

Synthesis and Structural Characterization of Lithium and Iron Complexes Containing a Chelating Phenolate Phosphane Ligand

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Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

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The preparation and characterization of lithium and iron(II) complexes containing a potentially tridentate biphenolate phosphane ligand are reported. Deprotonation of 2,2'-phenylphosphanyl-bis(4,6-di-*tert*-butylphenol) (H_2L^{Ph}) with one or two equivalents of *n*BuLi in diethyl ether solutions at $-35\text{ }^\circ\text{C}$ produces binuclear $\{Li(HL^{Ph})(OEt_2)\}_2$ or tetranuclear $Li_4(L^{Ph})_2(OEt_2)_3$, respectively. An X-ray study of $\{Li(HL^{Ph})(OEt_2)\}_2$ showed it to be a C_i -symmetric dimer composed of two $Li(HL^{Ph})(OEt_2)$ units linked with dative O–Li bonds in-

volving phenolate oxygen donor atoms whereas that of $Li_4(L^{Ph})_2(OEt_2)_3$ revealed a C_2 -symmetric structure in which the two biphenolate phosphane ligands are linked with four lithium atoms that bind to three diethyl ether molecules. Treatment of $FeCl_2$ with one or two equivalents of $Na_2(L^{Ph})(DME)_2$ in THF at $-35\text{ }^\circ\text{C}$ generates binuclear $Fe_2(L^{Ph})_2(THF)_2$ or mononuclear $Fe(HL^{Ph})_2(THF)_2$, respectively. The two iron(II) centers in $Fe_2(L^{Ph})_2(THF)_2$ are antiferromagnetically coupled.

Introduction

Cluster complexes that exhibit unusual structural and/or reactivity motifs have attracted considerable attention in the past decades. Specific molecular architectures may be deliberately constructed with the employment of smart bridging and blocking ligands. Unusual physical properties and/or chemical transformations may evolve significantly.^[1–8] For instance, lithium phenolate aggregates have been used as building blocks in the controlled assembly of metal–organic frameworks.^[9] We are currently exploring the reaction and structural chemistry with metal complexes of hybrid chelating ligands.^[10–17] In particular, a number of Group 1 derivatives of the biphenolate phosphane ligands 2,2'-phenylphosphanyl-bis(4,6-di-*tert*-butylphenolate) ($[L^{Ph}]^{2-}$)^[18] and 2,2'-*tert*-butylphosphanyl-bis(4,6-di-*tert*-butylphenolate) ($[L^{tBu}]^{2-}$)^[19] have been prepared and their structures characterized. The structural preferences of these complexes have been shown to be a function of several parameters, including substituents at the phosphorus donor, incorporation of solvent molecules, and the electrophilicity and sizes of the Group 1 metals. Examination of the relationship between complex structures and these constitutional parameters is

of interest. For instance, the molecular structures of Li_2L^{Ph} complexes vary noticeably upon DME or THF coordination.^[18,20] In this contribution, we describe the syntheses and structures of diethyl ether adducts of $Li(HL^{Ph})$ and Li_2L^{Ph} ; the structural motif of these molecules is notably distinct from those of $Li_2(L^{Ph})(DME)_2$ ^[18] and $\{Li_2(L^{Ph})(THF)_2\}_2$.^[20] Utilization of the established Group 1 complexes of $[L^{Ph}]^{2-}$ for the preparation of iron derivatives is also reported. Investigation of phenolate complexes of iron is intriguing in view of their relevance to metalloprotein chemistry.^[21–24] We note that biphenolate phosphane complexes of iron are unprecedented although ligands of this general type have been known since 1980.^[25]

Results and Discussion

The isolation of well-defined lithium complexes of $[L^{Ph}]^{2-}$ that are free of strong coordinating solvents was undertaken. The addition of two equivalents of *n*BuLi to a pentane or toluene solution of H_2L^{Ph} at $-35\text{ }^\circ\text{C}$ cleanly generated the dilithium derivative as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. The observed ^{31}P NMR chemical shift at approximately -32 ppm from these experiments is comparable to those acquired with well-defined compounds prepared in DME or THF solutions.^[18,20] Attempts to grow crystals of these solvent-free lithium complexes, however, led to amorphous precipitates, the 1H NMR spectra of which are unfortunately featureless. Similar reactions were

