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Co(III) Imidos Exhibiting Spin Crossover and C−H Bond Activation

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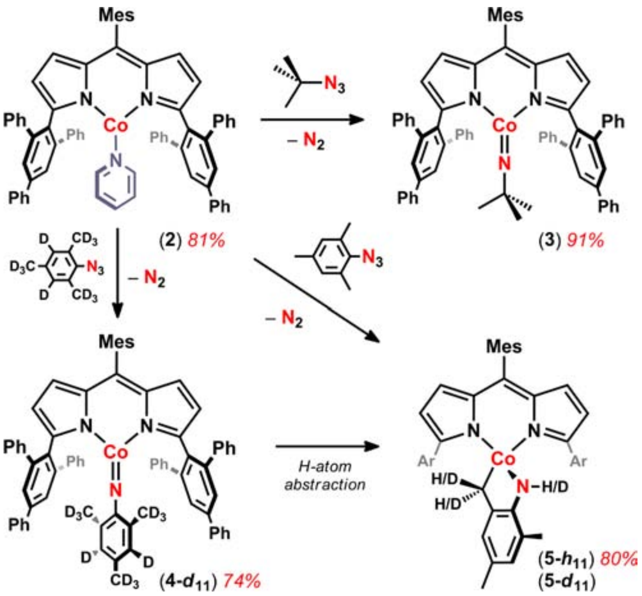
Ⓢ *Supporting Information*

ABSTRACT: The reaction of $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Co(py)}$ with $^{t}\mathrm{BuN_3}$ afforded the isolable three-coordinate Co−imido complex $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Co(N}^{t}\mathrm{Bu)}$, which is paramagnetic at room temperature. Variable-temperature (VT) ^{1}H NMR spectroscopy, VT crystallography, and magnetic susceptibility measurements revealed that $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Co(N}^{t}\mathrm{Bu)}$ undergoes a thermally induced spin crossover from an $S = 0$ ground state to a quintet ($S = 2$) state. The reaction of $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Co(py)}$ with mesityl azide yielded an isolable $S = 1$ terminal imido complex that was converted into the metallacycloindoline $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Co}(\kappa^2\text{-NHC}_6\mathrm{H}_2\text{-2,4-Me}_2\text{-6-CH}_2)$ via benzylic C−H activation.

The principal interest in synthesizing late, first-row transition metal coordination complexes featuring metal−ligand multiple bonds is that the terminally bound functionality may be transferred to unreactive substrates (e.g., olefins, C−H bonds).[1] A key determining factor for the reactivity of the multiply bonded functionality is the electronic structure of the transition metal ion to which it is bound.[2] Low-spin electronic configurations engender stability,[3−5] whereas open-shell configurations may populate the antibonding orbitals, thereby producing a reactive species for atom- or group-transfer processes.[6] While the ligand-field strength of the metal−ligand multiple bond is inherent, the use of weak-field ancillary ligands may permit high-spin (HS) configurations to be obtainable. This electronic structure−reactivity relationship has been most heavily scrutinized in high-valent Fe−oxo chemistry.[7] Unlike Fe-based metal−ligand multiple bonds, which have been observed to span a range of electronic configurations,[3,6] nearly all Co coordination compounds containing a metal−ligand multiple bond feature low-spin ground states,[4] producing inert complexes. The lone exception is Theopold's complex (Tp*)-$\mathrm{Co^{III}NAd}$, which undergoes radical decomposition at higher temperatures where a thermally accessible open-shell configuration may be accessible.[4e] Transient cobalt imides have been invoked in H-atom abstraction reactions on the basis of characterization of the resulting amides, but their spin states are unknown.[8] We report herein the synthesis of $\mathrm{Co^{III}}$ imido complexes featuring the weak-field dipyrrinato platform that undergo thermal spin crossover and can effect C−H bond activation.

