ORGANOMETALLICS

σ Bond Metathesis Reactivity of Allyl Scandium Metallocenes with Diphenyldichalcogenides, PhEEPh (E = S, Se, Te)

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Supporting Information

ABSTRACT:



The σ bond metathesis reactivity of $(C_5Me_4H)_3Sc$, which has a $(\eta^5 \cdot C_5Me_4H)_2Sc(\eta^1 \cdot C_5Me_4H)$ structure in the solid state, has been investigated and compared with that of a conventional $(C_5Me_4H)^-$ metallocene complex, $(C_5Me_4H)_2Sc(\eta^3 \cdot C_3H_5)$, 1. Complex 1 reacts with PhEEPh (E = S, Se, Te) in toluene to form the σ bond metathesis products $(C_3H_5)EPh$ and $[(C_5Me_4H)_2Sc(SPh)]_2$, $(C_5Me_4H)_2Sc(SePh)$, and $(C_5Me_4H)_2Sc(TePh)$, respectively. Analogous reactions in toluene/THF generate the THF solvates $(C_5Me_4H)_2Sc(EPh)(THF)$. The monometallic sulfur derivative $(C_5Me_4H)_2Sc(Spy-\kappa^2-S,N)$ forms from the reaction of 1 with 2,2'-dipyridyl disulfide, pySSpy. $(C_5Me_4H)_3Sc$ reacts similarly, showing that the $(\eta^1 \cdot C_5Me_4H)^-$ solid-state structure yields Sc-C bond reactivity in solution.

■ INTRODUCTION

The synthesis of sterically crowded complexes containing three pentamethylcyclopentadienyl rings, $(\eta^{5}-C_{5}Me_{5})_{3}M$ (M = Ln, Y, U), demonstrated that it was possible to make a series of complexes in which all the metal ligand bonds are longer than those previously observed.¹⁻⁶ Not only are these compounds unusual synthetically and structurally, but they also display unique reactivity. The long $M-C(C_{5}Me_{5})$ bonds translate into high reactivity and demonstrate a method to activate the normally inert ($\eta^{5}-C_{5}Me_{5}$)⁻ groups extensively used as ancillary ligands. Until recently, three general types of unexpected ($C_{5}Me_{5}$)⁻ reactivity have been observed with these sterically crowded ($C_{5}Me_{5}$)⁻ meativity;^{3,6-8} (b) a one-electron reduction process called sterically induced reduction (SIR);^{3,9,10} and (c) displacement of pentahapto ($\eta^{5}-C_{5}Me_{5}$)⁻ by a ligand of lower hapticity.^{11,12} Each of these reactions typically gives a single product in high yield.

Recently, it was observed that in reactions with diphenyldichalcogenide substrates, PhEEPh (E = S, Se, Te), the (C₅-Me₅)₃M complexes could react along two pathways.¹³ These reactions formed a single type of metallocene product, $[(C_5Me_5)_2M(EPh)]_2$, but mixtures of two types of byproducts were observed depending on M and E. (C₅Me₅)₂, the byproduct of sterically induced reduction, eq 1, was predominant in some

$$2(C_5Me_5)_3M + PhTeTePh \rightarrow [(C_5Me_5)_2M(TePh)]_2 + (C_5Me_5)_2$$
(1)

cases, but (C₅Me₅)EPh, the byproduct of σ bond metathesis, eq 2, was the major byproduct in other reactions.¹³ σ Bond

$$2(C_5Me_5)_3M + 2\underset{E=S, Se}{PhEEPh} \rightarrow [(C_5Me_5)_2M(EPh)]_2 + (C_5Me_5)EPh + (C_5Me_5)_2 \quad (2)$$
major minor

metathesis could occur via a pseudoalkyl intermediate, $(\eta^5 \cdot C_5 Me_5)_2 M(\eta^1 \cdot C_5 Me_5)$, but no crystallographic evidence for such a structure had been observed even in base adduct species, $(C_5 Me_5)_3 ML^{14-16}$ and $(C_5 Me_5)_3 ML_2$.^{12,16} Although σ bond metathesis is well established with substrates that can put H or Si in the position diagonal to the metal,¹⁷⁻²² reactions with chalcogens in the diagonal position are not so common.^{13,23,24}