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conducted in diethyl ether solutions, which also led to the clean formation of the anticipated dilithium derivative as indicated by $^3\text{P}\{\text{H}\}$ NMR spectroscopy. After standard work-up, the diethyl ether adduct $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ was successfully isolated as colorless crystals from a concentrated diethyl ether solution at -35°C . In a separate batch, colorless crystals of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$ were also obtained, though in rather low yield, with a crystal shape apparently different from that of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$. The formation of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$ was unexpected but ascribed tentatively to the partial protonation of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ as a result of trace amounts of moisture present in the solvent employed. Nevertheless, $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$ may be readily prepared from the reaction of $\text{H}_2\text{L}^{\text{Ph}}$ with one equivalent of $n\text{BuLi}$ in diethyl ether at -35°C . An analogous reaction involving $\text{H}_2\text{L}^{\text{Ph}}$ and NaH in DME gave $\text{Na}(\text{HL}^{\text{Ph}})(\text{DME})_2$.

Figure 1 illustrates the molecular structure of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$. Selected bond lengths and angles are summarized in Table 1. The crystals were of poor quality, suffering from disorder of the diethyl ether molecules, but sufficient to confirm the identity of this molecule. The C_i -symmetric dimer comprises two $\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)$ units bridged with two dative O–Li bonds. The inversion center lies at the central point of the Li_2O_2 tetragon. With the presence of a hydroxy group, the phenolate phosphane ligand is a monoanionic $\kappa^2\text{-O,P}$ donor to lithium. The coordination geometry at each lithium core is best described as a severely distorted tetrahedral.

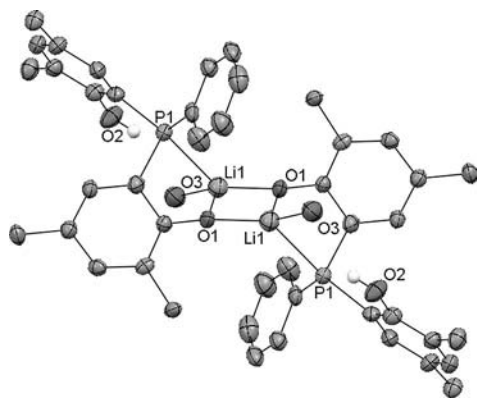


Figure 1. Molecular structure of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$ with thermal ellipsoids drawn at the 35% probability level. All methyl groups in *tert*-butyl and all ethyl groups in coordinated diethyl ether molecules have been omitted for clarity.

The molecular structure of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ is depicted in Figure 2. In view of the structural motifs of the previously established $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$,^[18] $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$,^[20] and $\{\text{Li}_2(\text{L}^{\text{Bu}})(\text{DME})\}_2$,^[19] the molecular structure of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ is of interest. It adopts three diethyl ether and two biphenolate phosphane ligands to bind to four lithium atoms in an overall C_2 -symmetric fashion, leading to the formation of two Li_2O_2 tetragons that are nearly orthogonal to each other. The C_2 axis coincides with the Li1-Li2 vector and penetrates through the central point of the Li3-O3-Li3A-O3A tetragon. The biphenolate phosphane ligand is $\kappa^2\text{-O,P}$ bound to Li2 and $\kappa^1\text{-O}$ bound

Table 1. Selected bond lengths [Å] and bond angles [°] for $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$, $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$, $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$, and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$.

