Hydrides in Biology

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Characterization of the Fe–H Bond in a Three-Coordinate Terminal Hydride Complex of Iron(I)**

Karen P. Chiang, Christopher C. Scarborough, Masaki Horitani, Nicholas S. Lees, Keying Ding, Thomas R. Dugan, William W. Brennessel, Eckhard Bill, Brian M. Hoffman,* and Patrick L. Holland**

Hydride complexes of transition metals play a central role in organometallic chemistry.[1,2] They are also implicated in biological inorganic chemistry, where hydrides are known or thought to be present in key intermediates in H_2 utilization by hydrogenases[3,4] and in N_2 reduction by iron–molybdenum nitrogenases.[5,6] In both cases, trapped intermediates exhibit large ^1H hyperfine couplings from hydrides bonded to paramagnetic iron ion(s).[7–11] As these biological hydrides arise in catalytic intermediates that are not amenable to crystallographic characterization, it is essential to identify the spectroscopic signatures of well-characterized transition-metal hydride complexes.[12]

As ENDOR spectroscopy of odd-electron enzyme intermediates has been a central tool in characterizing biological iron hydrides,[7–9,13–15] a key advance would be the preparation of simple mononuclear Fe–H complexes with an odd-electron iron(I) or iron(III) oxidation state for comparison. However, crystallographically characterized compounds of this type have been unknown, presumably because of the low oxidation state in iron(I) compounds and the high reactivity of hydrides. Because β-diketiminate ligands stabilize iron(I) complexes,[16] we chose the anion $[L^{tBu,iPr2}FeH]^-$ ($L^{tBu,iPr2}$ = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimido)heptyl) as a target. Herein we report the successful synthesis of this high-spin iron(I) complex and the detailed characterization of its Fe–H bonding through EPR and ENDOR spectroscopies. Computational studies also explain the distinctive ability of β-diketiminates to stabilize electron-rich iron(I) species.

Treatment of the iron(II) complex $[\{L^{tBu,iPr2}Fe(\mu\text{-}H)\}_2]$ with a slight excess of potassium graphite (KC_8) in diethyl ether gives the reduced iron(I) hydride complex $[\{KL^{tBu,iPr2}FeH\}_2]$ in 49% yield. An X-ray diffraction study shows that the iron atoms in $[\{KL^{tBu,iPr2}FeH\}_2]$ are three-coordinate (Figure 1). Its structure is similar to the previously reported cobalt(I) analogue.[17] The compound is a dimer, and the two crystallographically equivalent halves are held together by potassium cations that associate with aryl groups of the β-diketiminate ligands with potassium–centroid distances of 3.02 Å and 2.96 Å. The two diketiminate–iron planes are parallel but not coplanar, and the hydrides are 2.98(4) Å apart. The K^+ ions also interact with the hydrides, with K–H distances of 2.68(2) Å.

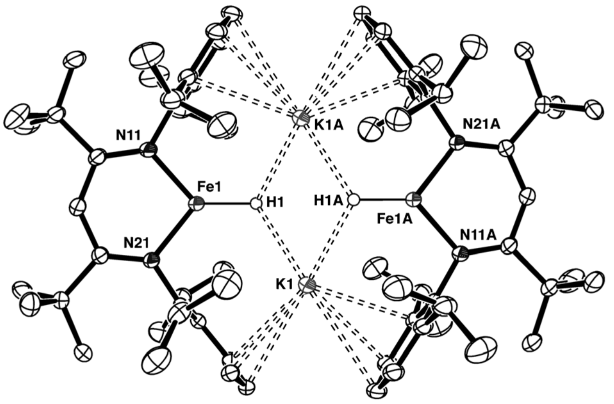

Figure 1. Thermal ellipsoid plot of $[\{KL^{tBu,iPr2}FeH\}_2]$. Ellipsoids are set at 50% probability. The two monomeric fragments are related by an inversion center. Selected bond lengths [Å] and angles [°]: Fe–N 1.914(1), 1.916(1), Fe–H 1.62(2); N-Fe-N 99.26(6), N-Fe-H 131.7(9), 129.0(8).