Recently, the first structurally characterizable example of a $(\eta^{5}-C_{5}R_{5})_{2}Ln(\eta^{1}-C_{5}R_{5})$ complex (Ln = rare earth, i.e., Sc, Y, lanthanide) was discovered with the combination of Sc³⁺ and $(C_{5}Me_{4}H)^{-}$, namely, $(\eta^{5}-C_{5}Me_{4}H)_{2}Sc(\eta^{1}-C_{5}Me_{4}H).^{25}$ This complex provided the first chance to test σ bond metathesis reactivity in a tris(polyalkylcyclopentadienyl) complex with demonstrated access to a $(\eta^{1}-C_{5}Me_{4}H)^{-}$ binding mode. However, the viability of σ bond metathesis of PhEEPh with more conventional scandium alkyl complexes had not yet been established.

This present study was initiated to remedy this deficiency and to provide information on σ bond metathesis between Sc–C and

Received: February 28, 2011 Published: May 09, 2011 PhEEPh in a conventional $(C_5Me_4H)^-$ metallocene complex. Reactions with $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1,²⁶ were studied because it is the only hydrocarbyl scandium $(C_5Me_4H)^-$ metallocene complex in the literature and also because allyl complexes of lanthanide metallocenes have proven to be conveniently synthesized, reliable sources of M–C bond reactivity.^{27–32} The reactivity of 1 with PhEEPh is reported here and compared to the reactivity of $(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)$.

EXPERIMENTAL SECTION

The manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium– potassium alloy, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use. PhEEPh (E = S, Se, Te) and 2,2'dipyridyl disulfide (pySSpy) were purchased from Aldrich and sublimed prior to use. $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1,²⁶ and $(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)^{25}$ were prepared according to literature methods. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. Infrared spectra were recorded as KBr pellets on a Varian 1000 FTIR spectrophotometer at 25 °C. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer. Mass spectrometry analyses were performed on a Thermo Trace MS+ GC-MS.

 $[(C_5Me_4H)_2Sc(\mu-SPh)]_2$, 2. In an argon-filled glovebox, PhSSPh (0.099 g, 0.45 mmol) was added to a stirred yellow solution of $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1 (0.149 g, 0.454 mmol), in toluene (10 mL). After 24 h, the solution was evaporated to dryness to yield a yellow powder. This was washed with a small amount of cold $(-35 \,^{\circ}\text{C})$ hexane in order to remove (C₃H₅)SPh³³ (identified by ¹H NMR and mass spectroscopy) and give yellow crystalline 2 (0.140 g, 78%). ¹H NMR (500 MHz, benzene-d₆): δ 7.65 (d, 2H, C₆H₅), 7.20 (m, 2H, C₆H₅), 7.03 (m, 1H, C₆H₅), 6.23 (s, 2H, C₅Me₄H), 2.08 (s, 12H, C_5Me_4H), 1.57 (s, 12H, C_5Me_4H). ¹³C NMR (126 MHz, benzene- d_6): δ 157.3 (C₆H₅), 134.1 (C₆H₅), 126.0 (C₆H₅), 125.6 (C₆H₅), 124.2 (C₅Me₄H), 121.0 (C₅Me₄H), 118.3 (C₅Me₄H), 12.5 (C₅Me₄H), 12.3 (C₅Me₄H). IR: 3071w, 3058w, 2966m, 2908m, 2860m, 2726w, 1575s, 1555m, 1475s, 1437s, 1382m, 1328w, 1297w, 1252m, 1178w, 1154w, 1072m, 1022s, 996m, 901m, 834s, 794s, 738s, 701m, 688s, 613m cm⁻ Anal. Calcd for C48H62S2Sc2: C, 72.70; H, 7.88. Found: C, 72.97; H, 7.73. Yellow crystals of 2 suitable for X-ray analysis were grown from a saturated toluene solution in the glovebox at -35 °C.