$\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$			
P(1)–Li(1)	2.725(15)	Li(1)–O(1A)	1.833(16)
O(3)–Li(1)	1.964(18)	O(1)–Li(1)	1.923(17)
O(1A)–Li(1)–O(1)	98.4(8)	O(1A)–Li(1)–O(3)	129.9(9)
O(1)–Li(1)–O(3)	117.7(8)	O(1A)–Li(1)–P(1)	126.7(8)
O(1)–Li(1)–P(1)	74.1(5)	O(3)–Li(1)–P(1)	97.4(6)
$\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$			
O(1)–Li(1)	1.833(4)	O(1)–Li(2)	1.894(5)
Li(3)–O(3A)	1.833(5)	O(2)–Li(3)	1.881(7)
O(4)–Li(1)	1.901(7)	P(1)–Li(2)	2.553(2)
O(3)–Li(3)	1.839(5)		
O(1)–Li(1)–O(1A)	101.0(3)	P(1)–Li(2)–P(1A)	142.5(2)
O(1)–Li(2)–P(1)	79.4(5)	O(1A)–Li(2)–P(1)	127.8(5)
O(1)–Li(1)–O(4)	128.1(1)	O(1)–Li(2)–P(1A)	127.8(5)
O(1A)–Li(1)–O(4)	128.4(1)	O(3)–Li(3)–O(2)	132.5(4)
O(3A)–Li(3)–O(2)	131.6(4)	O(3A)–Li(3)–O(3)	95.3(2)
O(1)–Li(2)–O(1A)	96.5(6)	O(1A)–Li(2)–P(1A)	79.4(5)
$\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$			
O(1)–Fe(1)	1.924(4)	O(2)–Fe(2)	1.890(4)
O(3)–Fe(2)	2.078(4)	O(3)–Fe(1)	2.086(4)
O(4)–Fe(1)	2.028(4)	O(4)–Fe(2)	2.268(4)
O(5)–Fe(1)	2.215(4)	O(6)–Fe(2)	2.206(5)
P(1)–Fe(1)	2.6443(17)	P(1)–Fe(2)	2.8221(17)
P(2)–Fe(2)	2.4081(16)	Fe(1)–Fe(2)	2.8237(14)
O(1)–Fe(1)–O(4)	129.51(16)	O(1)–Fe(1)–O(3)	139.28(16)
O(4)–Fe(1)–O(3)	88.46(14)	O(1)–Fe(1)–O(5)	91.88(16)
O(4)–Fe(1)–O(5)	97.29(15)	O(3)–Fe(1)–O(5)	97.76(15)
O(1)–Fe(1)–P(1)	79.58(12)	O(4)–Fe(1)–P(1)	88.90(10)
O(3)–Fe(1)–P(1)	88.30(10)	O(5)–Fe(1)–P(1)	171.42(12)
O(1)–Fe(1)–Fe(2)	141.57(12)	O(4)–Fe(1)–Fe(2)	52.68(10)
O(3)–Fe(1)–Fe(2)	47.18(10)	O(5)–Fe(1)–Fe(2)	126.52(11)
P(1)–Fe(1)–Fe(2)	62.04(4)	O(2)–Fe(2)–O(3)	156.19(15)
O(2)–Fe(2)–O(6)	89.06(17)	O(3)–Fe(2)–O(6)	94.26(18)
O(2)–Fe(2)–O(4)	95.40(15)	O(3)–Fe(2)–O(4)	82.55(14)
O(6)–Fe(2)–O(4)	175.01(14)	O(2)–Fe(2)–P(2)	122.48(12)
O(3)–Fe(2)–P(2)	80.30(10)	O(6)–Fe(2)–P(2)	99.00(13)
O(4)–Fe(2)–P(2)	76.72(9)	O(2)–Fe(2)–P(1)	72.50(12)
O(3)–Fe(2)–P(1)	83.81(10)	O(6)–Fe(2)–P(1)	103.45(13)
O(4)–Fe(2)–P(1)	80.08(9)	P(2)–Fe(2)–P(1)	153.31(6)
O(2)–Fe(2)–Fe(1)	116.35(12)	O(3)–Fe(2)–Fe(1)	47.42(11)
O(6)–Fe(2)–Fe(1)	133.95(15)	O(4)–Fe(2)–Fe(1)	45.34(9)
P(2)–Fe(2)–Fe(1)	97.93(5)	P(1)–Fe(2)–Fe(1)	55.86(4)
$\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$			
Fe(1)–O(1)	1.977(3)	Fe(1)–O(3)	2.260(4)
Fe(1)–O(4)	2.270(5)	Fe(1)–P(1)	2.5241(9)
O(1)–Fe(1)–O(1A)	174.40(15)	O(1)–Fe(1)–O(3)	92.80(7)
O(1A)–Fe(1)–O(3)	92.80(7)	O(1)–Fe(1)–O(4)	87.20(7)
O(1A)–Fe(1)–O(4)	87.20(7)	O(3)–Fe(1)–O(4)	180.0
O(1)–Fe(1)–P(1)	80.50(8)	O(1A)–Fe(1)–P(1)	99.83(8)
O(3)–Fe(1)–P(1)	86.67(3)	O(4)–Fe(1)–P(1)	93.33(3)
O(1)–Fe(1)–P(1A)	99.83(8)	O(1A)–Fe(1)–P(1A)	80.49(8)
O(3)–Fe(1)–P(1A)	86.67(3)	O(4)–Fe(1)–P(1A)	93.33(3)
P(1)–Fe(1)–P(1A)	173.35(5)		

to Li3 ; a coordination mode that is markedly different from those of $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$,^[18] $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$,^[20] and $\{\text{Li}_2(\text{L}^{\text{Bu}})(\text{DME})\}_2$,^[19] in which both $[\text{L}^{\text{Ph}}]^{2-}$ and $[\text{L}^{\text{Bu}}]^{2-}$ act as a $\kappa^3\text{-O,P,O}$ ligand bound to one of the lithium atoms. Notably, the lithium atoms in $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ are three- or four-coordinate whereas those in $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$,^[18] $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$,^[20] and $\{\text{Li}_2(\text{L}^{\text{Bu}})(\text{DME})\}_2$,^[19] are four-