$[\{KL^{tBu,iPr2}FeH\}_2]$ is highly soluble in nonpolar solvents such as benzene and pentane, suggesting that in solution it maintains a dimeric structure in which the potassium ions are surrounded by arenes. No X-band EPR signal is detected from frozen solutions of $[\{KL^{tBu,iPr2}FeH\}_2,]$, which is also suggestive of a dimer. Its ^1H NMR spectrum (Figure 2a) shows the expected seven paramagnetically shifted ligand resonances for the $L^{tBu,iPr2}$ ligand, indicating D_{2h} or D_{2d} symmetry. Because this symmetry is higher than the pseudo-C_{2h} symmetry in the solid state, there must be rapid motion that enables the hydrides to access both faces of the molecule

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[*] K. P. Chiang, Dr. K. Ding, T. R. Dugan, Dr. W. W. Brennessel, Prof. P. L. Holland
Department of Chemistry, University of Rochester
Rochester, NY 14627 (USA)
E-mail: holland@chem.rochester.edu
Dr. M. Horitani, Dr. N. S. Lees, Prof. B. M. Hoffman
Department of Chemistry, Northwestern University
Evanston, IL 60208 (USA)
E-mail: bmh@northwestern.edu
Dr. C. C. Scarborough, E. Bill
Max-Planck-Institut für Bioanorganische Chemie
45470 Mülheim an der Ruhr (Germany)
E-mail: bill@mpi-muelheim.mpg.de

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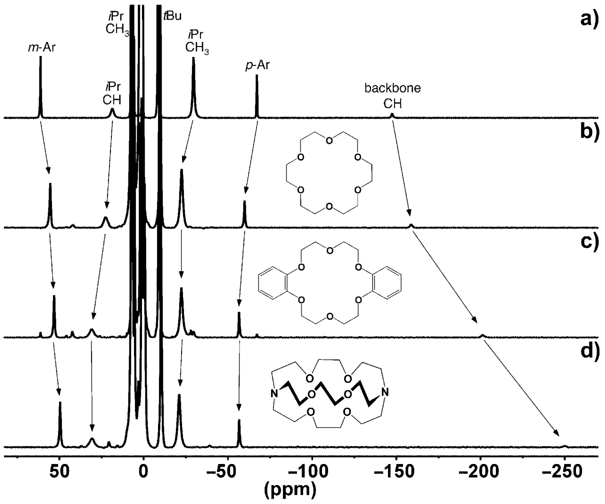

Figure 2. ^1H NMR spectra (C_6D_6, RT) of: a) [{$KL^{tBu,iPr2}FeH$}$_2$]; b) addition of [18]crown-6; c) addition of dibenzo[18]crown-6; d) addition of cryptand[2.2.2].

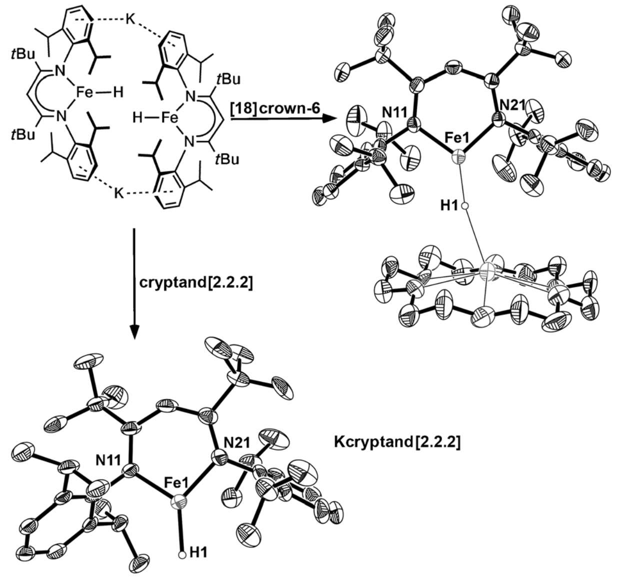

Figure 3. Synthesis and structures of monomeric iron(I) hydride complexes. ORTEPs of [K[18]crown-6][$L^{tBu,iPr2}FeH$] and [Kcrypt][$L^{tBu,iPr2}FeH$]; ellipsoids set at 50% probability. The cation in the Kcrypt salt is omitted for clarity. Selected bond lengths [Å] and angles [°]: [K[18]crown-6][$L^{tBu,iPr2}FeH$]: Fe–N 1.905(5), 1.912(5), Fe–H 1.76(8); N-Fe-N 101.0(2), N-Fe-H 136(3), 123(3). [Kcrypt][$L^{tBu,iPr2}FeH$]: Fe–N 1.916(2), 1.920(2), Fe–H 1.68(3); N-Fe-N 100.7(1), N-Fe-H 126(1), 133(1).