We have demonstrated the ability of the weak-field dipyrrin platform to stabilize low-coordinate Fe complexes in HS configurations.[6e,f,9] The sterically encumbered derivative 5-mesityl-1,9-(2,4,6-triphenylphenyl)dipyrromethene ($^{\mathrm{Ar}}$LH) stabilized a three-coordinate $\mathrm{Fe^{II}}$ chloride species and allowed for the isolation of a reactive $\mathrm{Fe^{III}}$ imido radical species following treatment of the $\mathrm{Fe^{II}}$ chloride with an aryl azide.[6f] The imido radical is capable of stoichiometric C−H bond amination and styrene aziridination, while less bulky versions of the dipyrrin ligand render the nitrene-transfer reaction catalytic.[6f] We hypothesized that use of the sterically encumbered dipyrrin ligands with Co might similarly lead to open-shell configurations with metal−ligand multiple-bonded functionalities, rendering these typically inert complexes reactive for imido-group transfer (Scheme 1).

Scheme 1. Reactions of $\mathrm{Co^I}$ Synthon 2



Metalation of $^{\mathrm{Ar}}$LH with Co followed directly from the previously reported protocols for preparing the Fe congeners.[6f] Reaction of $(^{\mathrm{Ar}}\mathrm{L})\mathrm{Li}$ with $\mathrm{CoCl_2(py)_2}$[10] afforded the dark-maroon pyridine (py) complex $(^{\mathrm{Ar}}\mathrm{L})\mathrm{CoCl(py)}$ (**1**), which exhibits a paramagnetically shifted ^{1}H NMR spectrum [$\mu_{\mathrm{eff}} = 4.2(1)\mu_{\mathrm{B}}$; $\mathrm{C_6D_6}$, 295 K] consistent with a quartet ground state. The presence of pyridine bound to Co was confirmed by structural elucidation [Figure S.1 in the Supporting Information (SI)]. Chemical reduction of **1** with $\mathrm{KC_8}$ in benzene at room temperature cleanly produced the $\mathrm{Co^I}$ pyridine adduct $(^{\mathrm{Ar}}\mathrm{L})$-Co(py) (**2**) as a purple solid. Like **1**, **2** is paramagnetic, and it has a triplet ground state, as corroborated by the solution [$2.9(1)\mu_{\mathrm{B}}$;

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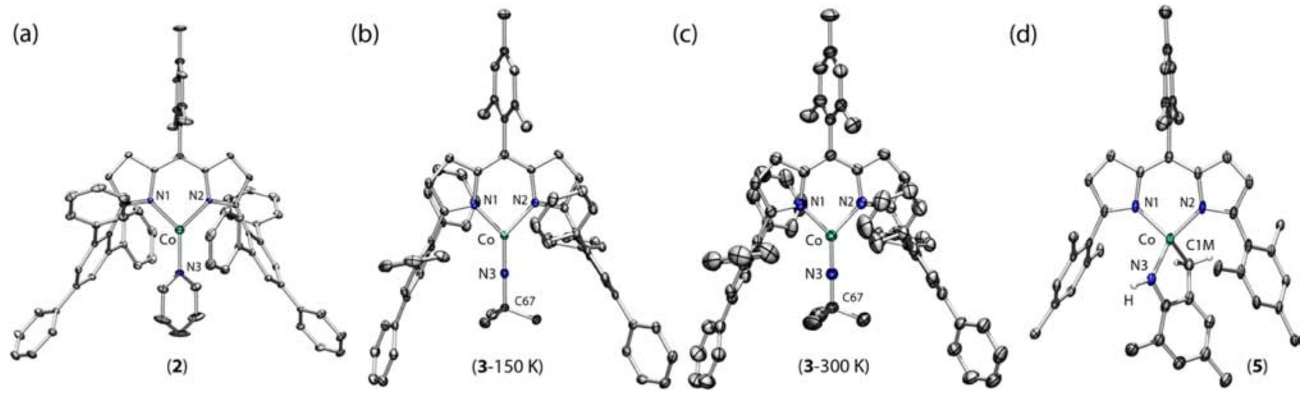