or five-coordinate. Such a discrepancy in molecular architectures highlights the weaker coordinating nature of diethyl ether compared with DME and THF. Though the bond lengths and angles of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ are all within the expected values for a biphenolate phosphane complex of lithium, the O–Li distances in $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ involving both phenolate and ethereal oxygen donors are slightly shorter than those of $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$ [lengths involving phenolate oxygen range from 1.897(6) to 1.985(7) Å and those involving DME oxygen range from 1.971(6) to 2.155(6) Å],^[18] $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$ [lengths involving phenolate oxygen range from 1.890(3) to 2.148(3) Å and those involving THF oxygen range from 1.981(3) to 1.994(3) Å],^[20] and $\{\text{Li}_2(\text{L}^{\text{tBu}})(\text{DME})_2\}_2$ [lengths involving phenolate oxygen range from 1.850(6) to 2.151(7) Å and those involving DME oxygen range from 2.006(7) to 2.078(7) Å],^[19] likely reflecting the lower coordination number of the lithium cores in the former. Consistent with the anticipated electronic nature of the phosphorus substituents, the P–Li distance of 2.553(2) Å in $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ is comparable to those of $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$ [2.573(5) Å]^[18] and $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$ (2.499(3) Å)^[20] but significantly longer than those of $\{\text{Li}_2(\text{L}^{\text{tBu}})(\text{DME})_2\}_2$ (2.43 Å average).^[19]

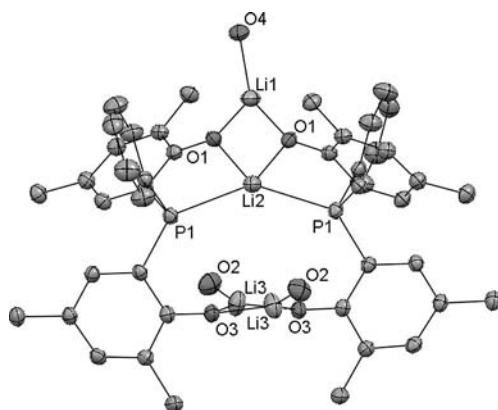


Figure 2. Molecular structure of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ with thermal ellipsoids drawn at the 35% probability level. All methyl groups in *tert*-butyl and all ethyl groups in diethyl ether molecules have been omitted for clarity.

The solution NMR spectroscopic data of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)_2\}_2$ are consistent with what is anticipated from the established X-ray structures; the *tert*-butyl groups are observed in the ^1H NMR spectra as three singlet resonances in a 2:1:1 ratio at room temperature whereas there are four well-resolved signals with equal intensity at -80°C . The solution structure of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ is apparently more symmetric than the solid-state, with the *tert*-butyl groups appearing as two singlet resonances with equal intensity in the ^1H NMR spectrum at room temperature, consistent with a dynamic equilibrium occurring in solution. The coordinated diethyl ether molecules in $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)_2\}_2$ and $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ are presumably labile as evidenced by only one set of diethyl ether signals observed in the ^1H NMR spectra of solutions containing an excess

amount of diethyl ether. Standing a $[\text{D}_8]\text{toluene}$ solution of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)_2\}_2$ or $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ at room temperature for several hours led to the occurrence of some precipitates. The ^1H NMR spectra of these solutions are indicative of the presence of C_1 -symmetric molecules, due possibly to the formation of higher aggregates.^[26–28] In agreement with this hypothesis, these precipitates re-dissolve in solution upon addition of an excess of diethyl ether. Similar phenomena were also found for $\{\text{Li}^{\text{tBu}}\text{Li}_2(\text{DME})_2\}_2$.^[19] Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)_2\}_2$ and $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ in $[\text{D}_8]\text{toluene}$ confirmed the coordination of the soft phosphorus donors to the hard lithium atoms with a 1:1:1:1 quartet resonance ($^1J_{\text{PLi}} = 61\text{ Hz}$), albeit at temperatures lower than -70°C . Consistently, the $^7\text{Li}\{^1\text{H}\}$ NMR spectrum of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)_2\}_2$ at -70°C exhibits a doublet resonance for the phosphorus-bound lithium atoms whereas that of $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ shows one triplet and two singlet resonances in a 1:1:2 ratio, reflecting the structural resemblance of these molecules between the solution and the solid state.