on the NMR timescale. No ^1H NMR signal is observed for the hydride hydrogen, presumably because it is relaxed quickly by the paramagnetic iron.

Solution and solid-state magnetic measurements of [{$KL^{tBu,iPr2}FeH$}$_2$] give magnetic moments of $(5.8 \pm 0.3)\ \mu_B$, as expected for two uncoupled $S = 3/2$ centers with g values of 2 ($\sqrt{2} \times 3.8 = 5.5\ \mu_B$). The temperature and field-dependence (4–300 K) of the solid-state magnetic moment fit to a very small antiferromagnetic exchange coupling of $J = -(0.14 \pm 0.1)\ \text{cm}^{-1}$ (Supporting Information, Figure S9, S10). The small coupling is expected from the long distance between the iron atoms (5.7619(6) Å) and the lack of connection through any route except electrostatic cation–π interactions. The zero-field Mössbauer spectrum of solid [{$KL^{tBu,iPr2}FeH$}$_2$] at 80 K shows one doublet, which is consistent with equivalent iron atoms (Supporting Information, Figure S1). Its isomer shift of $\delta = 0.48\ \text{mm s}^{-1}$ and quadrupole splitting of $\Delta E_Q = 1.90\ \text{mm s}^{-1}$ are distinctly different from those for the iron(II) species [{$L^{tBu,iPr2}Fe(\mu\text{-}H)$}$_2$] ($\delta = 0.59\ \text{mm s}^{-1}$, $\Delta E_Q = 1.58\ \text{mm s}^{-1}$),[18] and similar to those measured for another high-spin iron(I) diketiminate complex.[19]

Addition of potassium chelating agents [18]crown-6, dibenzo[18]crown-6, or cryptand[2.2.2] (crypt) to solutions of [{$KL^{tBu,iPr2}FeH$}$_2$] in C_6D_6 shifts the ^1H NMR resonances (Figure 2). The similar chemical shift pattern suggests that the electronic structures of the iron(I) sites are similar. The magnitude of the shift upon chelate addition correlates with the potassium-binding ability of the chelating agent. The highly sensitive products decompose upon exposure to even traces of oxygen or water, and are only stable to 60 °C in solution. In contrast to the neutral dimeric species, these ionic compounds are not soluble in pentane and are only slightly soluble in benzene, toluene, and diethyl ether.

Slow evaporation of Et_2O solutions gives crystals of [K[18]crown-6][$L^{tBu,iPr2}FeH$] in 65% yield, and [Kcrypt][$L^{tBu,iPr2}FeH$] in 78% yield (Figure 3). These are the first crystallographically verified monomeric open-shell hydride complexes to have a coordination number of three.[20,21] Each is a planar three-coordinate monomer in which the iron atom has bonds only to the diketiminate and the hydride, even though the hydride offers little steric protection. The positions of the iron-bound hydrogen atoms refine to give similar Fe–H distances of 1.76(8) Å and 1.68(3) Å, respectively. In the [18]crown-6 complex, the potassium cation interacts with the hydride (K–H 2.49(8) Å), while in the cryptand complex the cation is completely encapsulated.

Zero-field Mössbauer spectra of the monomeric hydride complexes reveals parameters much like those for the dimer (Table 1), as expected from the similar iron geometry and

Table 1: Metrical parameters, Mössbauer parameters, and observed g' values for iron(I) hydride complexes.