(C₅Me₄H)₂Sc(SePh), 3. As described for 2, complex 3 was obtained as a colorless crystalline solid (0.161 g, 76%), and (C₃H₅)SePh³⁴ was isolated from the reaction of PhSeSePh (0.148 g, 0.465 mmol) with 1 (0.156 g, 0.475 mmol) in toluene (10 mL). Colorless crystals of 3 suitable for X-ray analysis were grown from toluene at -35 °C. ¹H NMR (500 MHz, benzene-*d*₆): δ 7.91 (d, 2H, C₆H₅), 7.15 (m, 2H, C₆H₅), 7.07 (m, 1H, C₆H₅), 6.35 (s, 2H, C₃Me₄H), 2.08 (s, 12H, C₅Me₄H), 1.53 (s, 12H, C₅Me₄H). ¹³C NMR (126 MHz, benzene-*d*₆): δ 140.7 (C₆H₅), 137.0 (C₆H₅), 129.0 (C₆H₅), 125.5 (C₅Me₄H), 125.1 (C₆H₅), 121.3 (C₅Me₄H), 118.5 (C₃Me₄H), 12.6 (C₅Me₄H), 12.3 (C₃Me₄H). IR: 3112w, 3072w, 3060w, 3043w, 2976m, 2901m, 2860m, 2728w, 1664w, 1575s, 1470s, 1449s, 1435s, 1385s, 1372s, 1323m, 1176w, 1156m, 1114w, 1071s, 1061m, 1024s, 998m, 975w, 943w, 904w, 842vs, 824vs, 738vs, 694s, 667m, 629w, 615m cm⁻¹. Anal. Calcd for C₂₄H₃₁ScSe: C, 65.01; H, 7.05. Found: C, 64.90; H, 7.55.

 $(C_5Me_4H)_2Sc(TePh)$, 4. As described for 2, complex 4 was obtained as a yellow crystalline solid (0.101 g, 73%), and $(C_3H_5)TePh^{35}$ was isolated from the reaction of PhTeTePh (0.115 g, 0.281 mmol) and 1 (0.092 g, 0.028 mmol) in toluene (10 mL). Yellow crystals of 4 suitable for X-ray analysis were grown from toluene at -35 °C. ¹H NMR (500 MHz, benzene- d_6): δ 8.21 (m, 2H, C₆H₅), 7.09 (m, 3H, C₆H₅), 6.59 (s, 2H, C₅Me₄H), 2.04 (s, 12H, C₅Me₄H), 1.48 (s, 12H, C₅Me₄H). ¹³C NMR (126 MHz, benzene- d_6): δ 142.8 (C₆H₅), 129.3 (C₆H₅), 126.1 (C₆H₅), 125.6 (C₅Me₄H), 121.7 (C₅Me₄H), 118.3 (C₅Me₄H), 115.3 (C₆H₅), 13.1 (C₅Me₄H), 12.5 (C₅Me₄H), IR: 3105w, 3070w, 3056m, 3037w, 2974m, 2900s, 2859s, 2724m, 2660m, 1640w, 1596w, 1571s, 1469s, 1433s, 1385s, 1373s, 1323m, 1297w, 1260w, 1113w, 1061m, 1018s, 991m, 836vs, 822s, 733vs, 694s, 652w, 628w, 614m cm⁻¹. Anal. Calcd for C₂₄H₃₁ScTe: C, 58.58; H, 6.35. Found: C, 58.28; H, 6.29.