The preparation of iron(II) complexes of biphenolate phosphane ligands was undertaken. Reactions involving all established ethereal adducts of $\text{Li}_2\text{L}^{\text{Ph}}$, including those isolated and generated in situ, led to intractable materials from which no well-defined products have been identified thus far. In contrast, treating FeCl_2 with one equivalent of the sodium complex $\text{Na}_2(\text{L}^{\text{Ph}})(\text{DME})_2$ ^[18] in THF at -35°C afforded brownish-yellow crystals of binuclear $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ in 47% yield after recrystallization from a diethyl ether solution. As shown in Figure 3, this molecule has C_1 symmetry, with the Fe1 ion being six-coordinate and Fe2 seven. In addition to the coordination of two biphenolate phosphane ligands, each iron atom is bound to one THF molecule. The coordination modes of the two $[\text{L}^{\text{Ph}}]^{2-}$ ligands are different: the two iron atoms are bridged with one phosphorus donor from one $[\text{L}^{\text{Ph}}]^{2-}$ ligand and two phenolate oxygen donors from the other, although the P1–Fe2 distance of 2.822(2) Å and O4–Fe2 distance of 2.268(4) Å are somewhat long.^[24,29–32] The difference of 0.1778 Å between the P1–Fe1 and P1–Fe2 distances highlights the semi-bridging nature of this phosphane donor.^[33–35] The Fe–Fe distance of 2.824(1) Å in $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ is substantially longer than those found in the diiron site of Fe-only hydrogenase structures (ca. 2.60 Å)^[36,37] and their model complexes, such as $\text{Fe}_2(\mu\text{-S}_2\text{C}_3\text{H}_6)(\text{CO})_6$ [2.510(1) Å]^[38] and $[\text{Fe}_2(\mu\text{-S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{CN})_2]^{2-}$ [2.517(1) Å],^[39] but appears to be comparable to those in the model complexes of non-heme diiron enzymes, such as $[\text{Fe}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{H}_2\text{B}(\text{pz})_2)_2]^-$ [2.829(4) Å],^[40] $(\text{ToI}_2\text{C}_6\text{H}_3\text{-CO}_2)_4\text{Fe}_2(\mu\text{-OH})_2$ [2.8843(9) Å],^[41] and $(\text{Mes}_2\text{C}_6\text{H}_3\text{CO}_2)_4\text{-Fe}_2(\mu\text{-OCHMe})_2$ [2.998(1) Å].^[42] Solution NMR spectroscopic studies showed that $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ is ^{31}P NMR silent, indicating this compound to be paramagnetic. The effective magnetic moment (μ_{eff}) of this complex in solution at room temperature, determined by the Evans method,^[43,44] was found to be $7.15\mu_{\text{B}}$, indicating that the two high-spin Fe^{II} centers are antiferromagnetically coupled.

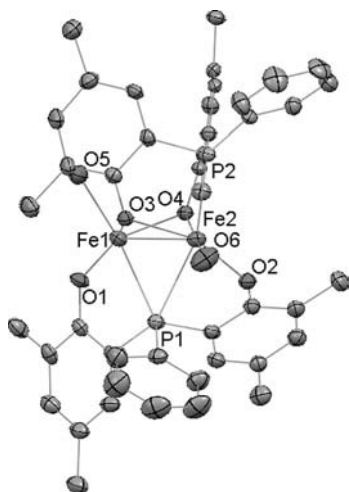


Figure 3. Molecular structure of $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ with thermal ellipsoids drawn at the 35% probability level. All methyl groups in *tert*-butyl and all methylene groups in THF molecules have been omitted for clarity.

Given the unexpected formation of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$, which contains a mono-protonated biphenolate phosphane ligand, we became curious if this phenomenon would occur similarly for reactions involving $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$. Indeed, a controlled experiment of $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ with a substoichiometric amount of water in THF at -35°C produced, though in low isolated yield, brown crystals of $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ as indicated by an X-ray diffraction study. Salt metathesis reactions of FeCl_2 with two equivalents of $\text{Na}_2(\text{L}^{\text{Ph}})(\text{DME})_2$ ^[18] or $\text{Na}(\text{HL}^{\text{Ph}})(\text{DME})_2$ in THF also generated $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ in 48 or 80% isolated yield, respectively. An X-ray study of $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ (Figure 4) showed it to be a six-coordinate octahedral species containing two *trans*-disposed THF and two *trans*-disposed phosphorus donors. This complex is thus C_2 -symmetric; the C_2 axis coincides with the vector defined by the two oxygen donor atoms of the coordinated THF. The phenolate phosphane ligands are $\kappa^2\text{-O,P}$ bound to iron. Similar to $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$, the mononuclear $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ is also ^{31}P NMR silent. The μ_{eff} value of $5.48 \mu_{\text{B}}$ measured by