Compound	Fe–H [Å]	K–H [Å]	δ_{expt} [mm s^{-1}]	δ_{calcd} [mm s^{-1}]	$\lvert\Delta E_Q\rvert_{expt}$ [mm s^{-1}]	$\Delta E_{Q\ calcd}$ [mm s^{-1}]	g'[a]
[{$KL^{tBu,iPr2}FeH$}$_2$]	1.62(2)	2.68(2), 2.64(2)	0.48	0.40	1.90	−2.09	N.A.
[K[18]crown-6] [$L^{tBu,iPr2}FeH$]	1.76(8)	2.49(8)	0.47	0.49	1.84	−1.84	[1.1, 0.88, 6.8]
[Kcrypt][$L^{tBu,iPr2}FeH$]	1.68(3)	6.28(3)	0.40	0.44	1.93	−1.93	[1.0, 0.88, 6.8]

[a] Determined by EPR spectroscopy.

identical oxidation state. Small impurities (< 10%) are evident from the Mössbauer spectra (Supporting Information, Figure S2, S3), and we have been unable to eliminate them owing to the extreme sensitivity of the iron(I) hydride complexes. The presence of impurities discouraged us from using solid-state magnetic susceptibility, but the solution magnetic moments of 4.4(2) μ_B and 3.5(2) μ_B in [D$_8$]THF are similar to the values for related $S = 3/2$ diketiminate cobalt(II) complexes.[17,22,23]

Density functional calculations on $S = 3/2$ models of the full molecules reveal the electronic structures of the iron(I) hydride complexes. The functionals, basis sets, solvation treatment, and effects of truncating the nacnac ligand were varied to match the experimental Mössbauer parameters (Table 1 and Supporting Information). Consistent with a recent report,[24] the TPSSh functional provides the best agreement, using the crystallographic geometries. The weak antiferromagnetic exchange coupling in [{KL$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH}$_2$] is modeled using broken-symmetry calculations. The Yamaguchi approach[25] indicates a small J of $-1.0\ \mathrm{cm}^{-1}$, in agreement with the experimental value of $-0.1\ \mathrm{cm}^{-1}$. Consistent with a small exchange coupling constant, modeling the dimer as an $S_{\mathrm{total}} = 3$ species (that is, two ferromagnetically coupled high-spin Fe$^{\mathrm{I}}$ ions) gives the same calculated Mössbauer parameters as a broken-symmetry (antiferromagnetically coupled) calculation.

The DFT-derived electronic structures of the three hydride complexes are very similar. Despite the potential influence of the coordinated K[18]crown-6 fragment, the electronic structure of [K[18]crown-6][L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH] is also nearly identical. The qualitative molecular orbital (MO) diagram of the simplest anion, [L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH]$^-$, is shown in Figure 4 as an example. They have high-spin iron(I) in agreement with experiment, with a nominal d^7 configuration in which all three spin-bearing orbitals have predominantly iron character. Nonetheless, some π backbonding into the diketiminate ligand is observed in these calculations: one of the ligand-field molecular orbitals is a bonding combination of a doubly-occupied metal $d_{xz/yz}$ orbital and the LUMO of the diketiminate π system. The calculated spin contamination is less than 10%, and analysis of the unrestricted corresponding orbitals (UCOs)[26] reveals that the spin contamination arises from slight reduction of the diketiminate ligand (Supporting Information, Figure S14). This π backbonding may explain the unusual ability of β-diketiminate ligands to support stable species in the rare iron(I) oxidation state.[16]

Solutions of the monomeric iron(I) hydrides give X-band EPR signals (Figure 5 a; Supporting Information, Figure S5) that integrate to no less than about 50% of the expected intensity. In particular, the EPR spectrum of [K[18]crown-6][L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH] (Figure 5 a) can be described in terms of a fictitious spin $S' = {}^1\!/_2$ with a highly anisotropic g tensor, $\boldsymbol{g}' = [1.1, 0.88, 6.8]$. Such values are expected for the $|m_s = \pm 3/2\rangle$ Kramers doublet of a spin quartet ($S = 3/2$) with large, rhombic zero-field splitting ($|D| \geqslant 0.3\ \mathrm{cm}^{-1}$) with $D < 0$ and a rhombicity parameter of $\lambda = |E/D| = 0.17$. Accurate fitting requires anisotropic intrinsic g values ($\boldsymbol{g}^{\mathrm{int}} = [2.04, 1.96, 2.31]$), which differ from $g^{\mathrm{int}} = g_e = 2.003$ for the a pure electron spin[27] owing to partially unquenched orbital momentum.