Figure 1. Solid-state structures of (a) $(^{Ar}L)Co(py)$ (**2**), (b, c) $(^{Ar}L)CoN^tBu$ (**3**) at (b) 150 and (c) 300 K, and (d) $(^{Ar}L)Co(\kappa^2\text{-}NHC_6H_2\text{-}2,4\text{-}Me_2\text{-}6\text{-}CH_2)$ (**5**) at 100 K, with 40% probability ellipsoids. H atoms, solvent molecules, and the ligand phenyl substituents in **5** have been omitted for clarity. Colors: Co, green; C, gray; H, white; N, blue. Selected bond lengths (Å) and angles (deg) for **2**: Co−N1, 1.961(3); Co−N2, 1.961(3); Co−N3, 1.942(4). For **3** at 150 K: Co−N1, 1.926(3); Co−N2, 1.916(3); Co−N3, 1.609(3); N3−Co−C67, 177.5(3). For **3** at 300 K: Co−N1, 1.930(3); Co−N2, 1.934(3); Co−N3, 1.632(3); N3−Co−C67, 178.2(3). For **5**: Co−N1, 1.927(3); Co−N2, 1.992(3); Co−N3, 1.848(4); Co−C1M, 2.018(5).

C_6D_6, 295 K] and solid-state ($\chi_M T = 1.07$ K cm^3/mol) magnetic moments. The molecular structure of **2** as determined by single-crystal X-ray diffraction (XRD) (Figure 1a) revealed a trigonal-planar geometry for the three-coordinate Co. With a suitable Co^I synthon in hand, we sought to examine its reactivity with two-electron group-transfer reagents.

Dropwise addition of a 1% (w/w) solution of $^tBuN_3$ in diethyl ether to a diethyl ether solution of **2** consumed the azide (as ascertained by the disappearance of ν_{N_3} by IR analysis) and cleanly afforded a new paramagnetic species. Crystals of this product were obtained from a benzene/hexane solution at −35 °C. The X-ray crystal structure of $(^{Ar}L)Co(N^tBu)$ (**3**) revealed a trigonal-planar three-coordinate cobalt imido (Figure 1b). The Co−N distance of 1.609(3) Å is shorter than those previously reported for either three- or four-coordinate cobalt imidos [1.621(3)−1.675(2) Å].[4] The Co−N3−C67 angle is nearly linear [178.8(1)°], and the imido does not deviate significantly from the plane formed by the dipyrrin nitrogens (N1 and N2) and the Co atom. The reaction of **2** or imido **3** with excess $^tBuN_3$ led to the formation of the tetrazole complex $(^{Ar}L)Co(\kappa^2\text{-}^tBuNNNN^tBu)$ (Figure S.4).

Imido **3** displays a paramagnetically shifted ^{1}H NMR spectrum at room temperature [δ 23.2 to −8.4 ppm; $\mu_{eff} = 2.96(2)\mu_B$; C_6D_6, 295 K]. However, cooling a sample of **3** in toluene-d_8 in the NMR probe resulted in a dramatic contraction of the chemical shift range to 8.85−0.29 ppm at −80 °C (Figure S.8). The ^{1}H resonances for the imido ^{t}Bu substituent appeared at 8.85 ppm [assigned via preparation of the deuterated analogue $(^{Ar}L)Co(N^tBu\text{-}d_9)$ (**3-*d*$_9$**)], still downfield from those of a diamagnetic ^{t}Bu group, indicating that the spin transition is incomplete at −80 °C. The recorded solution magnetic moment decreased accordingly (Figure S.13). The observed spectral features suggest a spin-crossover transition from an open-shell configuration (i.e., $S = 1$ or 2) to a singlet state, indicating that the ground state of **3** is diamagnetic.

To probe the magnetic behavior of **3** further, variable-temperature (VT) direct-current (dc) susceptibility data were collected over the temperature range 5−300 K. For **3**, $\chi_M T$ at 300 K was found to be 1.12 cm^3 K/mol ($2.99\mu_B$), consistent with the solution magnetic moment obtained at room temperature [$2.96(2)\mu_B$], but the plot of $\chi_M T$ was clearly rising at the temperature limit of the experiment (Figure 2a). As the temperature was lowered, $\chi_M T$ underwent a gradual decline to a value of 0.77 cm^3 K/mol near 50 K, followed by a subsequent decrease to 0.47 cm^3 K/mol ($1.94\mu_B$) at 5 K. As the susceptibility data never achieved a value consistent with a singlet ground state, we hypothesized that a fraction of the HS state remained at the low-temperature extreme. VT magnetization data were collected over the temperature range 1.8−10 K at fields of 1−7 T. The resulting plot of reduced magnetization (Figure S.12) featured a series of nonsuperimposable isofield curves, with the 7 T curve reaching a maximum value of $M = 0.62\mu_B$ at 1.8 K. The $\chi_M T$ versus T curve for **3** was fit as a spin transition (for x_{HS}, ΔH, and T_c) between a singlet state and either the triplet or quintet state using eq 1,[11] in which x_{HS} is the fraction of molecules trapped in the HS state at low T (see the SI for the expression used for x_{HS}).[12] The reduced magnetization data were fit using ANISOFIT[13] and the spin Hamiltonian shown in eq 2.