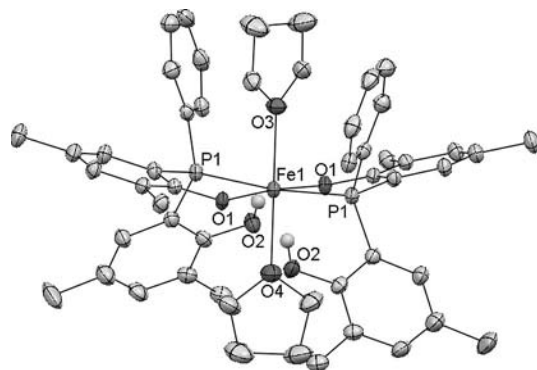


Figure 4. Molecular structure of $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ with thermal ellipsoids drawn at the 35% probability level. All methyl groups have been omitted for clarity.

the Evans method^[43,44] at room temperature is comparable to that anticipated for a mononuclear high-spin Fe^{II} complex.^[45]

Conclusion

In summary, we have prepared and structurally characterized a previously elusive diethyl ether adduct of $\text{Li}_2\text{L}^{\text{Ph}}$ and that of its singly protonated derivative $\text{Li}(\text{HL}^{\text{Ph}})$. With the incorporation of OEt_2 , a somewhat weaker coordinating motif than DME and THF, complex $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$ exhibits a molecular architecture distinct from $\text{Li}_2(\text{L}^{\text{Ph}})(\text{DME})_2$,^[18] $\{\text{Li}_2(\text{L}^{\text{Ph}})(\text{THF})_2\}_2$,^[20] and $\{\text{Li}_2(\text{L}^{\text{tBu}})(\text{DME})_2\}_2$.^[19] The formation of binuclear $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ is of particular interest in view of its diiron core structure containing two phenolate oxygen and one phosphane bridges. The isolation of $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$ and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ implies the compatibility of $[\text{HL}^{\text{Ph}}]^-$ be an effective chelating ligand to main-group and transition metals. The two iron(II) centers in $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ are antiferromagnetically coupled.

Experimental Section

General Procedures: Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. Compounds $\text{H}_2(\text{L}^{\text{Ph}})$ ^[46] and $\text{Na}_2(\text{L}^{\text{Ph}})(\text{DME})_2$ ^[18] were prepared according to literature procedures. All other chemicals were obtained from commercial vendors and used as received. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) are given in Hertz. ^1H NMR spectra are referenced using the residual solvent peak at $\delta = 2.09$ for $[\text{D}_8]\text{toluene}$ (the most upfield resonance). ^{31}P and ^7Li NMR spectra are referenced externally using 85% H_3PO_4 at $\delta = 0$ and LiCl in D_2O at $\delta = 0$, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

X-ray Crystallography: Crystallographic data are summarized in Table 2. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using SHELXL-97.^[47] All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The structures of $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$ contain disordered diethyl ether molecules. Attempts to obtain a suitable disorder model failed. The SQUEEZE procedure of Platon program^[48] was used to obtain a new set of F^2 (hkl) values without the contribution of solvent molecules, leading to the presence of significant voids in the structure. The refinement reduced $R1$ values to 0.0776 and 0.0713 for $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$, respectively. In $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$, one coordinated diethyl ether molecule is disordered with one ethyl and one methyl substituents over two conformations. In $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$, one coordinated diethyl ether molecule is disordered with two orientations crossing a symmetry element. In both $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$ and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$,

Table 2. Crystallographic data for $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$, $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$, $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$, and $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$.

