

Large Hyperfine Coupling Arising from Pseudo-²S Ground States in a Series of Lutetium(II) Metallocene Complexes

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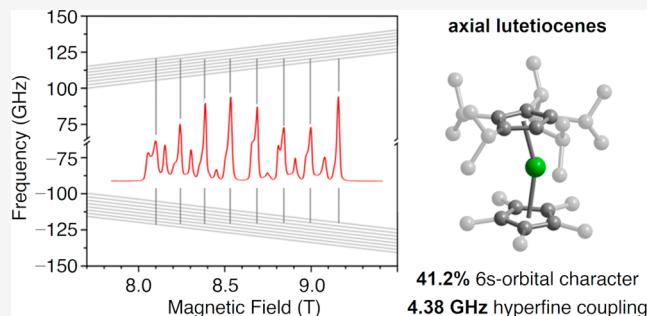
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ABSTRACT: The synthesis of molecules with strong coupling between electronic and nuclear spins represents an important challenge in molecular quantum information science. Here, we report the synthesis and characterization of the divalent lutetium metallocene complexes $\text{Lu}(\text{Cp}^{\text{Me}_5})(\text{Cp}^{\text{iPr}_5})$ (Cp^{Me_5} = pentamethylcyclopentadienyl; Cp^{iPr_5} = pentaisopropylcyclopentadienyl), $\text{Lu}(\text{Cp}^{\text{iPr}_4\text{Et}})_2$ ($\text{Cp}^{\text{iPr}_4\text{Et}}$ = ethyltetraisopropylcyclopentadienyl), and $\text{Lu}(\text{Cp}^{\text{iPr}_4})_2$ (Cp^{iPr_4} = tetraisopropylcyclopentadienyl). The molecular structures of these complexes, as determined through single-crystal X-ray diffraction, feature a common bent sandwich geometry, with average $\text{Cp}-\text{Lu}-\text{Cp}$ angles ranging from 159.9° to 152.6° . Analysis of continuous-wave electron paramagnetic resonance (EPR) spectra for the complexes reveals nearly isotropic g tensors with only a slight deviation from that of a free electron. Moreover, an extremely large splitting of the eight-line spectra indicates the presence of strong hyperfine coupling, and simulations provide isotropic hyperfine coupling constants of $A_{\text{iso}} = 4.38, 4.30$, and 4.17 GHz across the series, where the value of A_{iso} is found to decrease as the $\text{Cp}-\text{Lu}-\text{Cp}$ angle becomes more acute. Notably, these values are the largest yet observed for any lanthanide complex. Moreover, EPR and computational analysis show that the large values of A_{iso} stem from large s-orbital character—up to 41.2%—in the corresponding singly occupied molecular orbitals. To our knowledge, this degree of s-character in a molecular orbital is the largest yet reported for an open-shell isolable complex. These results outline a general strategy toward the isolation of paramagnetic molecules with strong hyperfine coupling and highly isotropic doublet electronic ground states.



INTRODUCTION

The presence of strong hyperfine coupling between nuclear and electronic spins in certain materials gives rise to exotic physics that underlies numerous applications in quantum information science, namely, the design of quantum bits—or qubits—which host highly coherent superpositions of quantum states that can be initialized, manipulated, and detected. For instance, the hyperfine transitions of ^{117}Sn vacancy centers in diamond can be optically addressed to effect initialization and readout of a nuclear spin owing to the large magnitude of the hyperfine coupling to the ^{117}Sn nucleus, which greatly exceeds the natural optical linewidth of the system.¹ Additionally, hyperfine coupling forms the basis of atomic clock physics, and the use of spin clock transitions has been well studied in defect states of various solid-state materials.^{2–8} In particular, bismuth defects in silicon possess an electronic structure with spin sublevels that are first-order insensitive to the applied magnetic field, forming the basis of a clock qubit.² Considerable computational and experimental effort has been directed toward discovering other spin defects with such properties.⁹ Beyond enabling optical initialization and readout as well as extending coherence times in qubits, large values of the

hyperfine constant A energetically resolve nuclear spin sublevels in Tb^{3+} single-molecule magnets, enabling electrically driven coherent control of nuclear spin states via the hyperfine Stark effect.¹⁰ Therefore, strong hyperfine interactions can facilitate various desirable functions within quantum information applications.

Despite considerable advances and applications in spin-defect quantum technology, solid-state-based quantum devices face several intrinsic limitations, such as the lack of atomic precision in the placement of individual quantum centers, the inability to scale these systems in a predictive manner, and the challenges of materials discovery. Alternatively, extending these phenomena to molecular systems offers an intriguing approach, as the composition and geometry of molecules can be programmed and tuned at the atomic level through simple

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coordination chemistry, and such compounds can be obtained in single-crystalline form.¹¹

Recent work has demonstrated that lanthanide complexes, including Lu²⁺ complexes with large hyperfine constants, can be employed as clock qubits with long coherence times.^{12–14} In conventional Zeeman-based spin qubits, minute changes in the local magnetic field lead to significant shifts in the frequency of the transition, thus promoting decoherence (Figure 1a). In contrast, for a hyperfine coupling-based clock

