3.0 Hz, 1H), 5.61 (s, 1H), 7.21–7.51 ppm (m, 25H); ^{13}C NMR (63 MHz, CDCl$_3$): $\delta = 36.5$, 54.8, 63.2, 69.3, 71.5, 72.2, 72.8, 74.8, 74.9, 75.2, 77.2, 80.4, 84.1, 98.2, 98.9, 101.5, 124.3, 126.3, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 129.0, 138.4, 138.6, 138.8 ppm; elemental analysis (%): calcd for $C_{48}H_{52}O_{10}$ (788.9): C 73.08, H 6.64; found: C 73.06, H 6.69. **35**: $R_f = 0.55$ (hexane/ethyl acetate 2:1); $[\alpha]_D = +0.15$ ($c = 0.20$ in CHCl$_3$); ^{1}H NMR (250 MHz, CDCl$_3$): $\delta =$ 1.86 (ddd, $J = 3.8$, 11.3, 13.2 Hz, 1H), 1.99 (m, 1H), 2.36 (dd, $J = 5.3$, 13.2 Hz, 1H), 2.45 (ddd, $J = 2.4$, 4.8, 13.2 Hz, 1H), 3.50–3.60 (m, 1H), 3.69–3.94 (m, 6H), 4.04–4.16 (m, 1H), 4.25 (dd, $J = 4.2$, 9.5 Hz, 1H), 4.37 (dd, $J = 4.8$, 9.8 Hz, 1H), 4.70 and 4.87 (q, $J = 11.8$ Hz, 2H), 4.72 and 4.85 (q, $J = 12.1$ Hz, 2H), 4.91 and 5.03 (q, $J = 14.5$ Hz, 2H), 5.05 (d, $J = 2.7$ Hz, 1H), 5.61 (s, 1H), 5.63 (s, 1H), 6.00 (dd, $J = 2.2$, 9.9 Hz, 1H), 7.24–7.64 (m, 23H), 8.03 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (63 MHz, CDCl$_3$): $\delta = 36.4$, 36.7, 63.5, 67.3, 67.5, 68.8, 69.3, 72.9, 73.2(2), 74.3, 82.8, 84.1, 92.6, 98.0, 101.5, 101.6, 126.2, 127.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.4(2), 128.5, 128.6, 129.0, 129.1, 131.2, 133,3, 137.5, 137.7, 138.3, 138.9, 140.8, 164.8 ppm; calcd for $C_{48}H_{48}O_{11}$ (800.9): C 71.98, H 6.04; found: C 71.78, H 6.10.

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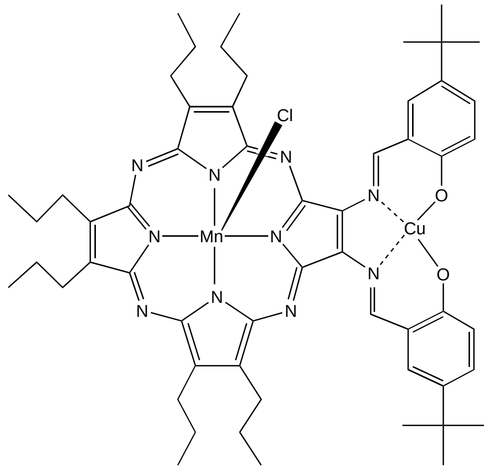
Spin Coupling between Metal Ions

Porphyrazines as Molecular Scaffolds: Periphery–Core Spin Coupling between Metal Ions of a Schiff Base Porphyrazine**

Min Zhao, Charlotte Stern, Anthony G. M. Barrett, and Brian M. Hoffman**

The periphery of a metalloporphyrazine (pz) can be readily functionalized with heteroatoms that coordinate additional metal ions, and this opens the way to high-spin molecules and molecular arrays based on exchange coupling between the metal ions.[1] We previously reported evidence for core–periphery spin coupling when a metal ion is bound to a peripheral dithiolene.[1–3] We show here that the pz molecule can be used as a scaffold on which to build complex peripheral chelating ligands, and that the resulting dimetallic complex shows some remarkable core–periphery spin coupling. We have synthesized the Schiff base appended porphyrazine (**1**) where the core metal ion is Mn^{III} with spin $S = 2$, and the peripheral ion is Cu^{II} with $S = 1/2$; have obtained its crystal structure, and characterized the $S = 3/2$ and 5/2 total-spin manifolds created by strong core–periphery M_1–M_2 spin coupling; and have