Compound	$\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$	$\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$	$\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$	$\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$
Formula	$\text{C}_{38}\text{H}_{56}\text{LiO}_3\text{P}$	$\text{C}_{80}\text{H}_{120}\text{Li}_4\text{O}_7\text{P}_2$	$\text{C}_{76}\text{H}_{106}\text{Fe}_2\text{O}_6\text{P}_2$	$\text{C}_{76}\text{H}_{108}\text{FeO}_6\text{P}_2$
<i>F</i> _w	598.74	1283.46	1289.25	1235.41
Crystal size [mm ³]	$0.13 \times 0.08 \times 0.02$	$0.75 \times 0.7 \times 0.65$	$0.24 \times 0.20 \times 0.11$	$0.66 \times 0.60 \times 0.40$
<i>D</i> _{calc} [Mg/m ³]	1.094	1.076	1.067	1.086
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>Ibca</i>
<i>a</i> [Å]	10.5366(5)	20.5594(3)	13.517(4)	13.2732(5)
<i>b</i> [Å]	11.1909(5)	21.5581(4)	17.121(4)	27.1423(10)
<i>c</i> [Å]	15.9578(9)	19.6062(4)	18.817(4)	41.9311(17)
α [°]	83.121(2)	90	78.679(19)	90
β [°]	89.630(2)	114.2490(10)	70.328(16)	90
γ [°]	76.706(2)	90	89.256(18)	90
<i>V</i> [Å ³]	1817.61(16)	7923.2(2)	4014.1(16)	15106.3(10)
<i>Z</i>	2	4	2	8
<i>T</i> [K]	200(2)	200(2)	200(2)	200(2)
2 θ range [°]	4.30, 50.64	4.42, 50.62	2.42, 50.06	1.94, 50.06
Index ranges (<i>h</i> ; <i>k</i> ; <i>l</i>)	−12, −12; −13, 13; −19, 19	−24, 24; −25, 25; −23, 17	−16, 15; −19, 20; −22, 22	−15, 11; −32, 27; −46, 49
Total number of reflections	25019	30787	25026	28179
Independent reflections	6571	7189	13685	6622
<i>R</i> _{int}	0.1610	0.0906	0.0856	0.0415
Absorption coefficient [mm ^{−1}]	0.108	0.104	0.445	0.288
Data / restraints / parameters	6571 / 0 / 417	7189 / 0 / 442	13685 / 0 / 734	6622 / 0 / 412
Goodness of fit	1.399	1.048	0.876	1.131
Final indices <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.1562	0.0622	0.0776	0.0713
Final indices <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.4110	0.1609	0.1803	0.2329
<i>R</i> 1 indices (all data)	0.2470	0.0922	0.1606	0.0934
<i>wR</i> 2 indices (all data)	0.4579	0.1807	0.2110	0.2587
Residual density [e/Å ³]	−0.876 to 0.931	−0.314 to 0.582	−0.598 to 0.715	−0.359 to 2.556

(THF)₂, two *tert*-butyl groups are disordered with the methyl substituents over two conformations.

CCDC-810499 (for $\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$), -810500 [for $\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$], -810501 [for $\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$], -810502 [for $\text{Fe}(\text{HL}^{\text{Ph}})_2(\text{THF})_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$\{\text{Li}(\text{HL}^{\text{Ph}})(\text{OEt}_2)\}_2$: *n*BuLi (77 μL , 2.5 M in hexane, 0.19 mmol) was added to a diethyl ether solution (7 mL) of $\text{H}_2\text{L}^{\text{Ph}}$ (100 mg, 0.19 mmol) at -35°C . The solution was stirred at room temperature for 1 h and the solvents evaporated to dryness under reduced pressure to give the product as an off-white solid; yield 98 mg (93%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at -35°C . ¹H NMR ([D₈]toluene, 500 MHz): δ = 7.44 (m, 8 H, ArH), 7.05 (m, 8 H, ArH), 6.91 (m, 4 H, ArH and OH), 2.90 (q, 8 H, OCH₂), 1.62 (s, 18 H, ArCMe₃), 1.49 (s, 18 H, ArCMe₃), 1.26 (br. s, 36 H, ArCMe₃), 0.78 (t, 12 H, OCH₂CH₃) ppm. ³¹P{¹H} NMR ([D₈]toluene, 121.5 MHz): δ = −33.3 (br. s) ppm. ⁷Li{¹H} NMR ([D₈]toluene, 194 MHz, -70°C): δ = 1.13 (d, ¹*J*_{PLi} = 65 Hz) ppm.

$\text{Li}_4(\text{L}^{\text{Ph}})_2(\text{OEt}_2)_3$: *n*BuLi (150 μL , 2.5 M in hexane, 0.38 mmol) was added to a diethyl ether solution (7 mL) of $\text{H}_2\text{L}^{\text{Ph}}$ (100 mg, 0.19 mmol) at -35°C . The solution was stirred at room temperature for 1 h and the solvents evaporated to dryness under reduced pressure to give the product as an off-white solid; yield 111 mg (99%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at -35°C . ¹H NMR ([D₈]toluene, 500 MHz): δ = 7.47 (m, 8 H, ArH), 7.17 (t, 4 H, ArH), 7.06 (m, 4 H, ArH), 6.97 (m, 2 H, ArH), 3.05 (q, 12 H, OCH₂), 1.51 (s, 36 H, ArCMe₃), 1.21 (s, 36 H, ArCMe₃), 0.70 (t, 18 H, OCH₂CH₃) ppm. ³¹P{¹H} NMR ([D₈]toluene, 121.5 MHz): δ

= −33.2 (br. s) ppm. ⁷Li{¹H} NMR ([D₈]toluene, 194 MHz, -70°C): δ = 4.26 (t, ¹*J*_{PLi} = 65 Hz, 1 Li), 1.76 (s, 1 Li), 1.23 (s, 2 Li) ppm.