(C₅Me₄H)₂Sc(SPh)(THF), 5. In a nitrogen-filled glovebox, PhSSPh (0.072 g, 0.33 mmol) was added to a yellow solution of 1 (0.108 g, 0.33 mmol) in toluene (10 mL) and THF (0.1 mL). After the mixture was stirred for 24 h, the solution was evaporated to dryness to yield a yellowwhite, tacky residue of 5 and (C₃H₅)SPh (identified by ¹H NMR).³³ Both compounds are soluble in hexane. Colorless crystals of 5 (0.107 g, 69%) suitable for X-ray analysis were grown from hexane at -35 °C. ¹H NMR (500 MHz, benzene-d₆): δ 7.66 (d, 2H, C₆H₅), 7.23 (m, 2H, C₆H₅), 7.04 (m, 1H, C₆H₅), 5.95 (s, 2H, C₅Me₄H), 1.96 (s, 12H, C_5Me_4H), 1.91 (s, 12H, C_5Me_4H). ¹³C NMR (126 MHz, benzene- d_6): δ 151.5 (C₆H₅), 137.2 (C₆H₅), 128.9 (C₆H₅), 123.5 (C₆H₅), 122.7 (C_5Me_4H) , 119.0 (C_5Me_4H) , 115.6 (C_5Me_4H) , 13.6 (C_5Me_4H) , 12.7 (C5Me4H). IR: 3090w, 3070w, 2968m, 2906m, 2861m, 2722w, 1580m, 1567w, 1509w, 1471s, 1450m, 1434m, 1373m, 1337w, 1295w, 1240w, 1177w, 1146w, 1111w, 1087s, 1064m, 1015s, 949w, 923m, 861s, 837s, 800s, 735vs, 699s, 690s, 619m cm⁻¹. Anal. Calcd for C_{2.8}H₃₉OScS: C, 71.76; H, 8.39. Found: C, 71.35; H, 8.88.

(C₅Me₄H)₂Sc(SePh)(THF), 6. As described for 5, the reaction of PhSeSePh (0.078 g, 0.25 mmol) and 1 (0.082 g, 0.25 mmol) in toluene (10 mL) and THF (0.1 mL) yields a yellow-white, tacky residue of 6 and (C_3H_5) SePh.³⁴ Since 6 is only slightly soluble in hexane, the product was washed with a minimal amount of cold hexane (-35 °C) to remove (C₃H₅)SePh. Colorless crystals of 6 (0.081 g, 63%) suitable for X-ray analysis were grown from toluene at -35 °C. ¹H NMR (500 MHz, benzene-d₆): δ 7.89 (d, 2H, C₆H₅), 7.17 (m, 2H, C₆H₅), 7.08 (m, 1H, C₆H₅), 6.15 (s, 2H, C₅Me₄H), 3.61 (s, 8H, C₄H₈O), 2.00 (s, 12H, C₅Me₄H), 1.77 (s, 12H, C₅Me₄H), 1.26 (s, 8H, C₄H₈O). ¹³C NMR (126 MHz, benzene- d_6): δ 141.7 (C_6H_5), 137.0 (C_6H_5), 128.8 (C_6H_5), 124.6 (C₆H₅), 123.5 (C₅Me₄H), 119.9 (C₅Me₄H), 116.5 (C₅Me₄H)), 72.8 (C₄H₈O), 25.9 (C₄H₈O), 13.3 (C₅Me₄H), 12.7 (C₅Me₄H). IR: 3112w, 3062w, 2970m, 2909m, 2860m, 2729m, 1644w, 1575s, 1470s, 1435s, 1450s, 1384s, 1372s, 1325w, 1242w, 1176w, 1112w, 1070s, 1022s, 1012s, 925m, 905m, 857s, 841s, 824s, 809s, 738vs, 695s, 667m, 615m cm⁻¹. Anal. Calcd for C₂₈H₃₉OScSe: C, 65.23; H, 7.63. Found: C, 64.81; H, 7.30.