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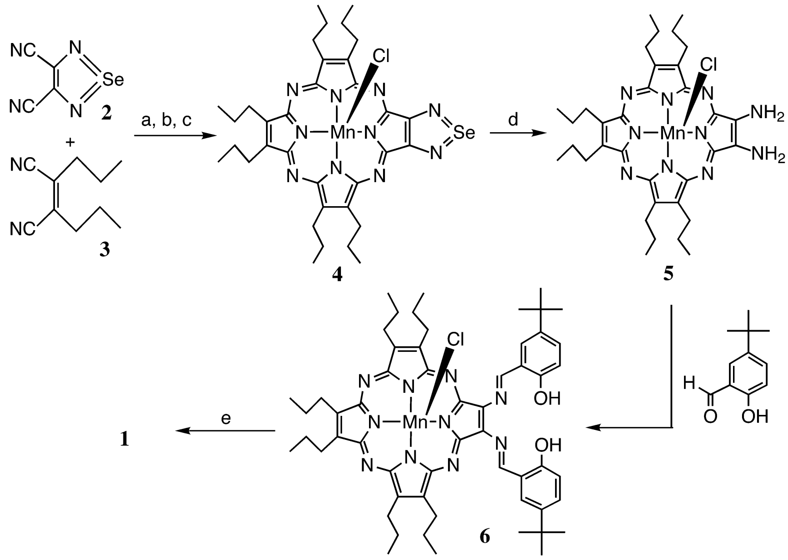

Scheme 1. a) $Mg(OBu)_2$/BuOH, reflux; b) trifluoroacetic acid; c) $MnCl_2$, chlorobenzene/*N*,*N*-dimethylformamide, 100 °C; d) H_2S/pyridine; e) $CuCl_2$, MeOH/$CHCl_3$.

determined the exchange-splitting between them through the use of EPR spectroscopy and magnetic susceptibility measurements.

The synthesis of **1** follows the procedures shown in Scheme 1. It involves the reaction of the [ClMn(pzdiamine)] (**5**) with two equivalents of 5-*tert*-butyl-2-hydroxybenzaldehyde to give **6**, followed by metalation of the Schiff base. Attempts to prepare **5** by a route that involves cocyclization of diaminomaleonitrile (DAMN) with dipropyl maleonitrile (**3**) were unsatisfactory, so we utilized the procedure devised by Baum et al.[4] in which DAMN is protected as 3,4-dicyano-1,2,5-selenodiazole (**2**) by oxidation with SeO_2 following the approach of Ercolani and co-workers.[5] This was cocyclized then with **3** by reaction with $Mg(OBu)_2$ in BuOH, demetalated in TFA to give the free-base form, which was metalated with $MnCl_2$ and air-oxidized to form **4**.[6] Deprotection with H_2S/pyridine generated **5**, which was treated in situ with 5-*tert*-butyl-2-hydroxybenzaldehyde to give the desired ligand **6**; the MnCu complex **1** was formed by stirring **6** with $CuCl_2$ in methanol/chloroform overnight.[7] Complex **1** was crystallized from dichloromethane/toluene/acetonitrile, and X-ray diffraction analysis[8] confirmed the structure (Figure 1).

Compound **1** crystallizes in the space group $P\bar{1}$, along with a molecule of CH_3CN and CH_2Cl_2 solvent. The pz core is planar to within 0.002 Å. As with other $ClMn^{III}$-complexed porphyrazines,[9] the manganese ion has a distorted square-pyramidal geometry, with the Mn center raised out of the N_4 coordination plane toward the apical chloride ion by 0.31 Å. The coordination environment of the copper ion of the Schiff base is planar to within 0.06 Å; the bonds to the O atoms are nearly equal in length, with an average value of 1.910 Å, which is slightly shorter than those to the N atoms, whose average value is 1.972 Å.