$\text{Na}(\text{HL}^{\text{Ph}})(\text{DME})_2$: A DME solution (2 mL) of $\text{H}_2\text{L}^{\text{Ph}}$ (65 mg, 0.125 mmol) was added to a DME suspension (12 mL) of NaH (3 mg, 0.125 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight, resulting in a colorless, homogeneous solution. All volatiles were removed under reduced pressure. The solid residue obtained was dissolved in pentane (10 mL). The pentane solution was then filtered through a pad of Celite and the solvents evaporated to dryness under reduced pressure to give the product as an off-white solid; yield 85 mg (95%). ¹H NMR (C₆D₆, 300 MHz): δ = 7.59 (br. s, 2 H, ArH), 7.55 (m, 2 H, ArH), 7.21 (m, 2 H, ArH), 6.99 (br. m, 4 H, ArH and OH), 3.09 (s, 8 H, OCH₂), 2.93 (s, 12 H, OMe), 1.65 (s, 18 H, CMe₃), 1.29 (s, 18 H, CMe₃) ppm. ³¹P{¹H} NMR (C₆D₆, 121 MHz): δ = −36.1 ppm.

$\text{Fe}_2(\text{L}^{\text{Ph}})_2(\text{THF})_2$: A pre-chilled THF solution (4 mL) of Na₂(L^{Ph})(DME)₂ (200 mg, 0.27 mmol) was added to a THF solution (1 mL) of FeCl₂ (34 mg, 0.27 mmol) at -35°C . The reaction solution was stirred at room temperature overnight and the solvents evaporated to dryness under reduced pressure. Toluene (10 mL) was added and the solution was filtered through a pad of celite and the solvents evaporated to dryness under reduced pressure. The tan solid obtained was dissolved in a minimal amount of diethyl ether (ca. 2 mL) and the solution was cooled to -35°C to give the product as brownish yellow crystals suitable for X-ray diffraction analysis; yield 81 mg (47%). (C₇₆H₁₀₆Fe₂O₆P₂)(C₄H₈O)₃ (1504.61): calcd. C 70.18, H 8.71; found C 69.97, H 8.53. ¹H NMR (C₆D₆, 300 MHz): δ = 70.42 (4 H), 49.24 (2 H), 33.18 (4 H), 29.34 (2 H), 18.35 (4 H), 9.25 (20 H), 6.75 (18 H), 3.92 (22 H), 2.74 (4 H), 1.63 (8 H), −25.51 (18 H) ppm.

Fe(HL^{Ph})₂(THF)₂. Method 1: A pre-chilled THF solution (4 mL) of Na₂(L^{Ph})(DME)₂ (300 mg, 0.40 mmol) was added to a THF solution (1 mL) of FeCl₂ (26 mg, 0.20 mmol) at −35 °C. The reaction solution was stirred at room temperature overnight and the solvents evaporated to dryness under reduced pressure. Diethyl ether (10 mL) was then added. The solution was filtered through a pad of celite and concentrated under reduced pressure until the volume was approximately 2 mL. Cooling the concentrated solution to −35 °C afforded the product as brown crystals suitable for X-ray diffraction analysis; yield 118 mg (48%).

Method 2: A THF solution (2 mL) of Na(HL^{Ph})(DME)₂ (40 mg, 0.055 mmol) was added to a THF solution (4 mL) of FeCl₂ (4 mg, 0.028 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. All volatiles were removed under reduced pressure. Diethyl ether (10 mL) was added. The diethyl ether solution was filtered through a pad of celite and the solvents evaporated to dryness under reduced pressure to give the product as a brown solid; yield 35 mg (80%). ¹H NMR (C₆D₆, 300 MHz): δ = 16.28 (2 H), 9.81 (10 H), 6.07 (36 H, CMe₃), 4.30 (36 H, CMe₃), 2.72 (12 H), 1.29 (8 H), −18.21 (4 H) ppm.

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