$$\chi_M T = x_{HS}(\chi_{HS}T) + (1 - x_{HS})(\chi_{HS}T)/[1 + e^{\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_c}\right)}] \quad (1)$$

$$\hat{H} = \mu_B g \mathbf{H}\cdot\hat{\mathbf{S}} + D\hat{S}_z^{\ 2} + E(\hat{S}_x^{\ 2} - \hat{S}_y^{\ 2}) \quad (2)$$

A satisfactory model for the reduced magnetization and susceptibility data could be obtained only by invoking a spin transition from a singlet to quintet configuration with a small fraction of the HS component present at low temperatures. Setting x_{HS} = 25.6% accounted for the plateau in the susceptibility below 100 K. Thus, the total fraction of the HS component is given by this baseline value plus the portion suggested by the Boltzmann distribution for the remaining fraction governed by the thermodynamic parameters $\Delta H = 472$ cm^{-1} and $T_c = 1397$ K, which were obtained by fitting our data to eq 1 using the x_{HS} expression for $S = 2$ with $D = -20.2$ cm^{-1} and $g_{avg} = 2.0$. The very small change in the fraction of the HS component between low temperature and room temperature (∼10%) is manifested in the very small structural perturbations observed crystallographically at 150 and 300 K. The 300 K structure reveals a modest elongation of the Co−N bond length from 1.609(3) to 1.632(3) Å (Figure 1c), consistent with electronic population of σ^* and π^* molecular orbitals (MOs) (see below). Population of Co−N antibonding MOs would suggest weakening of the Co−imido bond, making it reactive for H-atom abstraction or viable for imido-group transfer. While reaction with a two-electron reductant, PMe_2Ph, did facilitate imido-group transfer to give the phosphinimide $PhMe_2P(N^tBu)$

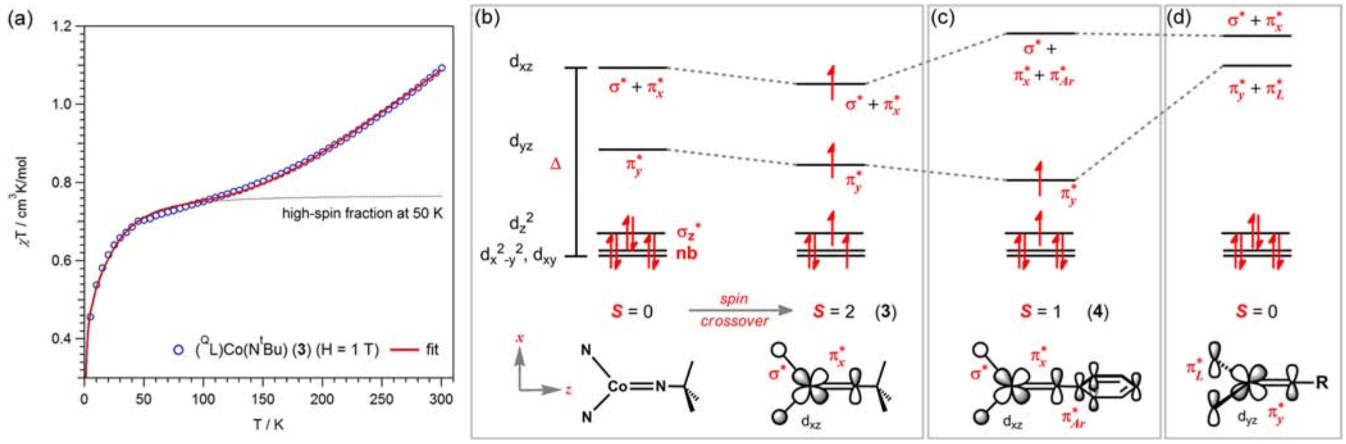

Figure 2. (a) VT magnetic susceptibility data for **3** in an applied dc field of 1 T (○) and the fit described in the text (red solid line). (b−d) Frontier MO description of Co^{III}(NR) featuring an ancillary ligand with (b) no ancillary π donation, (c) conjugation to the imido *N*-aryl π system, and (d) ancillary ligand π-donating substituents.