Figure 2 displays an X-band EPR spectrum of **1** taken at 77 K. It shows two overlapping "perpendicular" features at $g_\perp = 6$ and $g_\perp = 4$, each of which displays a sextet splitting from interaction with the ^{55}Mn ion ($I = 5/2$); the spectrum further shows unresolved intensity from the associated $g_\parallel$ features around $g = 2$. The hyperfine splittings show that these signals are associated with the Mn^{III} ion. However, an "isolated" Mn^{III} ion incorporated in a $[ClMn^{III}pz]$ has a high-spin ($S = 2$), d^4 configuration and at X-band is EPR silent; high-field EPR spectra show that an axial zero-field splitting (zfs) interaction resolves the four $S = 2$ spin sublevels into ±1/2 and ±3/2 doublets that are separated in zero field by $2D^{Mn} = -4.6\ cm^{-1}$, which is far greater than the X-band microwave quantum.[10] The d^9 Cu^{II} ion in an isolated Schiff base complex has $S^{Cu} = 1/2$; its frozen-solution EPR spectrum shows a quartet of $^{63/65}$Cu ($I = 1/2$) hyperfine lines centered at $g_\parallel = 2.2$, and a broad, but unsplit, "perpendicular" feature at $g_\perp \approx 2.05$.[11] Thus, the spectrum shown in Figure 2 cannot be associated with

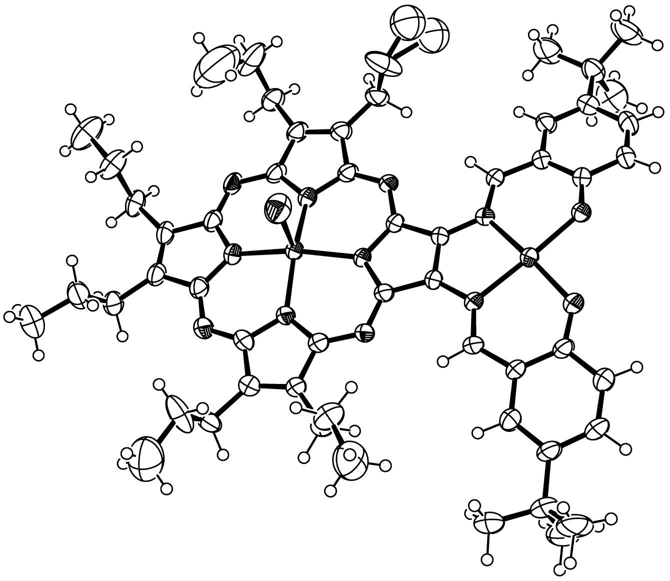

Figure 1. Crystal structure of **1**.

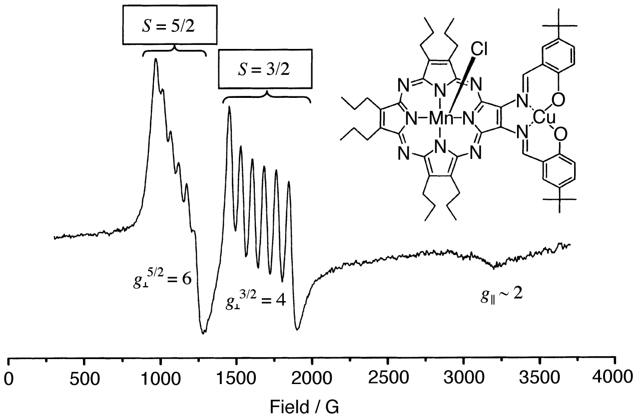

Figure 2. Frozen-solution X-band EPR spectrum of **1** dissolved in toluene/pyridine (1/1) (77 K).

either uncoupled spin center and must reflect interactions between them.

