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Synthesis of Vanadium and Titanium Complexes of the Type RM[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] (R = Cl, Alkyl) and the Structure of ClV[(Me$_3$SiNCH$_2$CH$_2$)$_3$N]

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Summary: Vanadium and titanium complexes of the type ClM[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] have been synthesized by adding Li$_3$[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] to MCl$_4$L$_2$ (M = Ti, L = THF; M = V, L$_2$ = DME). An X-ray study of ClV[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] ($P2_1/a$, a = 15.167 (2) Å, b = 10.242 (2) Å, c = 16.301 (1) Å, β = 93.705 (8)°, V = 2527 (1) Å^3, Z = 4, T = −72 °C, R = 5.8%, R_w = 5.6%) showed it to be a monomer having pseudo-C_3 symmetry. Addition of LiR (M = Ti, R = *n*-Bu, *s*-Bu; M = V, LiR = [Li·TMED]CH$_2$SPh) to ClM[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] gave isolable alkyl derivatives, RM[(Me$_3$SiNCH$_2$CH$_2$)$_3$N]. When it is either heated (70 °C) or treated with H$_2$ (3 atm, 25 °C), *s*-BuTi[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] cleanly cyclometalates via an observable Ti(IV) hydride intermediate (Ti–H δ 8.29).

The bis(trimethylsilyl)amide ligand has been used for years to prepare complexes of the type M[N(SiMe$_3$)$_2$]$_3$ (M = Sc, Ti, V, Cr, or Fe,[1] Al,[2] Gd,[3] and U or Nd[4]) or XM[N(SiMe$_3$)$_2$]$_3$ (M = Ti, Zr, Hf, X = Cl, Me;[5–7] M = Th, U, X = H, Cl, Me, BH$_4$;[8–10] M = Hf, X = Br, I, N$_3$, CN;[11] M = Ge, Sn, Pb, X = Br, N$_3$;[12,13] M = Cr, X = NO;[14] MX = NbO;[15] MX = ReO[16]). We report here the synthesis of complexes containing a related tetradentate triamido ligand, (Me$_3$SiNCH$_2$CH$_2$)$_3$N. We hope to take advantage of what is likely to be a relatively rigid four-coordinate core with a "pocket" at the fifth coordination position in order to synthesize high-oxidation-state inorganic or organometallic complexes with unusual structures and reactivities, among them as yet unknown first-row d^0 alkylidene[17] and alkylidyne[18] complexes, or complexes that contain neutral or partially reduced dinitrogen (N$_2$H$_x$ ligands).[19,20]

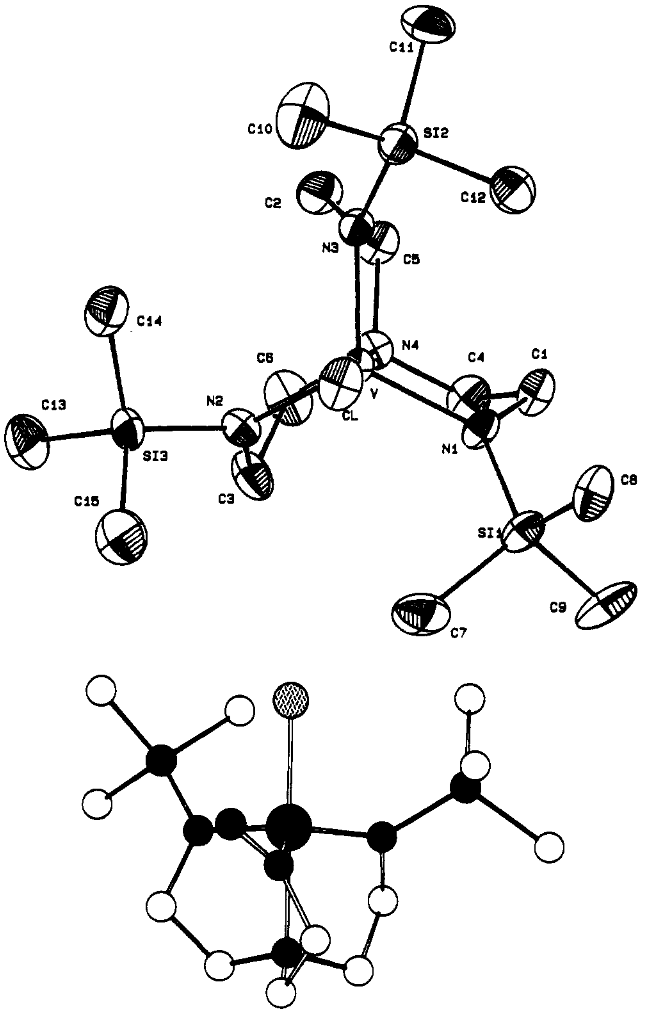

Figure 1. (a, top) ORTEP drawing of ClV[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] with ellipsoids at the 35% probability level. (b, bottom) Drawing of ClV[(Me$_3$SiNCH$_2$CH$_2$)$_3$N] emphasizing the steric compression about the V–Cl functionality. Methyl groups on the frontmost SiMe$_3$ fragment have been omitted for clarity.