quantitatively at 80 °C, we observed no evidence for C−H bond activation using **3** with either 1,4-cyclohexadiene or 9,10-dihydroanthracene.

The reaction of **2** with 1 equiv of mesityl azide (N_3Mes) in benzene resulted in consumption of the azide (as ascertained by the disappearance of ν_{N_3} by IR analysis) and cleanly afforded a new paramagnetic species upon sublimation of the benzene. XRD analysis of crystals obtained from this reaction revealed not an imido product but instead a metallacycloindoline product, (^{Ar}L)Co(κ^2-NHC_6H_2-2,4-Me_2-6-CH_2) (**5**) (Figure 1d). The mesitylnitrene unit was modified via net H-atom transfer from a mesityl benzylic group to the imido N (ν_{N-H} = 3357 cm^{-1}), enabling it to bind to Co as a dianionic chelate via a Co−anilido bond and a Co−alkyl bond to a mesityl benzylic carbon. Within the metallacycloindoline, the Co−N3 bond distance of 1.848(4) Å and the Co−C1M distance of 2.018(5) Å are consistent with single bonds to Co.

Given the stability of imido **3**, we propose that **5** arises via formation of the terminal imido product (^{Ar}L)Co(NMes) followed by H-atom abstraction from one of the proximal *o*-methylene groups by the imido with subsequent radical recombination between Co and the pendant benzylic radical. The intermediacy of the mesityl imido was supported by the observation of a new species by ^{1}H NMR spectroscopy immediately following the addition of N_3Mes to **2**. Reaction of an *n*-hexane slurry of **2** with N_3Mes-d_{11} (using the deuterated azide to suppress H-atom abstraction) over 48 h at room temperature permitted the isolation of a paramagnetic product that precedes the formation of metallacycloindoline **5-*d*₁₁**. As isolated, the new purple species was stable in the solid state for days but converted to **5-*d*₁₁** slowly in solution and upon attempts at crystallization. We propose the kinetic product to be (^{Ar}L)Co(NMes-d_{11}) (**4-*d*₁₁**), which exhibits a paramagnetically shifted ^{1}H NMR spectrum [μ_{eff} = 3.6(2)μ_B] at room temperature. Unlike **3**, however, imido **4** does not undergo a spin-state transition, as shown by VT ^{1}H NMR (Figure S.9) and magnetic moment susceptibility analysis (3.65μ_B at 300 K; Figure S.11d), suggesting that the triplet configuration of aryl imido complex **4** is the likely electronic ground state.

Several unusual features of the Co−imido complexes presented herein are unique to the (dipyrrin)Co platform: (1) alkyl imido **3** undergoes spin crossover from a singlet to quintet configuration; (2) aryl imido **4** features a well-isolated triplet ground state with no apparent spin-crossover behavior yet undergoes H-atom abstraction along the Co−N_{Ar} bond; and finally, (3) all previously reported Co^{III}−imido complexes have singlet ground states. These observations can be rationalized by considering the frontier MO perturbations caused by the various ligand substitutions. The Co−imido MOs arise from the imido N→Co σ interaction (N 2sp_z + Co 3d_{z^2}) and two Co−N π interactions, one (labeled π_x^*) arising from N 2p_x−Co 3d_{xz} overlap and the other (labeled π_y^*) from N 2p_y−Co 3d_{yz} overlap (Figure 2b). Symmetry-allowed mixing of the Co 4s and 3d_{z^2} orbitals stabilizes the 3d_{z^2} orbital, mitigating the destabilizing effect of populating the Co−N σ_z^* interaction. For four-coordinate imido complexes, the Co 3d_{xz} and 3d_{yz} orbitals are degenerate and contribute to bonding of the three ancillary ligand σ donors and the Co−imido π manifold, leading to a large energy gap between the occupied 3d_{z^2} orbital and the empty 3d_{xz}/3d_{yz} orbital set, favoring low-spin configurations.[2c,4a−c,e−g] For three-coordinate species, the Co−imido π manifold is composed of two nondegenerate bonding interactions, as the Co 3d_{xz} orbital also bears σ* character with respect to the ancillary bidentate ligand whereas the 3d_{yz} orbital does not.