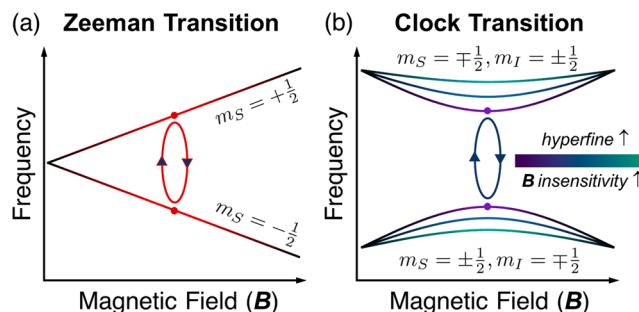


Figure 1. Cartoon depiction of spin transitions in Zeeman (a) and clock (b) qubits. The first-order field insensitivity of a clock qubit renders its transition frequency insensitive to fluctuations in the magnetic field (represented by a flatter frequency–magnetic field profile), thus engendering longer coherence times. Increasing the frequency of the clock transition Δ also increases the second-order field insensitivity of the clock transition and thus extends the flat region across a greater range of magnetic field.

qubit, avoided energy crossings appear in the Zeeman splitting of qubit basis states as a result of strong hyperfine coupling of nuclear and electronic spins. At the avoided crossing, the frequency (f) of the electron paramagnetic resonance (EPR) is first-order insensitive to local magnetic induction (B) and consequently to magnetic field fluctuations, thereby extending the coherence time (Figure 1b).

Molecular clock qubits^{13–20} offer the tunability required to iteratively design species with spin clock transitions that are more impervious to decoherence, namely, by targeting the second-order insensitivity to the local magnetic induction, as described by the equation $d^2f/dB^2 = \gamma_e^2/\Delta$, where γ_e is the electron gyromagnetic ratio and Δ is the frequency of the spin clock transition.^{17,19} As the frequency of the clock transition Δ increases, the clock transition incurs greater second-order insensitivity to magnetic field fluctuations and consequently prolonged coherence.^{19,20} As such, the synthesis of molecular complexes with spin clock transitions characterized by systematically increasing Δ can pave the way toward clock qubits with long coherence times, especially once Δ approaches commercial pulsed EPR spectrometer frequencies beyond the X-band such as the Q-band (34 GHz).

One synthetic strategy to isolate molecules with strong hyperfine coupling is through targeting species with singly occupied molecular orbitals (SOMOs) of high s-orbital parentage.^{21–23} Since s orbitals feature nonzero electron density at the nucleus, such complexes can exhibit significant interaction between electronic and nuclear spins, corresponding to large values of the hyperfine constant. Nevertheless, for the vast majority of paramagnetic molecules, little s-orbital character of the ground state is observed—across a range of molecular archetypes, including main group radicals and transition metal coordination complexes—owing to the

presence of SOMOs of primarily p-, d-, or f-orbital character. Such small degrees of s-orbital character are manifested as only modest values of the hyperfine coupling constant. Indeed, chemical species with rigorous ²S ground states arising from spherical symmetry are limited to gas-phase ions and atoms, with several of these species constituting state-of-the-art technologies in the field of quantum information science.^{24–26}

In exceptional cases, certain molecules have been reported with point group symmetries that permit greater s-orbital admixture from an excited state to the ground state. Among these rare examples are the anionic trigonal Lu²⁺ complexes $[\text{Lu}(\text{Cp}^{\text{SiMe}_3})_3]^-$ ($\text{Cp}^{\text{SiMe}_3} = \text{C}_5\text{H}_5\text{SiMe}_3$), $[\text{Lu}(\text{NR}_2)_3]^-$ ($\text{NR}_2 = \text{N}(\text{SiMe}_3)_2$), $[\text{Lu}(\text{OAr})_3]^-$ ($\text{OAr} = 2,6\text{-Ad}_2\text{-}4\text{-}t\text{-Bu-C}_6\text{H}_2\text{O}$, where Ad is adamantyl) with GHz-scale hyperfine constants determined by EPR spectroscopy corresponding to SOMOs with s-orbital parentages of 10%, 23%, and 33%, respectively.^{14,27} The presence of such large s-orbital character in the electronic ground states of these molecules can be understood through a qualitative orbital energy correlation diagram (Figure 2). First, consider the electronic structure of a free

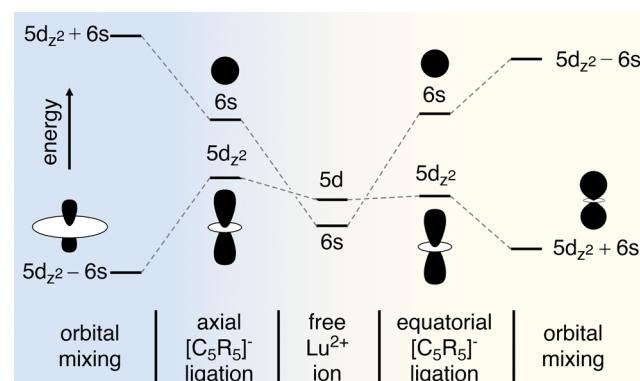


Figure 2. Qualitative energy correlation diagram for the 6s and $5d_z^2$ orbitals of a Lu²⁺ ion upon ligation of cyclopentadienyl ligands $[\text{C}_5\text{R}_5]^-$ in an equatorial arrangement versus an axial arrangement, prior to and after symmetry-allowed orbital mixing considerations. Metal-based orbitals are of a totally symmetric irreducible representation. Ligation considers interaction with ligand-based symmetry-adapted linear combinations of atomic orbitals, which transform under the totally symmetric irreducible representation. The closer 6s and $5d_z^2$ orbital energies in the case of axial cyclopentadienyl ligation gives rise to enhanced s-orbital character in the singly occupied molecular orbitals of the corresponding axial Lu²⁺ metallocene molecules.