(C₅Me₄H)₂Sc(TePh)(THF), 7. As described for 5, the reaction of PhTeTePh (0.299 g, 0.730 mmol) and 1 (0.240 g, 0.731 mmol) in toluene (10 mL) and THF (0.1 mL) gave 7 as a colorless crystalline solid (0.267 g, 65%) and (C₃H₅)TePh.³⁵ Colorless crystals of 7 suitable for X-ray analysis were grown from benzene at 25 °C. ¹H NMR (500 MHz, benzene- d_6): δ 8.19 (m, 2H, C₆ H_5), 7.09 (m, 3H, C₆ H_5), 6.36 (s, 2H, C₅Me₄H), 3.58 (s, 4H, C₄H₈O), 1.97 (s, 12H, C₅Me₄H), 1.70 (s, 12H, C₅Me₄H), 1.29 (s, 4H, C₄H₈O). ¹³C NMR (126 MHz, benzene-d₆): δ 142.8 (C₆H₅), 129.0 (C₆H₅), 125.7 (C₆H₅), 123.6 (C_5Me_4H) , 120.2 (C_5Me_4H) , 116.4 (C_5Me_4H) , 116.0 (C_6H_5) , 71.4 (C₄H₈O), 25.9 (C₄H₈O), 13.4 (C₅Me₄H), 13.1 (C₅Me₄H). IR: 3103w, 3061w, 3048w, 2970s, 2941s, 2906s, 2860s, 2724w, 1571s, 1470s, 1450s, 1430s, 1381m, 1337w, 1293w, 1240w, 1173w, 1150w, 1109w, 1061w, 1016s, 924w, 858s, 831s, 817s, 734vs, 696s, 652w, 616w cm⁻¹. Anal. Calcd for C₂₈H₃₉OScTe: C, 59.61; H, 6.97. Found: C, 59.26; H, 6.87.

 $(C_5Me_4H)_2Sc(Spy-\kappa^2-S,N)$, 8. In a nitrogen-filled glovebox, 2,2'dipyridyl disulfide, pySSpy (0.097 g, 0.44 mmol), was added at -35 °C to a precooled (-35 °C), stirred yellow solution of 1 (0.144 g, 0.438 Scheme 1. Reactivity of $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1, with PhEEPh



mmol) in toluene (10 mL). The reaction mixture was allowed to warm to ambient temperature. After the mixture was stirred for 24 h, the solution was evaporated to dryness to yield a yellow-white, tacky residue of 8 and (C₃H₅)Spy.³⁶ The product was washed with cold hexane (-35 °C) to remove (C_3H_5) Spy and dried under vacuum to yield 8, as a colorless solid (0.137 g, 79%). ¹H NMR (500 MHz, benzene- d_6): δ 7.19 (m, 2H, C₅H₄N), 6.66 (m, 1H, C₅H₄N), 6.15 (m, 1H, C₅H₄N), 6.02, (s, 1H, C₅Me₄H), 1.99 (s, 6H, C₅Me₄H), 1.91 (s, 6H, C₅Me₄H), 1.86 (s, 6H, C₅Me₄H), 1.41 (s, 6H, C₅Me₄H). ¹³C NMR (126 MHz, benzened₆): δ 145.4 (C₄H₄NCS), 136.4, (C₄H₄NCS), 123.8 (C₅Me₄H), 121.5 (C₅Me₄H), 119.3 (C₅Me₄H), 117.2 (C₅Me₄H), 115.2 (C₄H₄NCS), 112.1 (C5Me4H), 14.2 (C5Me4H), 13.9 (C5Me4H), 12.7 (C5Me4H), 11.2 (C_5Me_4H). Two of the carbon atoms of the pyridyl ring, including the quaternary carbon, could not be unambiguously assigned in the ¹³C NMR spectrum. IR: 3092w, 3077w, 3060w, 3044w, 2962m, 2934m, 2903m, 2860m, 2721w, 2660w, 1731w, 1591vs, 1538s, 1479w, 1447s, 1413vs, 1380s, 1368s, 1326m, 1263m, 1183m, 1136vs, 1086m, 1022m, 1003m, 986w, 868w, 802s, 756vs, 728s, 644m, 617m cm⁻¹. Anal. Calcd for C23H30NSSc: C, 69.49; H, 7.61; N, 3.52. Found: C, 69.22; H, 7.54; N, 3.53. Colorless crystals of 8 suitable for X-ray analysis were grown from benzene at 25 °C.