Transition-metal complexes have been reported that contain related ligands such as (OCH$_2$CH$_2$)$_3$N and (MeNCH$_2$CH$_2$)$_3$N,[21–23] but the relatively bulky SiMe$_3$ derivative of the latter has not been added to transition metals to our knowledge. Triply silylated tris(2-aminoethyl)amine (tren)[24] has recently been prepared in conjunction with studies of silicon chemistry, and silylated diamido ligands recently have been used to prepare metal(IV) tetraamido complexes of Ti, V, and Cr.[25]

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Table I. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{ClV[(Me_3SiNCH_2CH_2)_3N]}$

	Bond Distances		
V–Cl	2.278 (2)	Si(3)–N(2)	1.741 (6)
V–N(1)	1.883 (6)	Si(3)–C(13)	1.86 (1)
V–N(2)	1.875 (6)	Si(3)–C(14)	1.85 (1)
V–N(3)	1.890 (6)	Si(3)–C(15)	1.87 (1)
V–N(4)	2.238 (6)	N(1)–C(1)	1.474 (9)
Si(1)–N(1)	1.743 (6)	N(2)–C(3)	1.47 (1)
Si(1)–C(7)	1.84 (1)	N(3)–C(2)	1.480 (9)
Si(1)–C(8)	1.854 (9)	N(4)–C(4)	1.49 (1)
Si(1)–C(9)	1.87 (1)	N(4)–C(5)	1.477 (9)
Si(2)–N(3)	1.727 (6)	N(4)–C(6)	1.474 (9)
Si(2)–C(10)	1.87 (1)	C(1)–C(4)	1.49 (1)
Si(2)–C(11)	1.87 (1)	C(2)–C(5)	1.49 (1)
Si(2)–C(12)	1.871 (9)	C(3)–C(6)	1.52 (1)
	Bond Angles		
Cl–V–N(1)	100.0 (2)	V–N(2)–Si(3)	128.1 (3)
Cl–V–N(2)	99.2 (2)	V–N(2)–C(3)	112.0 (5)
Cl–V–N(3)	99.2 (2)	Si(3)–N(2)–C(3)	119.9 (5)
Cl–V–N(4)	179.4 (2)	V–N(3)–Si(2)	127.6 (4)
N(1)–V–N(2)	120.4 (3)	V–N(3)–C(2)	111.5 (5)
N(1)–V–N(3)	117.0 (3)	Si(2)–N(3)–C(2)	120.8 (5)
N(1)–V–N(4)	80.2 (2)	V–N(4)–C(4)	107.0 (5)
N(2)–V–N(3)	114.6 (3)	V–N(4)–C(5)	106.3 (4)
N(2)–V–N(4)	80.2 (2)	V–N(4)–C(6)	107.7 (4)
N(3)–V–N(4)	81.3 (2)	C(4)–N(4)–C(5)	110.8 (6)
V–N(1)–Si(1)	126.1 (3)	C(4)–N(4)–C(6)	112.4 (6)
V–N(1)–C(1)	113.6 (5)	C(5)–N(4)–C(6)	112.4 (6)
Si(1)–N(1)–C(1)	119.8 (5)		

$\mathrm{Li_3[(Me_3SiNCH_2CH_2)_3N]}$ can be prepared readily as white microcrystals (eq 1). It reacts cleanly with $\mathrm{MCl_4L_2}$ complexes in pentane (M = Ti,[26] V[27]) to give $\mathrm{ClM[(Me_3SiNCH_2CH_2)_3N]}$ complexes (eq 2).[28] The monochloro species were isolated as crystals from pentane at −40 °C.