Lu²⁺ ion, where the 6s orbital is slightly lower in energy than the $5d_z^2$ orbital.²⁸ Upon equatorial cyclopentadienyl ligation, the 6s orbital undergoes a larger energetic destabilization than does the $5d_z^2$ orbital, situating the 6s orbital higher in energy than the $5d_z^2$ orbital. Finally, symmetry-allowed mixing between these orbitals in the totally symmetric irreducible representation gives rise to a $5d_z^2 + 6s$ hybrid orbital that is lower in energy and a $5d_z^2 - 6s$ hybrid orbital that is higher in energy, with the degree of mixing determined by the energy gap between the 6s and $5d_z^2$ orbitals.

Inspection across the series of previously reported trigonal Lu²⁺ complexes reveals a gradual structural distortion from a trigonal planar to a trigonal pyramidal coordination geometry, which accompanies an increase in 6s-orbital parentage. This trend likely reflects a greater relative crystal-field-induced destabilization of the $5d_z^2$ orbital compared to the 6s orbital

upon distortion to a trigonal pyramidal geometry; the consequently smaller energetic gap between the two orbitals results in greater $6s-5d_z^2$ mixing (Figure 2). Following this logic, we hypothesized that a more pronounced structural distortion toward an axial bis-cyclopentadienyl geometry would induce an even greater relative energetic destabilization of the $5d_z^2$ orbital compared to the $6s$ orbital (Figure 2), allowing these two orbitals to mix more extensively and give rise to higher degrees of ground state s -orbital character. Indeed, previous work has shown that encapsulating divalent ions such as Y^{2+} ($A = 500$ MHz, 40% s -orbital character),²⁹ La^{2+} (2 GHz, 33%),²⁹ and Tl^{2+} (35 GHz, 17%)^{30,31} in axial coordination environments can give rise to significant s -orbital character in the ground state. Moreover, density functional theory calculations have suggested the presence of considerable s -orbital character in axial lanthanide metallocene, or $Ln(C_5R_5)_2$ complexes.²⁹

Herein, we report the synthesis and crystal structures of three Lu^{2+} metallocene complexes, with EPR spectroscopy and computational analysis showing significant hyperfine coupling stemming from the nearly maximal s -orbital character of the doublet ground state. Moreover, within the series of three Lu^{2+} metallocene molecules, the hyperfine coupling and $6s$ orbital character are found to systematically increase as the $Cp-Lu-Cp$ angle approaches linearity.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The axial Lu^{2+} metallocene complexes $Lu(Cp^{Me_5})(Cp^{iPr_5})$ (1), $Lu(Cp^{iPr_5}Et)_2$ (2), and $Lu(Cp^{iPr_5})_2$ (3) (Figure 3) were

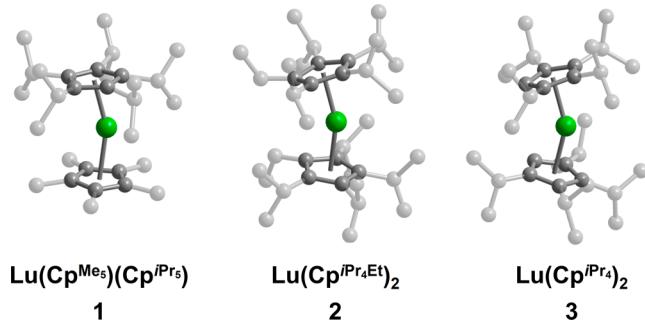


Figure 3. Molecular structures of complexes 1–3 from single-crystal X-ray diffraction. Green and gray spheres represent Lu and C atoms, respectively. In the case of 1, the structure shown corresponds to the structural isomer with 87% abundance. Hydrogen atoms have been omitted for clarity. Only one of the two molecules in the unit cell of 3 is shown for clarity.

synthesized via salt metathesis followed by chemical reduction using methods based on the previously published lanthanocenes, $Ln(Cp^{iPr_5})_2$.^{29,32} For heteroleptic 1, the trivalent dimer, $(Cp^{iPr_5})_2Lu_2I_4$, which was synthesized from LuI_3 and $NaCp^{iPr_5}$ in a manner similar to the previously published $(Cp^{iPr_5})_2Lu_2I_4$ compounds,³³ was subjected to salt metathesis with $NaCp^{Me_5}$ in toluene at high temperature to yield the putative compound $Lu(Cp^{Me_5})(Cp^{iPr_5})I$. The crude intermediate was dissolved in benzene and reduced to the divalent Lu^{2+} metallocene by stirring with excess KC_8 over several days at room temperature. Following solvent removal and crystallization from hexane, pure $Lu(Cp^{Me_5})(Cp^{iPr_5})$ was isolated as yellow plate-shaped

crystals whose electronic absorption spectra and infrared spectra are documented in Figures S5 and S14–S16.