[(C₅Me₄H)₂Sc(μ -SPh)]₂, **2**, from (η^{5} -C₅Me₄H)₂Sc(η^{1} -C₅Me₄H), **9**. In a nitrogen-filled glovebox, PhSSPh (0.020 g, 0.092 mmol) was added to a stirred orange solution of **9** (0.037 g, 0.091 mmol) in toluene (5 mL). After 5 d, the pale yellow solution was evaporated to dryness to yield a tacky, yellow solid, which was washed with a minimal amount (~0.5 mL) of cold hexane (-30 °C) to yield **2** as a very pale yellow powder (34 mg, 95%), as confirmed by ¹H NMR spectroscopy. The hexane washing was evaporated to dryness to yield a tacky, pale yellow solid (22 mg), which by ¹H NMR spectroscopy contained a small amount of **2** and (C₅Me₄H)SPh.³⁷ (C₅Me₄H)₂ was not observed by ¹H NMR spectroscopy or by GC-MS.

(C₅Me₄H)₂Sc(SePh), 3, from (η^{5} -C₅Me₄H)₂Sc(η^{1} -C₅Me₄H), 9. In a nitrogen-filled glovebox, PhSeSePh (0.028 g, 0.090 mmol) was added to a stirred orange solution of 9 (0.036 g, 0.088 mmol) in toluene (4 mL). After 24 h, the pale yellow solution was evaporated to dryness to yield a tacky, yellow solid, which was washed with a minimal amount (~0.5 mL) of cold hexane (-30 °C) to yield 3 as a very pale yellow powder (24 mg, 61%), as confirmed by ¹H NMR spectroscopy. The hexane washing was evaporated to dryness to yield a tacky, pale yellow solid (40 mg), which by ¹H NMR spectroscopy contained a small amount of additional 3 and (C₅Me₄H)SePh.³⁷ (C₅Me₄H)₂ was not observed by ¹H NMR spectroscopy or by GC-MS.

(C₅Me₄H)₂Sc(TePh), 4, from (η^5 -C₅Me₄H)₂Sc(η^1 -C₅Me₄H), 9. In a nitrogen-filled glovebox, PhTeTePh (0.041 g, 0.10 mmol) was added to a stirred orange solution of 9 (0.040 g, 0.098 mmol) in toluene (4 mL). After 24 h, the orange solution was evaporated to dryness to yield a tacky, orange solid, which was washed with a minimal amount (~0.5 mL) of cold hexane (-30 °C) to yield 4 as a yellow powder (27 mg, 56%), as confirmed by ¹H NMR spectroscopy. The hexane washing was evaporated to dryness to yield a tacky, orange solid (52 mg), which by ¹H NMR spectroscopy contained a small amount of additional 4 and (C_5Me_4H) TePh.³⁷ $(C_5Me_4H)_2$ was not observed by ¹H NMR spectroscopy or by GC-MS.

RESULTS

Reactivity of $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, **1**, with PhEEPh (E = S, Se, Te). $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, **1**, reacts with PhSSPh to form the dimeric arylsulfide complex $[(C_5Me_4H)_2Sc(SPh)]_2$, **2**, and with PhSeSPh and PhTeTePh to form the monomeric analogues $(C_5Me_4H)_2Sc(SePh)$, **3**, and $(C_5Me_4H)_2Sc(TePh)$, **4**, respectively, Scheme 1. In each case, (C_3H_5) EPh was isolated as a byproduct. For E = S and Se, the (C_3H_5) EPh compounds^{33,34} were characterized by NMR and mass spectroscopy. The less stable (C_3H_5) TePh³⁵ was characterized by NMR spectroscopy. Complexes **2**–**4** were isolated in crystalline form in at least 60% yield and were characterized by X-ray crystallography, Table 1. Complexes **2** and **4** are shown in Figures 1 and 2, respectively, and structural details are discussed below.

When the reaction of 1 with PhEEPh is performed in the presence of THF, the monomeric THF adducts $(C_5Me_4-H)_2Sc(EPh)(THF)$ (E = S, 5; Se, 6; Te, 7) are isolated, eq 3, and $(C_3H_5)EPh$ is again observed as a byproduct. Each solvated scandium complex was isolated in over 60% yield and characterized by X-ray crystallography, Table 2. Complex 5 is shown in Figure 3 as a representative example of 5-7.