$$\mathrm{(Me_3SiN(H)CH_2CH_2)_3N} \xrightarrow[\text{-3BuH, pentane, -78 to +25 °C}]{3\mathrm{Li}\text{-}n\text{-}\mathrm{Bu}} \mathrm{Li_3[(Me_3SiNCH_2CH_2)_3N]} \tag{1}$$

$$\mathrm{Li_3[(Me_3SiNCH_2CH_2)_3N]} \xrightarrow[\text{-3LiCl, pentane, -40 to +25 °C}]{\mathrm{MCl_4L_2}} \mathrm{ClM[(Me_3SiNCH_2CH_2)_3N]} \tag{2}$$

$$\mathrm{M = Ti,\ L_2 = 2\ THF;\ M = V,\ L_2 = dimethoxyethane}$$

Proton and carbon NMR spectra of yellow-orange $\mathrm{ClTi[(Me_3SiNCH_2CH_2)_3N]}$ are consistent with the molecule having 3-fold symmetry,[28] while the proton NMR spectrum of blue-black $\mathrm{ClV[(Me_3SiNCH_2CH_2)_3N]}$ (δ 1.73, $\Delta\nu_{1/2}$ = 31 Hz, $\mathrm{SiMe_3}$; δ −15.09, $\Delta\nu_{1/2}$ = 130 Hz, $\mathrm{CH_2}$; δ −46.13, $\Delta\nu_{1/2}$ = 310 Hz, $\mathrm{CH_2}$) is what one might expect for a paramagnetic ($\mathrm{d^1}$) complex. The EPR spectrum of $\mathrm{ClV[(Me_3SiNCH_2CH_2)_3N]}$ at 92 K (toluene glass) consists of a signal similar to that observed for $\mathrm{V(CH_2SiMe_3)_4}$,[29] with $g = 1.963$ and hyperfine coupling to $^{51}\mathrm{V}$ of 14.7 mT. Since the IR spectra[28] of the titanium and vanadium complexes match peak for peak, these species may be assumed to be isostructural.

An X-ray study of $\mathrm{ClV[(Me_3SiNCH_2CH_2)_3N]}$[30] (Figure 1) showed that the molecule has pseudo-C_3 symmetry, the C_3 axis along the Cl–V–N(4) vector (Cl–V–N(4) angle 179.4°) not being crystallographically imposed. Bond distances and angles vary little between the three five-membered rings of the core (Table I). Overall the molecular structure is best described as intermediate between a trigonal bipyramid and a face-capped tetrahedron, with the vanadium atom displaced from the plane of the three amide nitrogen atoms by 0.310 Å in the direction of the chloride ligand and the average of the Cl–V–N(amide) angles being 99.5°. The amine nitrogen atom (N(4)) is well within bonding distance of the metal (V–N(4) = 2.238 (6) Å). The V–Cl bond distance (2.278 (2) Å) is slightly longer than the Ti–Cl bond distance (2.259 (6) Å) reported for $\mathrm{ClTi[N(SiMe_3)_2]_3}$,[6] while the V–N(amide) bonds are shorter (average 1.883 Å vs 1.940 Å).

Alkyl derivatives could be prepared smoothly as shown in eq 3.[31-36] The highly soluble titanium n-Bu and s-Bu

$$\mathrm{ClM[(Me_3SiNCH_2CH_2)_3N]} \xrightarrow[\text{-LiCl, pentane, -40 to +25 °C}]{\mathrm{LiR}} \mathrm{RM[(Me_3SiNCH_2CH_2)_3N]} \tag{3}$$

$$\mathrm{M = Ti,\ R} = n\text{-Bu}, s\text{-Bu};\ \mathrm{M = V,\ LiR = [Li{\cdot}TMED]CH_2SPh}$$

complexes[37] (yellow and orange, respectively) are stable at room temperature, and their pentane solutions can be

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(28) $\mathrm{ClTi[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.364 (t, $\mathrm{CH_2}$), 2.276 (t, $\mathrm{CH_2}$), 0.353 (s, $\mathrm{SiMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 63.174 ($\mathrm{CH_2}$), 50.807 ($\mathrm{CH_2}$), 1.614 ($\mathrm{SiMe_3}$); IR (pentane, KBr; cm^{-1}) 1266 (m), 1246 (m), 1073 (m), 1062 (m), 931 (s), 904 (m), 839 (s), 783 (s), 750 (m), 738 (m). Anal. Calcd for $\mathrm{C_{15}H_{39}ClN_4Si_3Ti}$: C, 40.66; H, 8.87; N, 12.64; Cl, 8.00. Found: C, 40.36; H, 8.64; N, 12.53; Cl, 8.05. $\mathrm{ClV[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.73 ($\Delta\nu_{1/2}$ = 31 Hz, $\mathrm{SiMe_3}$), −15.09 ($\Delta\nu_{1/2}$ = 130 Hz, $\mathrm{CH_2}$), −46.13 ($\Delta\nu_{1/2}$ = 310 Hz, $\mathrm{CH_2}$); IR (pentane, KBr; cm^{-1}) 1263 (m), 1246 (m), 1074 (m), 1058 (m), 934 (s), 907 (m), 839 (s), 778 (s), 751 (m), 737 (m). Anal. Calcd for $\mathrm{C_{15}H_{39}ClN_4Si_3V}$: C, 40.38; H, 8.81; N, 12.56. Found: C, 40.42; H, 8.99; N, 12.48.