In the case of 2 and 3, salt metathesis between LuI_3 and the corresponding sodium cyclopentadienide salts in toluene solvent at high temperature led to the putative iodide intermediates $Lu(Cp^{iPr_5}Et)_2I$ and $Lu(Cp^{iPr_5})_2I$. The crude residues were dissolved in benzene and converted to the desired Lu^{2+} metallocenes by stirring with excess KC_8 at room temperature for several days. Following solvent removal and crystallization from hexane or pentane, analytically pure 2 and 3 were isolated as dark yellow prismatic crystals whose electronic absorption spectra and infrared spectra are documented in Figures S6, S7, and S17–S22. Both solid-state samples and alkane solutions of the Lu^{2+} metallocenes were found to be stable at room temperature over many months under argon and can be recrystallized from boiling hexane without noticeable decomposition but decay rapidly in the presence of air and moisture.

The solid-state structures of 1, 2, and 3 were determined by single-crystal X-ray diffraction analyses (Tables 1, S2–S4, S6–S8, Figures S9–S11). All exhibit a bent geometry with average $Cp-Lu-Cp$ angles ranging from $152.57(7)^\circ$ to $159.91(9)^\circ$.

In heteroleptic complex 1, the lutetium atom is disordered over two positions in an 87:13 ratio. Such positional disorder of the central lanthanide ion is commonly observed in bent lanthanide metallocenes.^{34,35} This positional disorder yields two sets of $Cp-Lu-Cp$ angles and $[Lu-Cp^{Me_5}, Lu-Cp^{iPr_5}]$

Table 1. Summary of Parameters Obtained from X-ray Diffraction and EPR Analysis^a

	1	2	3
$\angle Cp-Lu-Cp$ (deg)	158.8(7) ^a 161.0(5) ^b	156.96(17)	152.68(10) ^c 152.46(11) ^f
$Cp-Lu$ (Å)	2.253(2) ^{a,c} 2.314(2) ^{a,d} 2.206(7) ^{b,c} 2.345(8) ^{b,d}	2.315(3)	2.296(3) ^c 2.306(3) ^e 2.295(3) ^f 2.311(3) ^f
$\angle Cp-Lu-Cp_{mean}$ (deg)	159.91(9)	156.96(17)	152.57(7)
$Cp-Lu_{mean}$ (Å)	2.282(1)	2.315(3)	2.302(2)
g_x	1.982	1.986	1.985
g_y	1.982	1.986	1.985
g_z	1.995	1.996	1.990
$ g_x - g_e $	0.019	0.016	0.017
$ g_y - g_e $	0.019	0.016	0.017
$ g_z - g_e $	0.007	0.006	0.012
$g_{iso,exp.}$	1.987	1.989	1.987
$g_{iso,calc.}$	1.989	1.992	1.991
A_x (GHz)	4.35	4.25	4.10
A_y (GHz)	4.35	4.25	4.10
A_z (GHz)	4.43	4.40	4.30
$A_{iso,exp.}$ (GHz)	4.38	4.30	4.17
$A_{iso,calc.}$ (GHz)	4.34	4.28	4.18
Q_z (MHz) ^g	70	100	60
SOMO 6s orbital character	41.2%	40.5%	39.2%

^aIn 1, angles and distances correspond to two structurally disordered components with occupancies of ^a87% and ^b13% as derived from single-crystal X-ray diffraction analysis. Additionally, in heteroleptic 1, distances correspond to the ^a Cp^{Me_5} and ^d Cp^{iPr_5} ligands. In 3, angles and distances correspond to those of two^{ef} crystallographically inequivalent molecules of 3 in the asymmetric unit of the crystal structure. ^g $Q_x - Q_y = 0$ for 1–3.

