4$] molecules but now both have near-ideal square-planar geometries in which the lithium centers are alternately above and below the FePh$_4$ plane as one circumnavigates the periphery of the anion (Figure 2).

The coordinates for this new arrangement correspond to the space group $P\bar{4}2_1c$. Because this same atomic arrangement can be produced with the asymmetric unit in Shilov's structure and the symmetry operations for $P\bar{4}2_1c$, the two descriptions differ in the choice of point group used to generate the three-dimensional structure from the basic structural motif. Shilov used 222 instead of $\bar{4}$. Thus, in the original $P4_22_12$ solution, the atoms within the asymmetric unit were properly positioned and oriented but the incorrect choice of space group caused the dispositions of the asymmetric units with respect to each other within the unit cell to be wrong.

If the new model is correct, then it must give diffraction intensities that agree with the experimentally

determined intensities for **1**. Unfortunately, structure factors for **1** have not been deposited, and despite several attempts, we have been unable to grow crystals of **1** by the published method so that a new data set could be collected (see below, however). Therefore, we calculated the intensities from the published coordinates and displacement parameters under the space group $P4_22_12$ and used this simulated data set to determine whether the new model is consistent with the diffraction pattern.[5] In fact, the simulated data set can be *solved* in the space group $P\bar{4}2_1c$, and the resulting coordinates are virtually identical to those generated by the transformation described above. Refinement against the simulated data set gives a reasonably low residual R_1 of 0.12.[6]

The absences for $P4_22_12$ are 00*l* ($l \neq 2n$) and *h*00 ($h \neq 2n$), whereas those for $P\bar{4}2_1c$ are *hhl* ($l \neq 2n$) and *h*00 ($h \neq 2n$). Thus, $P\bar{4}2_1c$ has extra absences of the form *hhl* with $h \neq 0$ and $l \neq 2n$. In the simulated data set generated from the space group and atomic parameters given by Shilov et al., the 111 and 113 reflections have nonzero calculated intensities (15% and 8% of the most intense reflection, respectively; all of the other *hhl* reflections with $h \neq 0$ and *l* odd have $I/I_{max} < 4\%$). We do not know, however, what the intensities were in the original experimental data set, but if all of the *hhl* ($l \neq 2n$) reflections were in fact absent, then the true space group is almost certainly $P\bar{4}2_1c$. If not, then the correct space group is probably $P2_12_12$.

In most published crystallographic studies in which an incorrect space group has inadvertently been chosen, the correct space group is one of three types: it is a supergroup,[7,8] an enantiomorphous space group,[9] or (more rarely) a subgroup[10] of the incorrect one. If the actual space group for compound **1** is $P\bar{4}2_1c$, then the present example falls into none of these classes. What is interesting about the $P4_22_12$ refinement is that it gives a false solution that is mathematically satisfactory but chemically unbelievable. This phenomenon resembles (but is not identical to) that described for structures in which the correct space group is chosen but the model refines into a false minimum.[11]

The new model for the structure of **1** eliminates all of the chemically unreasonable features that were

(5) The displacement parameters given by Shilov et al. for the non-hydrogen atoms are β's (not *B*s as indicated), and the off-diagonal coefficients in the table are evidently multiplied by 10^5 (not 10^4 as indicated). We used the program XFOG, which is part of the SHELXTL software package, to calculate the diffraction pattern from the published coordinates and displacement parameters. The estimated standard deviations of the intensities were set equal to the square root of the calculated intensity plus a background factor chosen so that the number of reflections with $F_o^2 > 2\sigma(F_o^2)$ was approximately the same ($\sim$500) as reported by Shilov et al.

(6) Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions with C–H = 0.96 Å. The displacement parameters for the hydrogen atoms were set equal to 1.2 times U_{eq} for the attached carbon atom. The displacement parameters for lithium and the atoms of the diethyl ether molecule were constrained to be similar. The refinement was carried out on $\sum w(F_o^2 - F_c^2)^2$: wR_2 (all data) = 0.373 for 111 parameters and 1059 total data. For the background factor chosen, there were 535 data with $F_o^2 > 2\sigma(F_o^2)$. The final electron density difference map was essentially featureless ($\Delta\rho_{max}$ = 0.93 e Å^{-3}).

(7) Marsh, R. E. *Acta Crystallogr.* **1995**, *B51*, 897–907.

(8) Baur, W. H.; Tillmanns, E. *Acta Crystallogr.* **1986**, *B42*, 95–111.

(9) Stout, G. H.; Turley, S.; Sieker, L. C.; Jensen, L. H. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 1020–1022.

(10) Burrell, A. K.; Cotton, F. A.; Daniels, L. M.; Petricek, V. *Inorg. Chem.* **1995**, *34*, 4253–4255.

characteristic of the original refinement. The iron center adopts an almost perfect square-planar geometry, with interligand angles of 90(1)° between mutually cis ligands and 180(1)° between mutually trans groups. The phenyl groups are canted with respect to the FeC_4 plane and are arranged as dictated by the $\bar{4}$ symmetry of the molecule. The short C···C contacts of 2.09 Å between the ipso carbons of adjacent phenyl groups are no longer present. The coordination geometries about the lithium centers now resemble those seen in other lithium salts of arylmetalate anions. Each lithium center forms five contacts (instead of three previously): one contact of ~2.0 Å with the oxygen of an ether molecule, two contacts of ~2.2 Å with the ipso carbons of *both* of the two nearest phenyl groups, and two longer contacts of 2.4−2.6 Å with ortho carbons. The chemically reasonable nature of this new model strongly suggests that the $P\bar{4}2_1c$ refinement is the correct one.