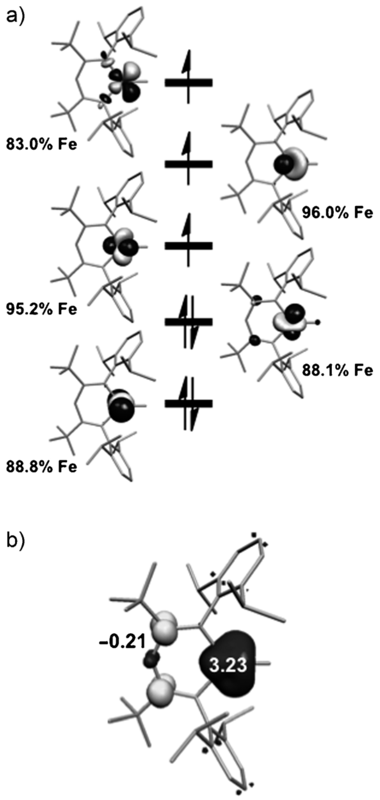

Figure 4. a) Frontier molecular orbitals of [L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH]$^-$ with qualitative ordering of orbital energies. b) The Mulliken spin-density distribution on the metal and ligand.

Combining EPR-derived $\boldsymbol{g}'$ values with a fit to the SQUID magnetization data gives $D = -14(\pm 4)\ \mathrm{cm}^{-1}$.[28] These values of $\boldsymbol{g}^{\mathrm{int}}$ and D are typical for d^7 systems.[19,29]

Figure 5 b (left) shows a partial 2D field-frequency ^{1}H CW ENDOR pattern composed of spectra collected across the low-field portion of the EPR envelope of [K[18]crown-6][L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH].[30] The spectrum collected at g_1 shows the high-frequency partner (ν_+) of a doublet signal from the hydride proton that is characterized by a large observed ($S' = {}^1\!/_2$) hyperfine interaction, $|A_1(^1\mathrm{H})'|$. As the field is increased, the splitting decreases until the ν_+ feature merges with other signals near the ^{1}H Larmor frequency. Although the hydride signal thus can be followed over only a portion of the EPR envelope, the full hyperfine tensor is obtained by simulating this pattern (Figure 4 b, gray lines). The observed 2D pattern corresponds to an effective hyperfine interaction with $A_1' \gg A_2', A_3'$, but upon correction for the g anisotropy,[31] the coupling tensor for the true $S = 3/2$ spin state is $\mathbf{A} = +[10.5, -29.1, -34.5]$ MHz, with isotropic coupling $a = -17.7$ MHz, and near-axial anisotropic coupling $\mathbf{T} = +[28.2, -11.4, -16.8]$ MHz, coaxial with $\boldsymbol{g}$ and $\boldsymbol{g}'$ within error.[32] Further correction of $\mathbf{T}$ and a for the effects of the anisotropy of the intrinsic $S = 3/2$ g tensor (pseudo-contact effects) yields the intrinsic $S = 3/2$ anisotropic interaction, $\mathbf{T} = +[28.9, -10.7, -16.1]$ and isotropic (σ-orbital) interaction, $a_{\mathrm{iso}} = -18.5$ MHz.

The intrinsic $\mathbf{T}$ tensor for [L$^{t\mathrm{Bu},i\mathrm{Pr2}}$FeH]$^-$ has the near-axial symmetry expected for a terminal hydride ligand, suggesting that the K$^+\cdots$H interaction does not greatly influence the