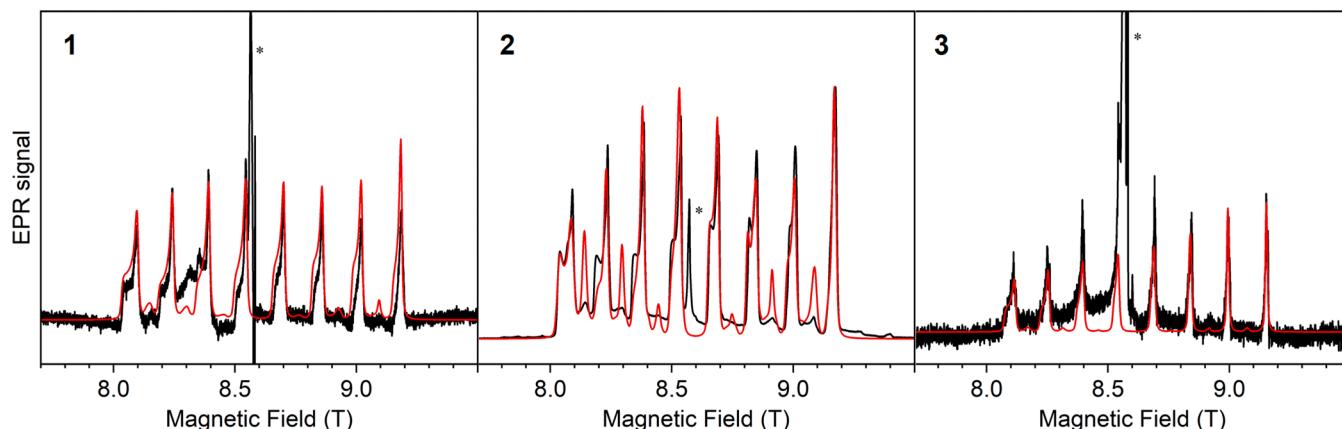


Figure 4. High-field, high-frequency (240 GHz) continuous-wave electron paramagnetic resonance spectra of **1**–**3** measured at 5 K. Experimental data and corresponding simulations are colored black and red, respectively. Asterisks designate peaks associated with an unidentified $g = 2$ impurity.

distance pairs. The 87%-occupancy disorder component—determined by allowing the lutetium occupancy to freely refine—exhibits a Cp–Lu–Cp angle of $158.8(7)^\circ$, a Lu–Cp^{Me₅} distance of $2.253(2)$ Å, and a Lu–Cp^{iPr₅} distance of $2.314(2)$ Å. Meanwhile, the 13%-occupancy disorder component exhibits a Cp–Lu–Cp angle of $161.0(5)^\circ$, a Lu–Cp^{Me₅} distance of $2.206(7)$ Å, and a Lu–Cp^{iPr₅} distance of $2.345(8)$ Å. In total, **1** exhibits a weighted average Cp–Lu–Cp angle of $159.91(9)^\circ$ and a weighted average Cp–Lu distance of $2.282(1)$ Å.

In **2**, asymmetry in the steric profile of the [Cp^{iPr₄Et}][–] ligand leads to a more acute Cp–Lu–Cp angle, as the steric clash between opposite [Cp^{iPr₄Et}][–] ligands is mitigated at the ethyl substituent compared to the more sterically encumbered isopropyl substituents. Homoleptic compound **2** exhibits a Cp–Lu–Cp angle of $156.96(17)^\circ$ and a Cp–Lu distance of $2.315(3)$ Å. The more acute average Cp–Lu–Cp angle and longer average Cp–Lu distances indicate a less axial crystal field in **2** compared to **1**.

In the crystal structure of **3**, two crystallographically nonequivalent molecules exhibit Cp–Lu–Cp angles of $152.46(11)^\circ$ and $152.68(10)^\circ$, each containing short Cp–Lu distances of $2.295(3)$ and $2.296(3)$ Å, respectively, and long Cp–Lu distances of $2.311(3)$ and $2.308(3)$ Å, respectively, resulting in an average Cp–Lu–Cp angle of $152.57(7)^\circ$ and an average Cp–Lu distance of $2.302(2)$ Å. Particularly low steric encumbrance at the unsubstituted position of the [Cp^{iPr₄}][–] ring in **3** leads to the most acute Cp–Lu–Cp angle among **1**–**3**, and thus **3** features the least axial crystal field among the three Lu²⁺ metallocene complexes.

Electron Paramagnetic Resonance Spectroscopy. To probe the extent of hyperfine coupling in **1**–**3**, continuous-wave electron paramagnetic resonance (CW-EPR) spectra were collected on ground microcrystalline powders of **1**–**3** at $T = 5$ K, at frequencies up to 384 GHz and magnetic fields of up to 15 T (see **Supporting Information** for experimental details; additional variable-field CW-EPR spectra are included in **Figures S23–S25**). CW-EPR spectra, collected at $f = 240$ GHz and $T = 5$ K, at magnetic fields of up to 10 T, for **1**–**3** (**Figure 4**) all exhibit an eight-line pattern characteristic of an $S = 1/2$ state split via the interaction with an $I = 7/2$ ¹⁷⁵Lu nucleus (97.41% natural abundance). Simulations of the spectra reveal the presence of nearly isotropic g tensors for **1**–**3**, with all g

tensor components g_x , g_y , and g_z deviating less than 0.02 from the free electron value of 2.0023. Importantly, the isotropic nature of these g values is in contrast to those previously reported for divalent lutetium molecules with trigonal crystal fields,^{14,27} consistent with the presence of higher s-orbital character in the SOMOs of these axial Lu²⁺ metallocene complexes.

Explicitly, the degree of deviation from the free electron value of $g_e = 2.0023$ for the g tensor of a spin due to second-order orbital angular momentum can be described by the following proportionality expression:

$$|g - g_e| \propto \lambda \cdot \langle j | \hat{H} | i \rangle / \Delta_{ij} \quad (1)$$

where λ is the spin–orbit coupling constant, $\langle j | \hat{H} | i \rangle$ is the matrix element corresponding to spin–orbit coupling-induced mixing of ground (i) and excited (j) state orbitals, and Δ_{ij} is the energy gap between states i and j .³⁶ In the case of **1**–**3**, a large value of λ arises owing to the large atomic number of Lu. As such, the observed isotropy of the unpaired spin in these complexes instead likely stems from a combination of insignificant spin–orbit coupling-induced mixing of the electronic states and a substantial energy gap Δ_{ij} . Indeed, $\langle j | \hat{H} | i \rangle$ is expected to be minimal for orbitals with significant s character due to the spherical symmetry of the s orbital. Moreover, the energy gap Δ_{ij} should increase with the degree of 6s orbital mixing and consequently stabilize the 6s–5d_z² hybrid orbital, thereby energetically isolating it from higher-energy 5d orbitals. These results suggest that the isotropy observed for the unpaired spin in **1**–**3** stems from a SOMO with a significant degree of s-orbital character.