Heisenberg exchange coupling between the $S=2$ and $S=1/2$ individual spins ($\hat{H}_{\mathrm{ex}}=JS^{\mathrm{Mn}}S^{\mathrm{Cu}}$) would produce two total-spin manifolds with $S=3/2$ and $5/2$ which are separated by $\Delta=5J$. Each of these manifolds exhibits an axial zfs interaction whose principal value (D^{S}) is determined by that of the uncoupled Mn$^{\mathrm{III}}$ ion: $D^{3/2}=(3/5)D^{\mathrm{Mn}}$, $D^{5/2}=(7/5)D^{\mathrm{Mn}}$. As these zfs parameters are much larger than the X-band microwave quantum one expects the X-band spectra to display only transitions within the $m_s=\pm 1/2$ doublet for each total-spin manifold. These would be characterized by g tensors with $g_{\perp}^{3/2}=4$, $g_{\perp}^{5/2}=6$, and $g_{\parallel}^{3/2}=g_{\parallel}^{5/2}=2$. The spectrum shown in Figure 2 is clearly a superposition of the spectra expected for the $S=3/2$ and $S=5/2$ total-spin manifolds, and the observation of such a superposition at 77 K establishes the existence of a strong Heisenberg coupling between the partner spins, while implying there is thermal population of both manifolds at this temperature.

This interpretation is confirmed by the observed ^{55}Mn hyperfine splittings. It is straightforward to show that the exchange-coupled system should exhibit splittings of $A_{\mathrm{Mn}}^{3/2}=(6/5)A_{\mathrm{Mn}}$ and $A_{\mathrm{MMn}}^{5/2}=(4/5)A_{\mathrm{Mn}}$, where A_{Mn} is the coupling for the isolated Mn$^{\mathrm{III}}$ ion. The resulting prediction that $A_{\mathrm{Mn}}^{3/2}/A_{\mathrm{Mn}}^{5/2}=3/2$, clearly matches the ratio of the observed couplings $A_{\mathrm{Mn}}^{3/2}/A_{\mathrm{Mn}}^{5/2}=80\,\mathrm{G}/53\,\mathrm{G}=1.51$; the resulting hyperfine interaction for the uncoupled Mn$^{\mathrm{III}}$ ion ($A_{\mathrm{Mn}}=66$ G) is typical for such ions.[12] Despite the assignment of these signals to an exchange-coupled MnCu center, they surprisingly show no hyperfine splittings by the $^{63/65}$Cu ion. This too, however, is explained by the exchange model: The resolved features are "perpendicular", and $A_{\perp}^{\mathrm{Cu}}$ value for a $^{63/65}$Cu ion ($I=3/2$) of a Schiff base is normally small ($A_{\perp}^{\mathrm{Cu}}=$ ca. 30 G).[11] A coupling of this magnitude would still give substantial hyperfine broadening and indeed would preclude resolution of the ^{55}Mn couplings, especially for the $S=5/2$ state of **1**. However, spin-coupling calculations further show that the hyperfine coupling of the copper ion is sharply reduced in the total-spin manifolds generated by the spin exchange: $A_{\perp}(\mathrm{Cu})^{3/2}=A_{\perp}(\mathrm{Cu})^{5/2}=\pm(1/5)A_{z}(\mathrm{Cu})$. These considerations explain why the ^{55}Mn splittings are well resolved in the EPR spectra associated with the $S=3/2$, $5/2$ spin manifold, and why no evidence of $^{63/65}$Cu splittings is detectable.

The detailed analysis of the spectrum in Figure 2 shows definitively that **1** exhibits strong Heisenberg spin exchange between the partner metal-ion spins, but cannot yield a value of the exchange parameter Δ that splits the $S=3/2$ and $S=5/2$ manifolds. The magnetic susceptibility of **1** was measured between temperatures of 2 and 300 K using a SQUID magnetometer to determine the value of Δ (Figure 3). The high-temperature limiting value is $\chi T\approx 3.5\,\mathrm{cm^3\,mol^{-1}\,K}$, which is consistent with the presence of partners with $S=2$ and $S=1/2$ spins, each having intrinsic g values of roughly 2. The fall-off with decreasing temperature is indicative of antiferromagnetic coupling ($J>0$ for the $\hat{H}_{\mathrm{ex}}$ condition defined above), which places the $S=3/2$ manifold lower in energy than the $S=5/2$ one. The measured $\chi(T)$ value was fit to the theoretical expression for such a spin-coupled center, [Eq. (1)].[13]