The dipyrrin σ-donor strength is attenuated relative to that of non-N-heterocyclic donors,[14] reducing the 3d_{xz} destabilization [i.e., Δ(3d_{xz} − 3d_{xy}) is diminished; see Figure 2b]. The N-based π electrons in the dipyrrin ligand are incorporated into the ligand conjugated π framework and therefore do not destabilize the 3d_{yz} orbital. As the 3d_{yz} energy decreases, the 3d_{yz}−3d_{z^2} energy gap is reduced to less than the mean spin-pairing energy, permitting an open-shell configuration to be obtained. For complex **3** (Figure 2b), the combination of these two effects allows for population of 3d_{yz} and the thermally induced spin transition between the singlet and quintet states. Singlet−quintet spin crossover is most commonly observed for six-coordinate Fe^{II} complexes,[15] but Co^{III} spin-crossover complexes are not without precedent.[16] Complex **3**, much like recently reported Ni[17] and Fe[6g] imido complexes, showcases spin-crossover behavior in a complex bearing a metal−ligand multiple bond.

Substitution of N^{t}Bu by NMes decreases the N_{imido} 2p_y energy relative to the alkyl imido via orbital conjugation with the coplanar mesityl aryl ring (Figure 2c). Furthermore, orienting the mesityl unit perpendicular to the dipyrrin plane to minimize steric interactions raises the imido N 2p_x energy by introducing a π* interaction with the mesityl aromatic π electrons (labeled

π^*_{Ar}). Consequently, the Co $3d_{xz}$–N $2p_x$ orbital interaction is destabilized further, increasing Δ relative to the value for complex **3** and favoring the triplet configuration $d^2_{x^2-y^2}d^2_{xy}d^1_{z^2}d^1_{yz}$ (Figure 2c). The perpendicular orientation of the aryl imido ligand positions the mesityl *o*-methyl groups directly above the frontier MO possessing radical character ($3d_{yz}$), facilitating H-atom transfer. Radical recombination to afford metallacycloindoline **5** is entropically favored, as opposed to direct C–N bond formation to make the four-membered bicycloazetine product.

For the previously reported three-coordinate $\mathrm{Co^{III}}$–imido complexes, the ancillary ligands employed (β-diketiminato[4d] and guanidinato[4h]) are π-donating N-based ligands. They destabilize the $3d_{yz}$ orbital through π^*_{L} interactions with respect to the ancillary ligand as well as the imido interaction, leading to a large $3d_{yz}$–$3d_{z^2}$ energy gap akin to that in the four-coordinate systems, and similarly favor singlet ground states (Figure 2d). As mentioned previously, the N-based π electrons in the dipyrrin ligand are incorporated into the dipyrrin π framework and do not destabilize the $3d_{yz}$ orbital in a similar fashion. This feature, coupled with the weaker σ-donating capabilities of the dipyrrin, permits the open-shell configurations to be obtainable.

The synthesis and characterization of the dipyrrin $\mathrm{Co^{III}}$ imidos demonstrate that limiting the ancillary ligand field strength can provide access to electronic structures with higher spin. Ligands that enforce low coordination number can be used to create a sufficiently compressed ligand field that favors unpaired arrangements of electrons. This was demonstrated by the observation of reactivity atypical of singlet $\mathrm{Co^{III}}$ imidos: an alkylcobalt imido that partially populates a quintet state at room temperature carried out nitrene transfer to phosphine, and a triplet arylcobalt imido underwent intermolecular H-atom abstraction. These results in combination with the magnetic and structural characterization show that targeting metal–ligand multiple bonds with open-shell configurations may unveil reactive species for atom- or group-transfer processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; spectral, crystallographic, VT NMR, and magnetic data; and a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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