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Communications

Synthesis and Characterization of a New Organometallic Magnetic Coupler Based on the Silole Ring

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Summary: The synthesis, X-ray structure, and magnetic properties of a new aminoxyl biradical linked by a silacyclopentadienyl ring is reported. Connection across the 2,5-positions of the silole is characterized by intramolecular antiferromagnetic interactions leading to a singlet ground state, which is one of the requirements for accessing photoinduced/photoswitching magnetic spin systems.

Intramolecular spin alignment and exchange interactions in purely organic spin systems are essential topics in the field of molecule-based magnetism.[1,2] Since most studies have been limited to the ground state, synthetic efforts have been actually devoted to design high-spin compounds that are based on conjugated polyradicals with topologically polarized π-spins able to give rise to ferromagnetic interactions between the spin carriers. Therefore, topologies that are expected to allow antiferromagnetic interactions, yielding a singlet or low-spin ground state, have been generally discredited. Recently, the observation of high-spin excited states in purely organic π-conjugated spin systems with a singlet ground state has opened a new strategy for photoinduced/photoswitching magnetic spin systems and has rekindled an interest in systems with the “wrong” topology.[3]

One of the major requirements for the organic coupler in such a strategy is that it has to have luminescent properties associated with an accessible photoexcited triplet state. In this context, the silacyclopentadienes, usually abbreviated siloles, are promising candidates. In comparison to conventional π-systems, the silole ring would take advantage of the $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the silicon moiety and the π^* orbital of the butadiene fragment, leading to an unusually low-lying LUMO.[4] This allows the siloles to exhibit very interesting luminescent properties, which may be associated with potential magnetic interactions through this system.[5] We report here the preparation and the structural characterization of the novel diradical 1,1-dimethyl-2,5-bis(3-*N*-*tert*-butyl-*N*-aminoxylphenyl)-3,4-diphenylsilole (**3**), as well as the determination of its magnetic ground state.

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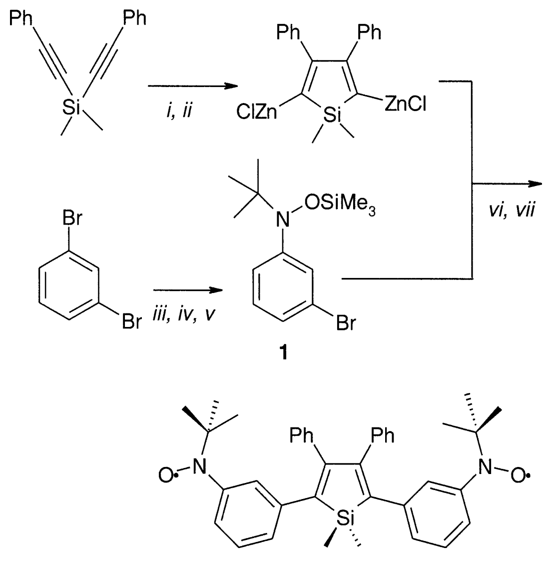
Scheme 1[a]



3

[a] Legend: (i) NpLi; (ii) $ZnCl_2$, TMEDA; (iii) BuLi; (iv) ^{t}BuNO; (v) Me_3SiCl, NEt_3; (vi) $PdCl_2(PPh_3)_2$; (vii) Ag_2O.

The biradical **3** was synthesized according to an adaptation of the general reported described by Tamao et al. (Scheme 1).[4a] It involves the intramolecular reductive cyclization of the dimethylbis(phenylethynyl)silane in the presence of lithium naphthalenide. The Pd^0-catalyzed cross-coupling reaction of the organozinc intermediate with 1-[*N*-*tert*-butyl-*N*-(trimethylsiloxy)amino]-3-bromobenzene (**1**) gives 1,1-dimethyl-2,5-bis(*m*-phenyl-*N*-*tert*-butylhydroxylamine)-3,4-diphenylsilole (**2**), which is oxidized by silver oxide to lead to the expected diradical **3** after purification by preparative TLC. Monocrystals suitable for X-ray analysis were obtained by layering a dichloromethane solution of **3** with hexane.[6]

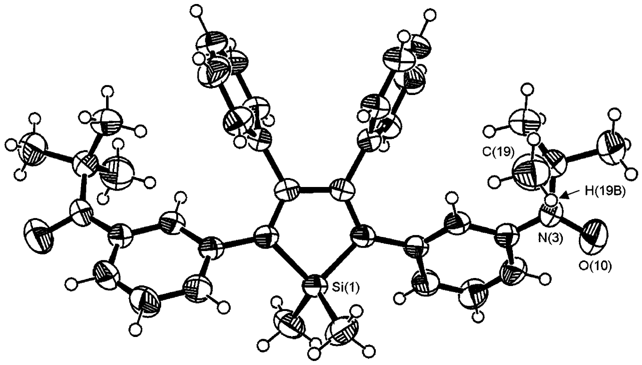


Figure 1. ORTEP view of **3** (50% probability). The Si atom lies on a 2-fold axis.