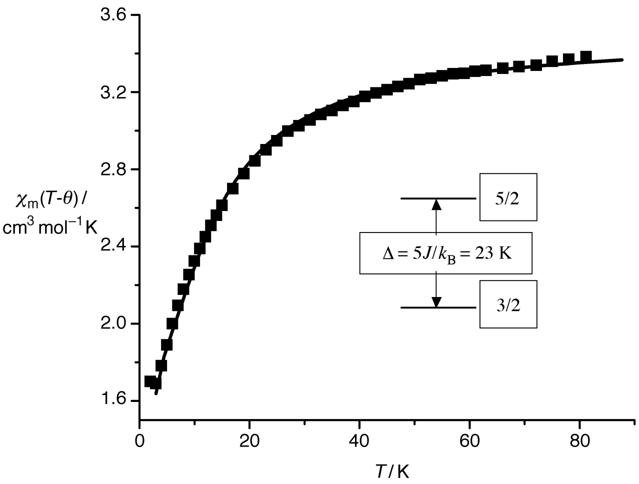

Figure 3. Plot of the molar magnetic susceptibility of a powdered sample of **1** plotted as (χT), which corresponds to the effective moment squared. The solid line is a fit to the data by Eq. (1), with $\theta=-8$ K, $g=2.05$, $D^{3/2}=(3/5)D^{\mathrm{Mn}}=-1.38\,\mathrm{cm^{-1}}$, and $\Delta/k_{\mathrm{B}}=23$ K.

$$\chi=\chi^{3/2}\frac{2}{2+3\,\mathrm{e}^{-\Delta/k_{\mathrm{B}}T}}+(C/4)\frac{35\,\mathrm{e}^{-\Delta/k_{\mathrm{B}}T}}{2+3\,\mathrm{e}^{-\Delta/k_{\mathrm{B}}T}} \tag{1}$$

$C=N\mu_{\mathrm{B}}^{2}g^{2}/k_{\mathrm{B}}(T-\theta)$ and the symbols have their usual meanings; the function $\chi^{3/2}$ is associated with the $S=3/2$ manifold and incorporates the effects of the zero-field splitting, where $D^{3/2}$ is fixed as described above [Eq. (2)].

$$\chi^{3/2}=C\left[\frac{1}{3}\frac{1+9\,\mathrm{e}^{-2D^{3/2}/k_{\mathrm{B}}T}}{4\,(1+\mathrm{e}^{-2D^{3/2}/k_{\mathrm{B}}T})}+\frac{2}{3}\frac{4+\frac{3k_{\mathrm{B}}T}{D^{3/2}}(1-\mathrm{e}^{-2D^{3/2}/k_{\mathrm{B}}T})}{4(1+\mathrm{e}^{-2D^{3/2}/k_{\mathrm{B}}T})}\right] \tag{2}$$

The fits give $\Delta/k_{\mathrm{B}}=23$ K and the Curie–Weiss constant $\theta=-8$ K.

The present results show that the pz macrocycle can be used as a scaffold on which to build a peripheral chelate, and that exchange coupling between core and peripheral metal ions with different intrinsic spin values yields a spin-coupled "ferrimagnetic" system with high residual spin. Other combinations of metal ions are being examined so as to define the systematics of spin coupling within this system, and we further anticipate that systems being prepared with more than one peripheral chelate will show exciting new features.

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[6] Yield: 59%. UV/Vis (CH_2Cl_2) $\lambda_{max} = 361, 618, 679$ nm; FAB MS: m/z 725.5 $[M-Cl]^+$, calcd for $C_{34}H_{42}N_{10}SeMn$: m/z 725.2.

[7] Yield: 41%. UV/Vis (CH_2Cl_2) $\lambda_{max} = 344$, 381, 656, 694 nm; atmospheric pressure CI-MS: m/z 1066.5 $[M+H]^+$, 1030.5 $[M-Cl]^+$; calcd $C_{56}H_{69}N_{10}O_2MnCuCl$: m/z 1066.4, calcd $C_{56}H_{68}N_{10}O_2MnCu$: m/z 1030.4; elemental analysis calcd for $C_{56}H_{71}N_{10}O_3MnCuCl$ (**1**+H_2O): C 61.98, H 6.50, N 12.91; found: C 62.01, H 6.27, N 13.12.