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(30) Data were collected at −72 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 3670 reflections were collected to a 2θ value of 44.9°, of which 3517 were unique ($\mathrm{R_{int}}$ = 0.041); equivalent reflections were merged. The structure was solved by a combination of Patterson and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1920 observed reflections ($I > 3.00\sigma(I)$) and 217 variable parameters and converged (largest parameter shift was less than 0.009 times its esd) with R = 0.058 and $\mathrm{R_w}$ = 0.056. A final difference-Fourier map showed no chemically significant features. Crystal data are a = 15.167 (2) Å, b = 10.242 (2) Å, c = 16.301 (1) Å, β = 93.705 (8)°, V = 2527 (1) Å^3, space group $P2_1/a$, Z = 4, mol wt 446.15, and ρ(calcd) = 1.173 g/cm^3.

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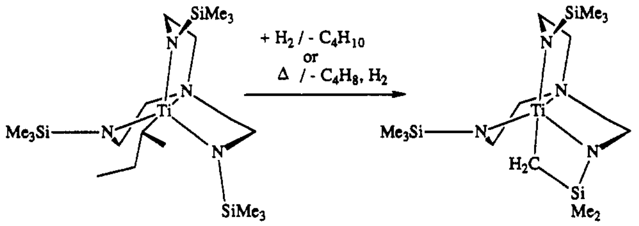
(37) n-$\mathrm{BuTi[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.345 (t, $\mathrm{NCH_2}$), 2.154 (t, $\mathrm{NCH_2}$), 2.150 (m, $\mathrm{CH_2}$), 1.475 (m, $\mathrm{CH_2}$), 1.392 (m, $\mathrm{CH_2}$), 1.033 (t, $\mathrm{CH_3}$), 0.333 (s, $\mathrm{SiMe_3}$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 72.898 ($\mathrm{TiCH_2}$), 61.991 ($\mathrm{NCH_2}$), 50.385 ($\mathrm{NCH_2}$), 35.316 ($\mathrm{CH_2}$), 29.403 ($\mathrm{CH_2}$), 13.901 ($\mathrm{CH_2}$), 1.680 ($\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{19}H_{48}N_4Si_3Ti}$: C, 49.10; H, 10.41; N, 12.05. Found: C, 48.92; H, 10.10; N, 12.40. s-$\mathrm{BuTi[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.402 (ddd, 3, $\mathrm{NCH_2}$), 3.305 (ddd, 3, $\mathrm{NCH_2}$), 2.652 (ddq, 1, $\mathrm{CH_2}$), 2.171 (t, 6, $\mathrm{NCH_2}$), 1.768 (ddq, 1, $\mathrm{CH_2}$), 1.748 (d, $\mathrm{CH_3}$), 1.063 (t, $\mathrm{CH_3}$), 0.852 (ddq, TiCH), 0.329 (s, $\mathrm{SiMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 82.877 (d, TiCH), 62.513 (t, $\mathrm{NCH_2}$), 50.515 (t, $\mathrm{NCH_2}$), 32.905 (t, $\mathrm{CH_2}$), 22.219 (q, $\mathrm{CH_3}$), 15.030 (q, $\mathrm{CH_3}$), 1.966 (q, $\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{19}H_{48}N_4Si_3Ti}$: C, 49.10; H, 10.41; N, 12.05. Found: C, 48.69; H, 10.14; N, 12.06. $\mathrm{Ti[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.723 (t, $\mathrm{NCH_2}$), 3.226 (ddd, 2, $\mathrm{NCH_2}$), 3.116 (ddd, 2, $\mathrm{NCH_2}$), 2.337 (t, $\mathrm{NCH_2}$), 2.270 (dd, 2, $\mathrm{NCH_2}$), 2.253 (dd, 2, $\mathrm{NCH_2}$), 1.313 (s, $\mathrm{TiCH_2Si}$), 0.366 (s, $\mathrm{SiMe_2}$), 0.318 (s, $\mathrm{SiMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 58.473 (t, J_{CH} = 135 Hz, $\mathrm{NCH_2}$), 56.905 (t, J_{CH} = 136 Hz, $\mathrm{NCH_2}$), 55.866 (t, J_{CH} = 124 Hz, $\mathrm{TiCH_2Si}$), 53.659 (t, J_{CH} = 134 Hz, $\mathrm{NCH_2}$), 48.836 (t, J_{CH} = 134 Hz, $\mathrm{NCH_2}$), 1.871 (q, $\mathrm{SiMe_2}$), 1.476 (q, $\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{15}H_{38}N_4Si_3Ti}$: C, 44.30; H, 9.42; N, 13.78. Found: C, 44.03; H, 9.39; N, 13.78. $\mathrm{PhSCH_2V[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.14 ($\Delta\nu_{1/2}$ = 177 Hz, $\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{22}H_{46}N_4SSi_3V}$: C, 49.49; H, 8.68; N, 10.49. Found: C, 49.70; H, 8.67; N, 10.38. $\mathrm{CH_3V[(Me_3SiNCH_2CH_2)_3N]}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.93 ($\Delta\nu_{1/2}$ = 42 Hz, $\mathrm{SiMe_3}$), −9.35 ($\Delta\nu_{1/2}$ = 175 Hz, $\mathrm{CH_2}$), −35.83 ($\Delta\nu_{1/2}$ = 955 Hz, $\mathrm{CH_2}$).