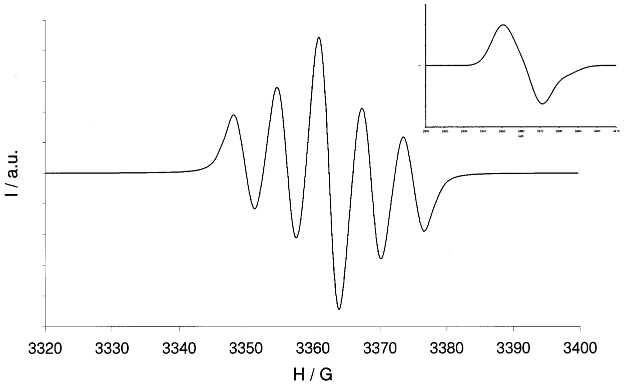


Figure 2. ESR spectra of a dichloromethane solution of **3** recorded at room temperature and at 100 K (inset).

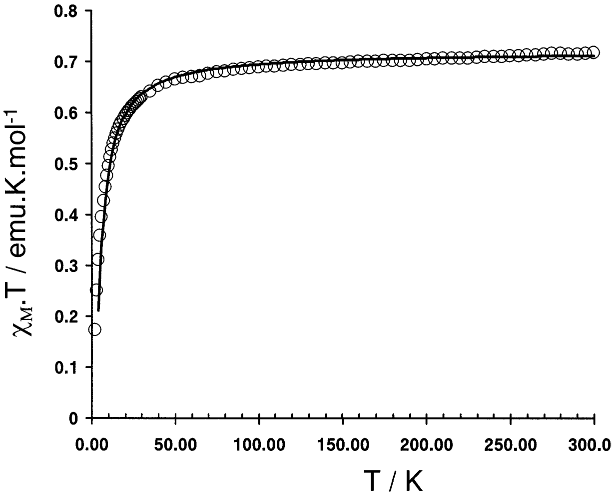


Figure 3. Plot of experimental (○) and calculated (—) $\chi_{\mathrm{mol}}T$ values versus temperature for the biradical **3** (see text).

Compound **3** crystallizes in the monoclinic space group *C*2/*c*.[7] The molecule displays a propeller-like arrangement of the four benzene rings, as usually observed with the other tetraarylsiloles (Figure 1).[4] The intramolecular distance between the radical centers is 14.6 Å; the torsion angle between the N−O• bond and the benzene ring of 15.8° may result from the minimization of the steric interactions between the *tert*-butyl group and the adjacent aromatic hydrogen atom. The dihedral angles between the mean plane of the central silacyclopentadienyl heterocycle and the phenyl rings bearing the aminoxyl radicals have a value of 49.2°, which is still compatible with an efficient π-conjugation. Examination of the crystal packing shows a pattern consisting of zigzag alternating chains of silole units running along the *ac* plane.[6] In these chains, the silole units are linked together by a complementary hydrogen bond involving the H19B hydrogen of the *tert*-butyl group and the oxygen of the aminoxyl group (H19B−O10′ = 2.75 Å); as a consequence, the closest intermolecular distance between two radicals in the crystal lattice is 4.90 Å.

The room-temperature ESR spectrum of **3** in degassed dichloromethane (Figure 2) exhibits the quintet of lines expected for a bis-aminoxyl radical system ($a_N/2 = 6.59$ G) in which the exchange coupling parameter J is substantially larger than the nitrogen hyperfine coupling ($|J| \gg a_N$). Cooling the sample down to cryogenic

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(6) Detailed information is provided in the Supporting Information.

(7) Crystal data for **1**: $C_{38}H_{42}N_2O_2Si$, $M_r = 572.83$, monoclinic, space group *C*2/*c*, $a = 25.176(5)$ Å, $b = 10.454(5)$ Å, $c = 13.062(5)$ Å, $\beta = 99.910(5)°$, $V = 3386(2)$ Å^3, $Z = 4$, 9891 collected reflections, 99.9% completeness to $\theta = 24.7°$, 2888 unique observed reflections, $R_{\mathrm{int}} = 0.05$, 195 refined parameters, $R1_{\mathrm{obsd}} = 0.047$, $wR2_{\mathrm{obsd}} = 0.11$, $R1_{\mathrm{all}} = 0.085$, largest difference peak and hole 0.22/−0.20 e Å^{-3}. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Si1−C21 = 1.854(3), Si−C7 = 1.873(2), Si−C7−C5 = 124.1(1), N3−O10 = 1.283(3), N3−C6 = 1.418(3), N3−C14 = 1.500(3), C6−N3−O10 = 116.2(2), C6−N3−C14 = 126.4(2), Si−C7−C5−C8 = 49.2(1), C13−C6−N3−O10 = 15.8(1), C5−C7−C2−C11 = 4.2(1).

temperature gives a slightly structured signal in the $\Delta M_s = 1$ region (Figure 2) which may be simulated by using the following parameters: $S = 1$, $|D| = 16$ G, $|E| = 0$ G, $g(x) = 2.008$, $g(y) = 2.005$, $g(z) = 2.002$. The interspin distance is estimated to ca. 12 Å by using the zero-field-splitting (ZFS) parameter D in the point-dipole approximation. In comparison to the interspin distance obtained from the crystal structure (14.6 Å, vide supra), this value reflects an effective spin delocalization through the aromatic rings.