The hyperfine coupling constant, A , which provides a quantitative measure of the strength of interaction between electronic and nuclear spins, is directly correlated to the degree of s-orbital character of the electronically populated orbital, since the nonzero electron density at the nucleus of an s orbital gives rise to significant electronic–nuclear coupling. To extract the hyperfine coupling constants associated with **1**–**3**, simulations of the EPR spectra at 5 K were performed according to the Hamiltonian in **eq 2** using EasySpin:³⁷

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g}_e \cdot \hat{S} - \mu_N g_N \vec{B} \cdot \hat{I} + \hat{S} \cdot \vec{A} \cdot \hat{I} + \hat{I} \cdot \vec{Q} \cdot \hat{I} \quad (2)$$

where μ_B is the Bohr magneton, μ_N is the nuclear magneton, \vec{B} is the applied magnetic field, \vec{g}_e is the g -tensor of the electron,

Table 2. Comparison of EPR Parameters for Lu²⁺ Complexes with Strong Hyperfine Coupling^{abc}

	g_x, g_y, g_z	g_{iso}	$g_e - g_{\text{iso}}$	A_{iso} (GHz)	SOMO 6s character	ref.
	1.966, 1.966, 1.998	1.977	0.025	1.1	10%	27 ^a
	1.882, 1.898, 2.000	1.927	0.075	2.4	23%	14 ^b
	1.915, 1.915, 2.000	1.943	0.059	3.5	33%	14 ^c
	1.985, 1.985, 1.990	1.987	0.015	4.17	39.2%	this work
	1.986, 1.986, 1.996	1.989	0.013	4.30	40.5%	this work
	1.982, 1.982, 1.995	1.987	0.015	4.38	41.2%	this work

^a(Cp^{SiMe₃})⁻ = C₅H₄SiMe₃⁻. ^bNR₂⁻ = N(SiMe₃)₂⁻. ^cOAr⁻ = 2,6-Ad₂-4-^tBu-C₆H₂O⁻.

g_N is the g -factor for the nucleus, \hat{S} is the electron spin operator, \hat{I} is the nuclear spin operator, \hat{A} is the hyperfine coupling tensor, and \hat{Q} is a matrix that represents the nuclear quadrupole interaction tensor.

The eight lines present in each EPR spectrum correspond to eight allowed transitions from the $M_S = -1/2$ to the $M_S = +1/2$ manifold (Figure 4). In line with the observed g tensor isotropy and minimal deviations from $g_e = 2.0023$, these simulations reveal the presence of immense hyperfine coupling across the series of Lu²⁺ metallocenes, with isotropic coupling constants of $A_{\text{iso}} = 4.38 \pm 0.05$ GHz, 4.30 ± 0.05 GHz, and 4.17 ± 0.05 GHz, respectively, for 1, 2, and 3 (Table 1). The hyperfine tensors $A = [4.35, 4.35, 4.43]$ GHz, $A = [4.25, 4.25, 4.40]$ GHz, and $A = [4.10, 4.10, 4.30]$ GHz, for 1, 2, and 3, respectively, display little anisotropy, once again highlighting the isotropic nature of the doublet ground states in 1–3 (Table 1). The peak structure of these eight allowed transitions is governed by slight g and A anisotropy, as well as quadrupolar splitting whose magnitude is comparable to that of previously reported [Lu(OAr)₃]⁻; beyond this eight-line pattern, additional peaks indicative of hyperfine coupling to the $I = 7$ ¹⁷⁶Lu nucleus (2.59% natural abundance) are observed (Figures S24 and S26, Tables 1 and S9).¹⁴

To our knowledge, the value of the hyperfine coupling constant obtained for 1 is the largest yet observed for any lanthanide complex, eclipsing cubic Pr^{IV} sites in Pr:BaSnO₃ ($A_{\text{iso}} = 1.8$ GHz),³⁸ the axial lanthanocene complex La(Cp^{iPr₅})₂