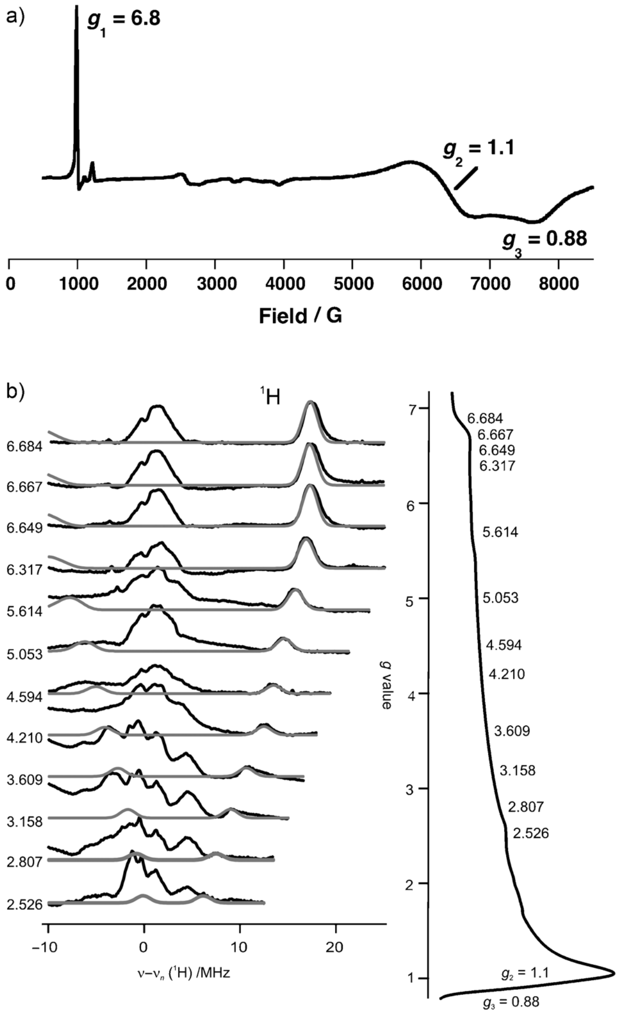

Figure 5. a) X-band CW EPR spectrum of [K[18]crown-6][$L^{tBu,iPr2}$FeH] in 1:3 benzene/toluene frozen solution. Parameters: $T = 8$ K, frequency = 9.3834 GHz, modulation amplitude = 9.8 G. b) Q-band CW ^{1}H ENDOR spectra. Black: experiment; gray: simulations with the GENDOR program (using *A* and *g*′ tensors given in the text). The strong anisotropy of *g*′ shifts the hyperfine-split doublets away from the ^{1}H Larmor frequency. ENDOR parameters: $T = 2$ K, microwave frequency = 35.364 GHz; modulation amplitude = 1.3 G; RF scan speed = 1 MHz s^{-1}. The absorption-display EPR spectrum is shown on the right.

Fe–H bond. A point-dipolar Fe–H distance calculated from **T** (1.85 Å) is close to the crystallographic distance of 1.76 ± 0.08 Å.[33] The agreement between the crystallographic and ENDOR analyses validates the ability of ENDOR to reveal the presence of a terminal Fe–H in metalloenzyme intermediates where other forms of characterization are difficult or impossible.

Thus, a negative overall charge and steric encumbrance enable the isolation of high-spin, 13-electron iron(I) hydride complexes with only three bonds to the metal ion. The very electron-rich metal center is partially stabilized by back-bonding into the β-diketiminate ligand. These complexes allow the first ENDOR characterization of a crystallographically defined Fe–H bond. These results may be compared to the recent spectroscopic characterization of a five-coordinate $S = 1/2$ molybdenum(III) hydride.[12] The anisotropic interaction tensors **T** for the two complexes are very similar, with a modestly larger value for $T_{\max}$ of $[L^{tBu,iPr2}FeH]^-$ reflecting the shorter Fe–H bond. The value of a_{iso} for Fe-H is almost twice that for the Mo-H upon correction for a factor 1/*S* in the definition of a_{iso}. Because the molybenum complex has yet to be crystallographically characterized, the differences in structure and bonding that give rise to this difference in a_{iso} remain unknown. However, the two studies combined suggest that the key signature for a terminal metal-bound hydride is independent of the metal ion involved (Mo, Fe), its local symmetry (C_{3v}, C_{2v}), or spin state ($S = 1/2, 3/2$). This signature is a large, axial anisotropic interaction, combined with a large isotropic coupling of the opposite sign as the unique anisotropic element. Recognizing this signature will be useful for the identification of terminal hydrides in biological systems.

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