Consistent with the formation of the THF adducts **5**–7, a pyridyl analogue, $(C_5Me_4H)_2Sc(Spy-\kappa^2-S,N)$, **8**, was obtained from the reaction of $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$ with 2,2'-dipyridyl disulfide, pySSpy, eq 4. A 79% yield was observed, and the expected σ bond metathesis byproduct, $(C_3H_5)Spy,^{36}$ was isolated. The X-ray crystal structure of **8** is shown in Figure 4.



Structural Analysis. $[(C_5Me_4H)_2Sc(EPh)]_x$, 2–4. $[(C_5Me_4-H)_2Sc(SPh)]_2$, 2 (Figure 1), crystallizes as a dimer in which each metal is formally eight coordinate. This dimeric structure is common for rare earth metallocene complexes, and the structure

	2	3	4
empirical formula	$C_{48}H_{62}S_2Sc_2 \cdot C_7H_8$	$C_{24}H_{31}ScSe \cdot C_7H_8$	$C_{24}H_{31}ScTe \cdot C_7H_8$
fw	885.15	535.54	584.18
temperature (K)	143(2)	148(2)	143(2)
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_{1}/n$	Pnma	Pnma
a (Å)	9.1827(5)	11.2833(5)	11.5128(11)
b (Å)	15.5610(8)	11.7599(6)	11.8430(11)
c (Å)	16.4433(9)	19.9881(10)	20.2121(19)
α (deg)	90	90	90
β (deg)	98.9859(6)	90	90
γ (deg)	90	90	90
volume (Å ³)	2320.8(2)	2652.2(2)	2755.8(4)
Ζ	2	4	4
$ ho_{calcd} (Mg/m^3)$	1.267	1.341	1.408
$\mu \ (\mathrm{mm}^{-1})$	0.419	1.667	1.321
R1 $[I > 2.0\sigma(I)]^a$	0.0346	0.0469	0.0406
wR2 (all data) ^a	0.0963	0.1570	0.1340
^{<i>i</i>} Definitions: wR2 = $[\Sigma[w(F_o^2)]$	$(-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]]^{1/2}$, R1 = $\Sigma F_{o} - $	$F_c \parallel \Sigma F_o \parallel$.	





Figure 1. $ORTEP^{44}$ of $[(C_5Me_4H)_2Sc(SPh)]_2$, 2, drawn at the 50% probability level. Hydrogen atoms and toluene solvent molecule are omitted for clarity.



Figure 2. ORTEP of $(C_5Me_4H)_2Sc(TePh)$, 4, drawn at the 50% probability level. Hydrogen atoms and toluene solvent molecule are omitted for clarity. $(C_5Me_4H)_2Sc(SePh)$, 3, is isomorphous (see Supporting Information).

of **2** is similar to that of $[(C_5Me_5)_2Y(SPh)]_2^{38}$ and $[(C_5-Me_5)_2Sm(SPh)]_2^{39}$ when the differences in ionic radii⁴⁰ are taken into account, Table 3. A similar structure with the much smaller scandium is probably possible since **2** contains $(C_5Me_4H)^-$ and not

Table 2. X-ray Data Collection Parameters for $(C_5Me_4H)_2Sc(SPh)(THF)$, 5, $(C_5Me_4H)_2Sc(SePh)(THF)$, 6, $(C_5Me_4H)_2Sc(TePh)(THF)$, 7, and $(C_5Me_4H)_2Sc(Spy-\kappa^2-S, N)$, 8