($A_{\text{iso}} = 2$ GHz),²⁹ and most notably the trigonal pyramidal complex [Lu(OAr)₃]⁻ ($A_{\text{iso}} = 3.5$ GHz),¹⁴ exceeding the previous lanthanide record by nearly 25% (see Table 2). This value of 4.38 GHz also eclipses the previous non-Tl record holder, a Bi^{II} complex Bi^{II}((ArN)[Si]O[Si](NAr)) (Ar = 2,6-diisopropylphenyl, [Si] = SiMe₂) with $A = [-2.804, -3.930, -4.764]$ GHz ($|A_{\text{iso}}| = 3.833$ GHz) and $g = [1.621, 1.676, 1.832]$ ($g_{\text{iso}} = 1.710$).³⁹ Not only do 1–3 exhibit larger A_{iso} and more isotropic A tensors than this Bi^{II} complex, 1–3 also have more isotropic g tensors and an s-orbital character at least eight times that of the 5% in the Bi^{II} complex. Similar to Bi, which boasts $A_{\text{iso},\text{max}} = 77.53$ GHz for theoretical 100% s-orbital character,⁴⁰ Tl possesses inherently a large Fermi contact interaction with $A_{\text{iso},\text{max}} = 183.80$ GHz,⁴⁰ giving rise to large hyperfine coupling constants. Indeed, the largest hyperfine coupling constant observed in a molecule belongs to a linear, two-coordinate Tl^{II} anion (NBu₄)₂Tl^{II}(Pt(C₆F₅)₄)₂³¹ with $A = [35.88, 35.88, 33.97]$ GHz ($A_{\text{iso}} = 34.61$ GHz) and $g = [1.924, 1.924, 2.489]$ ($g_{\text{iso}} = 2.113$), but the s-orbital character (17%) is less than half of that of 1–3. Additionally, the g tensors of this Tl^{II} complex are more anisotropic than those of 1–3. While the more anisotropic g tensors are partly due to the increased atomic number of Tl relative to Lu, we postulate that these differences in the EPR parameters arise mainly from the lower s-orbital character in (NBu₄)₂Tl^{II}(Pt(C₆F₅)₄)₂ compared to that of 1–3, the discussion of which follows.

The degree of s-orbital character in a spin-bearing molecular orbital can be estimated by examining how the experimentally

determined hyperfine constant compares to a theoretical maximum hyperfine constant for an ns orbital with single occupation.⁴⁰ For instance, considering the theoretical maximum of $A_{\text{iso},\text{max}} = 10.63$ GHz for the Lu nucleus and the experimental value of $A_{\text{iso}} = 4.38$ GHz for **1**, the s-orbital character can be estimated as $4.38 \text{ GHz} / 10.63 \text{ GHz} = 41.2\%$. This exceeds the previous highest percentage of s-orbital character observed in a molecule, 40%, as observed in $\text{Y}(\text{Cp}^{\text{iPr}_5})_2$.²⁹ **1** also exhibits an A_{iso} nearly an order of magnitude larger than the 505 MHz observed for $\text{Y}(\text{Cp}^{\text{iPr}_5})_2$. Notably, the A_{iso} values of **1–3** vastly exceed their early lanthanide counterpart $\text{La}(\text{Cp}^{\text{iPr}_5})_2$ ($A_{\text{iso}} = 2$ GHz, s-orbital character = 33%) likely due to the relativistic contraction of the 6s orbitals and relativistic expansion of the 5d orbitals moving from the early lanthanides to the late lanthanides; the resultant enhanced energetic proximity of the 6s and 5d orbitals for Lu corresponds to greater s-orbital character in **1–3** compared to $\text{La}(\text{Cp}^{\text{iPr}_5})_2$. This is also reflected in more isotropic g tensors in **1–3** compared to $\text{La}(\text{Cp}^{\text{iPr}_5})_2$ ($g_x = g_y = 1.92$, $g_z = 1.595$).²⁹ In summary, these results demonstrate a synthetic approach to isolating molecules with ground states approaching the ^2S limit.

While these results show that moving from trigonal to axial geometries engenders an increase in the hyperfine coupling constant via an increase in the s-orbital character of the SOMO, further manipulation of the degree of axiality within a series of axial Lu^{2+} metallocenes can allow for fine-tuning of the s-orbital character. Compound **3**, which exhibits the most acute Cp–Lu–Cp angle and thus the least axial crystal field, is associated with the lowest isotropic hyperfine coupling constant of $A_{\text{iso}} = 4.17$ GHz. A less acute Cp–Lu–Cp angle in **2** results in a larger $A_{\text{iso}} = 4.30$ GHz. Compound **1** exhibits the most axial Cp–Lu–Cp coordination geometry among **1–3**; the greater degree of $5d_z^2$ orbital destabilization results in the largest A_{iso} value among **1–3** of 4.38 GHz.

Although we observed two different Lu environments in **1** and **3** from the analysis of X-ray diffraction data in these compounds, each EPR spectrum was best modeled with one set of g and hyperfine tensors. Indeed, using a two-site model to simulate the EPR data did not yield more reasonable simulations than those obtained by the one-site model discussed here. This result indicates that the disordered components in the crystal structure of **1** display one effective structure within EPR line width considerations, and the same is likely true for the two distinct molecules in the crystal structure of **3**.

Computational Analysis. Density functional theory (DFT) calculations were carried out to assess the degree of s-orbital parentage in the title molecules and to provide support for the experimentally observed EPR parameters. Calculations at the exact two-component (X2C) Hamiltonian in the diagonal local approximation to the unitary decoupling transformation^{41,42} (DLU) and the B3LYP/x2c-TZVPall-s level^{43–45} indicate that the SOMOs (Figure 5) of **1–3** contain considerable 6s character, similar to previously reported divalent lanthanocenes.^{14,27,29,32,46} In the report of a 3.467 GHz hyperfine coupling observed for the $[\text{Lu}(\text{OAr})_3]^-$ system mentioned above, more standard DFT methods failed to capture the hyperfine coupling constants, overshooting by an order of magnitude.¹⁴ However, the more rigorous DLU-X2C framework has recently been shown to be effective in modeling