In 1992, Shilov reported that $[Li(Et_2O)]_4[FePh_4]$ reacts with H_2 to give an iron(II) dihydride of stoichiometry $[Li(Et_2O)]_4[FeH_2Ph_4]$ (**2**).[12] A crystal structure of **2** showed that the anion adopts a trans octahedral geometry in which the phenyl groups occupy the four equatorial positions. The presence of the hydride ligands was unequivocally demonstrated from deuteration studies and IR spectroscopy. Several aspects of the crystal structure of **2** are notable. First, the unit cell parameters for this dihydride are virtually identical to those reported for the tetraphenylferrate(0) salt **1**. Second, the structure of **2** was solved in the space group $P\bar{4}2_1c$. Third, the atomic coordinates reported for **2** correspond very closely with those of our $P\bar{4}2_1c$ model for **1**. Notably, the Fe−C distances in $[Li(Et_2O)]_4[FePh_4]$ and $[Li(Et_2O)]_4[FeH_2Ph_4]$ are virtually identical, a result that is *not* consistent with the presumption that the two iron centers are in different oxidation states. These considerations lead us to conclude that *the crystal originally reported to be [Li(Et₂O)]₄[FePh₄] was in fact a crystal of the dihydride* **2**. In short, the compound "$[Li(Et_2O)]_4[FePh_4]$" almost certainly does not exist.

The reformulation of $[Li(Et_2O)]_4[FePh_4]$ as an iron(II) hydride helps to explain why we could not synthesize it by the published method. Although Shilov reported[3] that addition of $FeCl_3$ to 10 equiv of phenyllithium in diethyl ether afforded crystals of "**1**" (i.e., **2**), we have been unable to obtain any crystalline material from this reaction despite many attempts. We attribute our result to the absence of an effective hydride source in solution. Although phenyl groups can serve as hydride sources (via formation of benzyne), in the

present case this reaction is evidently very inefficient. If, however, we add 2 equiv of *n*-butyllithium to the reaction solutions, crystals of the dihydride **2** form readily.[13] This result is significant because Shilov has claimed that aryliron(II) species react with *n*-propyllithium to afford iron(0) products.[14] The present results suggest instead that iron(II) hydrides are formed by means of β-hydrogen elimination processes.

We end with several conclusions. The data set collected for a crystal of the putative zerovalent compound "$[Li(Et_2O)]_4[FePh_4]$" ("**1**") was solved and refined in what we propose was an incorrect space group, $P4_22_12$. Despite the wrong choice of space group, the refinement proceeded to give a false solution that was satisfactory in all respects except that it was chemically unbelievable. In contrast, refinement in the space group $P\bar{4}2_1c$ gives a chemically sensible result.

Compound **1** almost certainly does not exist, or if it does, it has never been crystallized. We propose that the crystal thought to be **1** consisted, instead, of the iron(II) dihydride $[Li(Et_2O)]_4[FeH_2Ph_4]$ (**2**), in which the hydride ligands were generated by adventitious hydride sources in solution.

The claims that "$[Li(Et_2O)]_4[FePh_4]$" reacts with H_2 to form a dihydride and with N_2 to form a dinitrogen complex must be reevaluated in view of the questions raised about the existence of this iron(0) compound. We propose that iron(II) phenyl complexes are almost certainly the reactive species in both of these reactions. In our view, there is no convincing evidence that iron(0) compounds of any kind are formed upon treatment of $FeCl_3$ with phenyllithium.

Finally, the results reemphasize that the interpretation of X-ray diffraction data is not always straightforward. A mathematically satisfactory refinement is no guarantee that the deduced structure is correct.

Supporting Information Available: Tables of atomic coordinates and bond distances and angles for the $P\bar{4}2_1c$ refinement of "**1**" (3 pages). Ordering information is given on any current masthead page.

(11) Donohue, J.; Goodman, S. H. *Acta Crystallogr.* **1967**, *22*, 352−354. Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608−7617. Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 688−692. Lock, C. J. L.; Speranzini, R. A.; Zvagulis, M. *Acta Crystallogr.* **1980**, *B36*, 1789−1793 and references therein. Murphy, V. J.; Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 9762−9763.

(12) Bazhenova, T. A.; Kachapina, L. M.; Shilov, A. E.; Antipin, M. Yu.; Struchkov, Yu. T. *J. Organomet. Chem.* **1992**, *428*, 107−123.

(13) To a solution of phenyllithium (4.9 g, 61.6 mmol) in diethyl ether (75 mL) at −78 °C was added a chilled (−78 °C) solution of $FeCl_3$ (1.0 g, 6.2 mmol) in diethyl ether (75 mL). The mixture was stirred for 1 h at −78 °C and then for 3 h at room temperature. The dark red solution was filtered, cooled to −78 °C, and treated with *n*-butyllithium (6.2 mL of a 2.5 M solution in hexane, 15.4 mmol). The mixture was warmed to room temperature and allowed to stand for 12 h. The resulting black crystals were collected and then dried in a vacuum. Yield: 0.80 g (19%). The identity of the product was confirmed from its IR spectrum and unit cell parameters, which agree with those reported for **2**.

(14) Bazhenova, T. A.; Ivleva, I. N.; Kachapina, L. M.; Shilova, A. K.; Shilov, A. E.; Tchoubar, B. *J. Organomet. Chem.* **1985**, *296*, 95−101.