[8] Crystal data for **1**, $C_{59}H_{73}Cl_3CuMnN_{11}O_2$: triclinic, space group $P\bar{1}$, $a = 13.009(3)$, $b = 14.273(4)$, $c = 17.856(6)$ Å, $\alpha = 104.66(2)$, $\beta = 104.964(16)$, $\gamma = 104.781(14)°$, $V = 2910.9(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.358$ Mg m^{-3}, final $R1$ value of 0.0581 and wR_2 value of 0.1363 were based on 13690 independent reflections ($I > 2\sigma(I)$) out of 27297 reflections collected and 678 variable parameters. The data collection were performed at 153 K on a Bruker SMART-1000 CCD area detector, by using graphite monochromated Mo_K radiation ($\lambda = 0.71073$ Å), by the ϕ and ω-scan mode, within the limits $1.57 < \theta < 28.84°$. The linear absorption coefficient μ is 0.770 mm^{-1}. An integration absorption correction was applied. Minimum and maximum transmission factors were 0.8337 and 0.9801, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-97), expanded by using Fourier techniques (SHELXS-97), and refined by full-matrix least-squares on F^2. The non-hydrogen atoms were refined anisotropically except those on the disordered C33 methyl group. Hydrogen atoms were included in idealized positions, except those on the disorder carbon atoms, but not refined. The program Squeeze (A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C-34) was used to take out 84 electrons which correspond to the dichloromethane molecule. This solvent was refined as a diffuse contribution without specific atom positions, but the density and absorption coefficient reflect the full formula. All calculations were performed using the Bruker SHELXTL crystallographic software package. CCDC-190473 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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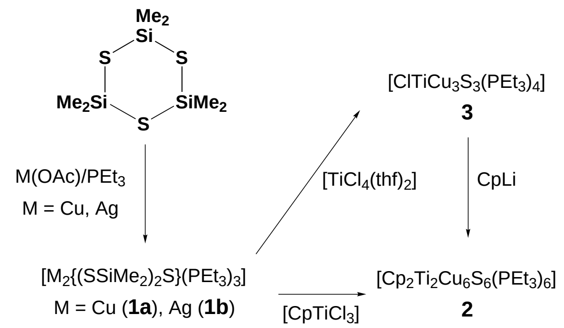
Cu and Ag Silanethiolato Complexes

Copper and Silver Complexes Containing the $S(SiMe_2S)_2^{2-}$ Ligand: Efficient Entries into Heterometallic Sulfido Clusters

Takashi Komuro, Tsukasa Matsuo, Hiroyuki Kawaguchi, and Kazuyuki Tatsumi*

The development of synthetic routes to mixed-metal sulfido clusters is a critical prerequisite to study these important materials.[1] It is well known that $(Me_3Si)_2S$ is a good sulfur-transfer reagent, and can replace a halide, alkoxide, acetate, or oxide with a sulfido ligand through the formation of energetically favorable Si–Cl or Si–O bonds.[2] Therefore, the corresponding M–SSiMe$_3$ species have the potential to be synthetic precursors of sulfido clusters.[3,4] However, because of the high lability of Si–S bond, there is a tendency to restrict the use of silanethiolato complexes. Thus, the stabilization of these complexes is required if they are to be used in the development of cluster syntheses. Cyclotrisilathiane has received less attention than $(Me_3Si)_2S$ for use in preparations of sulfido clusters.[5] In exploring of the utility of this reagent, we discovered the formation of thermally stable copper and silver complexes containing the intriguing $S(SiMe_2S)_2^{2-}$ ligand. Herein we report the synthesis of these complexes, and their reactions with titanium–chloride complexes.

Treatment of Cu(OAc) with cyclotrisilathiane in the presence of PEt_3 at room temperature generated $[Cu_2\{(SSiMe_2)_2S\}(PEt_3)_3]$ (**1a**) as colorless crystals in 74% yield (Scheme 1). The silver congener **1b** was obtained as colorless



Scheme 1. Synthesis of **1** and reactions with titanium chloride complexes to give **2** and **3**.

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