passed through a short alumina (activity 1) column before the complexes are recovered by crystallization. NMR spectra of the *n*-Bu derivative are similar to those for the chloro precursor, while the methylene protons in the $(Me_3SiNCH_2CH_2)_3N$ ligand are rendered diastereotopic in the *s*-Bu case.[37] Stable butyl derivatives of the early transition metals are rare, but known examples frequently contain electronegative, π-donating ancillary ligands in the coordination sphere.[31-36] Paramagnetic, crystalline brown $PhSCH_2V[(Me_3SiNCH_2CH_2)_3N]$[37] is formed cleanly using $[Li{\cdot}TMED]CH_2SPh$[38] (TMED = $Me_2NCH_2CH_2NMe_2$); the methyl analogue[37] was generated similarly but did not crystallize. Alkyls such as CH_2SPh may be of interest with respect to generation of a metal–carbon double bond.[39] A volatile, waxy aquamarine complex tentatively formulated as $V[(Me_3SiNCH_2CH_2)_3N]$ is obtained upon reducing $ClV[(Me_3SiNCH_2CH_2)_3N]$ with sodium amalgam in pentane; characterization of this paramagnetic species is underway.

The titanium *s*-Bu complex is cleanly converted to a metallacycle[37] either upon heating (k_{obs} = [2.0 (3)] × 10^{-4} at 66 °C) or upon treating the complex with H_2 (25 °C, 12 h, 3 atm) as in eq 4. Thermal conversion gives rise to butenes and H_2, while butane is produced in the dihydrogen reaction. A resonance at δ 8.29 observed in the proton NMR spectrum during the reaction with dihydrogen in a sealed NMR tube is tentatively assigned to a titanium(IV) monohydride intermediate. A related metallacycle is known for titanium,[40] and the proposition of a hydride intermediate in our case mirrors the loss of dihydrogen from $HM[N(SiMe_3)_2]_3$ (M = Th, U) with cyclization.[41] It would be one of the very few observable Ti(IV) hydride complexes[42,43] and therefore warrants further study.



(4)

We are continuing to investigate the chemistry of titanium and vanadium complexes containing the $(Me_3SiNCH_2CH_2)_3N$ ligand and will be attempting to prepare related complexes that contain metals in the chromium or manganese triads.

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Supplementary Material Available: Tables of final positional parameters and final thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Decamethylbimetallocenes

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Summary: Decamethylbimetallocenes have been synthesized for Fe, Co, and Rh, and the crystal structures of the 36-electron iron and rhodium complexes show a fully transoid conformation; electron-transfer studies indicate the 35-electron mixed-valence PF_6^- diiron salt is localized and suggest the neutral dicobalt and dirhodium bis-sandwich species have respectively 38 and 36 valence electrons.

The originality of transition-metal fulvalene chemistry is related to the large electronic delocalization of this bridging ligand, which results in considerable mutual influence of the two transition-metal centers.[1-7] For in-

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