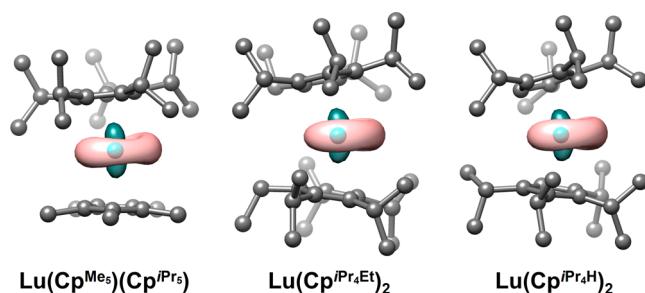


Figure 5. Singly occupied molecular orbitals (SOMOs) corresponding to complexes **1–3** at the B3LYP/x2c-TZVPall-s/scalar-relativistic DLU-X2C level are shown at an isosurface value of 0.07.

hyperfine tensors for systems with particularly large hyperfine coupling constants.^{47–51} This method was indeed found to accurately capture the experimentally measured g and hyperfine tensors for **1–3** at the $\omega\text{B97X-D/x2c-TZVPall-s}$ level^{51,52} (Tables S16–S21) as well as with other functionals (see included Supporting Information). All functionals screened strongly reflect the trend of decreasing hyperfine coupling from **1** to **2** and to **3**.

At the scalar-relativistic level of calculation, the large hyperfine coupling constants are almost entirely derived from the Fermi-contact interaction, with only vanishingly small contributions from both the paramagnetic spin–orbital interaction and the nuclear-electron spin–dipolar coupling interaction (Tables S13–S15 and S19–S21). The minor impact of spin–orbit terms is also confirmed by the results of the spin–orbit two-component calculations. This clearly confirms that the Fermi-contact term is the origin of the massive hyperfine coupling constants through pronounced 6s mixing; indeed, both the Fermi-contact contribution to the hyperfine coupling constant and the spin density at the ^{175}Lu nucleus decrease gradually from **1** to **2** to **3** (Figures S27 and S28). Natural population analysis (Table S22) on the SOMOs of **1–3** yields 6s orbital parentages of 43.3%, 42.7%, and 41.7% for **1**, **2**, and **3**, respectively, correlating (Figures S29 and S30) with 6s-orbital characters of 41.2%, 40.5%, and 39.2% derived from experimentally determined hyperfine coupling constants.

Note that an s-orbital character of 50% represents the maximum theoretical value for any system where the orbital that incurs an s-orbital admixture, in this case the $5d_z^2$ orbital, lies energetically below the corresponding admixing s-orbital prior to mixing considerations, in this case the 6s orbital. This energetic ordering of the $5d_z^2$ orbital below the 6s orbital prior to mixing considerations is validated by the greater $5d_z^2$ character than 6s character for **1–3** via natural population analysis (Table S23). If $5d_z^2$ is the majority contributor to the lower-energy $5d_z^2$ – 6s hybrid orbital, then naturally the $5d_z^2$ orbital must be energetically lower than the 6s orbital prior to orbital mixing considerations. Thus, since an s-orbital character of 50% represents the maximum theoretical value for systems such as these, the observed 41.2% s-orbital character for **1** corresponds to 82.4% of the maximum possible 6s orbital character for a Lu^{2+} complex.

CONCLUSIONS

The foregoing results demonstrate that the introduction of axial crystal fields—in the form of bulky cyclopentadienyl ligands—in Lu^{2+} complexes gives rise to hyperfine coupling of unprecedented magnitude among lanthanide complexes.

Further, EPR and computational analyses confirm that this large hyperfine coupling arises owing to the presence of a $5d_{z^2} - 6s$ SOMO marked by up to 41.2% 6s character, representing the highest degree of s-orbital character yet reported for the ground state of an open-shell molecule, as well as near-record magnitudes of hyperfine coupling constants greater than 4 GHz. Across the three Lu^{2+} metallocene complexes, varying degrees of axiality act to further fine-tune the core magnetic properties and establish a clear trend among the geometric structure, crystal field axiality, and s-orbital parentage of the singly occupied molecular orbitals. By combining isotopic substitution to ^{176}Lu —where the larger $I = 7$ nuclear spin also increases clock transition energies—with a further strengthening of the hyperfine coupling via crystal field considerations, it may be possible to realize Lu^{2+} clock qubits operative at even higher frequencies.

More broadly, these results outline a synthetic approach toward molecules with true 2S ground states, which may find use in areas of quantum information science within and beyond clock qubits, such as the design of optically or electrically addressable nuclear spin qubits. Toward this end, work is underway to further adjust the chemical periphery of bulky cyclopentadienyl ligands to enforce more linear geometries as well as to extend this approach to other axial ligand families and to other metal ions, especially metal ions inherently capable of even larger hyperfine interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c01947>.

Experimental section, synthetic procedures, IR, UV-vis–NIR, EPR spectroscopy data, X-ray crystallography data, and computational data ([PDF](#))

Computational data full spreadsheets and optimized structures ([ZIP](#))

Accession Codes

Deposition Numbers 2378861–2378863 and 2378890 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe [Access Structures service](#).

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Notes

The authors declare no competing financial interest.

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