The magnetic susceptibility of a polycrystalline sample of **3** was measured with a SQUID magnetometer in a field of 5 kOe, and the $\chi_M T$ vs T plot is shown in Figure 3. The room-temperature value of $\chi_M T$ of 0.72 emu K/mol is close to the expected value for two uncorrelated $^1/_2$ spins (0.75). The curve was analyzed in term of a modified singlet−triplet two-spin model ($H = -J\mathbf{S}_1\cdot\mathbf{S}_2$):

$$\chi_M = f\frac{2Ng^2\mu^2_B}{k_B(T-\Theta)}\frac{1}{3+\exp(-2J/k_BT)} \qquad (1)$$

where J is the exchange interaction, Θ indicates a Weiss constant employed to describe the additional of an eventual intermolecular interaction by mean field theory, and f was introduced to take into account the sample purity and experimental errors.[8] The best-fit parameters were $J/k_B = -6.0$ K, $\Theta = 0$ K, and finally, $f = 0.96$, which also corresponds to the estimation of the biradical purity from the room-temperature ESR results. The introduction of a nonzero Weiss constant Θ did not improve the fit. This result is consistent with negligible through-space intermolecular antiferromagnetic interactions, as expected from the observed NO···NO shortest intermolecular distance of 4.90 Å observed in the crystal.[9]

To confirm the nature of the magnetic interactions observed in the solid state, ESR studies were carried out on frozen solutions down to 4 K. The presence of a triplet state was evidenced by the observation of a half-field transition ($\Delta M_s = 2$) below 50 K at a field of 1717 G. The intensity of this transition was measured as a function of the temperature (4−30 K). The resulting Curie plot (Figure 4) showed a nearly linear increase of the signal intensity with increasing the inverse absolute temperature, consistent with a thermally accessible triplet state. The best fit of the data according to the Bleaney−Bowers model[8]

$$I_{ESR} = \frac{C}{T}\left[\frac{1}{3+\exp\left(\frac{\Delta E_{T-S}}{k_BT}\right)}\right] \qquad (2)$$

where C is a constant to fit the sample intensity and ΔE_{T-S} is the singlet−triplet energy gap, gave a result of $\Delta E_{T-S}/k_B = 8$ K. This result, which is close to the value of J/k_B ($\Delta E_{T-S} = -2J$) obtained from the SQUID measurements, clearly indicates the intramolecular nature of the antiferromagnetic interactions.

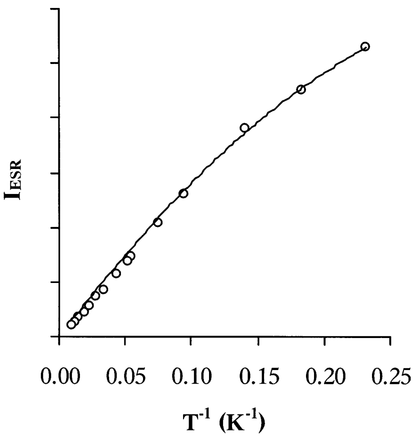

Figure 4. Curie plot for the biradical **3** compared with the Bleaney−Bowers model (see text).

From the above results, it follows that the connection of two *m*-phenylaminoxyl radicals across the 2,5-positions of a silole ring leads to a near-degeneracy of the singlet ground state with the thermally accessible triplet state. At first glance, the nearly planar conformation of a silole linker is in drastice contrast to the behavior of analogous acyclic diphenylsilane couplers, for which very weak magnetic interactions are observed.[5] However, it seems difficult to determine at the present time whether the magnetic exchange pathway implicates the silicon atom, since the butadiene moiety alone should also lead to a singlet ground state in the spin-polarization model.

From a structural point of view, **3** belongs to a class of biradicals termed as pseudo-disjoint, mainly constituted by nonalternating heteropentacyclic systems, in which spin-bearing units are connected to the central ring through sites bearing minimal spin density.[10] These systems usually displayed singlet ground states with low-lying multiplet excited states, whatever the heteroatom (X = O, NH, S), since the latter did not affect a singlet spin distribution. Therefore, **3** appears to follow the same trend, although no lone pair allowing magnetic interactions by a superexchange mechanism is present on the silicon atom.[11]

In summary, the connection of *m*-phenylaminoxyl radicals across the 2,5-positions of the luminescent silole ring is characterized by intramolecular antiferromagnetic interactions leading to a singlet ground state, which is one of the requirements to access photoinduced/photoswitching magnetic spin systems. Therefore, our further efforts will focus on their potential spin alignment in the photoexcited state. This work is currently underway.

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Supporting Information Available: Text, figures, and tables giving details of the synthesis, characterization, and crystal packing of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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