		5	0	'	0	
	empirical formula	C28H39OSSc	C ₂₈ H ₃₉ OScSe	C ₂₈ H ₃₉ OScTe	C23H30NSSc	
	fw	468.61	515.51	564.15	397.50	
	temperature (K)	148(2)	148(2)	93(2)	93(2)	
	cryst syst	triclinic	triclinic	triclinic	monoclinic	
	space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	
	a (Å)	8.9008(4)	8.8672(5)	9.3570(3)	16.3661(5)	
	b (Å)	9.4443(5)	9.7827(6)	16.8480(6)	8.4809(3)	
	c (Å)	15.9737(8)	15.3323(9)	18.5223(6)	15.8932(5)	
	α (deg)	81.1952(5)	94.6992(7)	67.1803(4)	90	
	β (deg)	75.3670(5)	102.8106(7)	79.3325(4)	108.00	
	γ (deg)	71.1870(5)	97.2083(7)	76.4365(4)	90	
	volume (Å ³)	1226.05(10)	1278.34(13)	2601.89(15)	2097.98(12)	
	Ζ	2	2	4	4	
	$ ho_{ m calcd}~({ m Mg/m}^3)$	1.269	1.339	1.440	1.258	
	$\mu (\text{mm}^{-1})$	0.403	1.729	1.399	0.457	
	R1 $[I > 2.0\sigma(I)]^{a}$	0.0302	0.0248	0.0217	0.0304	
	wR2 (all data) ^a	0.0817	0.0681	0.0549	0.0841	
^{<i>a</i>} Definitions: wR2 = $\left[\sum \left[w (F_0^2 - F_c^2)^2 \right] / \sum \left[w (F_0^2)^2 \right] \right]^{1/2}$, R1 = $\sum F_0 - \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} \right] = \sum F_0 ^2 + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} + \frac{1}{2} \sum \left[\frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} \sum \left[\frac{1}{2} + $						
]]	$ F_c /\Sigma F_o .$					
_						

 $(C_5Me_5)^-$ ligands. The hydrogen-substituted ring carbons in each metallocene in 2 are almost perfectly staggered: the two HC-(ring centroid)–Sc planes have a dihedral angle of 1.5° . The plane defined by the six carbon atoms in the aryl ring of 2 is twisted 38.0° from the plane defined by the two scandium and two sulfur atoms, larger than that observed in $[(C_5Me_5)_2Y(SPh)]_2$,³⁸ 20.1°, and $[(C_5Me_5)_2Sm(SPh)]_2$,³⁹ 21.5°. This suggests there is more crowding in 2.

The isolation of $(C_5Me_4H)_2Sc(SePh)$, 3, and $(C_5Me_4H)_2$ -Sc(TePh), 4, as monomers in contrast to dimer 2 can be rationalized by the difference in size of the chalcogens. Two Se or Te donor atoms may be too large for the small scandium even in the tetramethylcyclopentadienyl $[(C_5Me_4H)_2Sc]^+$ unit. On the other hand, in the series (pyridine)_4Yb(SPh)_2,



Figure 3. ORTEP of $(C_5Me_4H)_2Sc(SPh)(THF)$, **5**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. $(C_5Me_4H)_2-Sc(SePh)(THF)$, **6**, is isomorphous and $(C_5Me_4H)_2Sc(TePh)(THF)$, **7**, is similar but has two independent molecules in the unit cell (see Supporting Information).



Figure 4. ORTEP of $(C_5Me_4H)_2Sc(Spy-\kappa^2-S_5N)$, **8**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

(pyridine)₄Yb(SePh)₂ and (pyridine)₅Yb(TePh)₂, the higher coordination number for the tellurium complex is attributed to longer Ln–E bonds that place the phenyl groups further from the lanthanide.⁴¹ This secondary coordination sphere argument could also explain the structures of **2**–4. In addition, (SePh)⁻ and (TePh)⁻ are not as effective at binding as (SPh)⁻ and would be expected to form less favorable bridging interactions. The structures of $(C_5Me_4H)_2Sc(EPh)(THF)$, **5**–7, described below demonstrate that a (SePh)⁻ or (TePh)⁻ unit alone does not fully saturate the coordination sphere of scandium in $[(C_5Me_4H)_2Sc]^+$. The closest related structure is the pentamethylcyclopentadienyl complex $(C_5Me_5)_2Sc(TeCH_2C_6H_5)$, which also crystallizes as a monomer.⁴² Due to disordered toluene solvent in isomorphous complexes **3** and **4**, a detailed metrical analysis is not presented.

 $(C_5Me_4H)_2Sc(EPh)(THF)$, 5–7. Complexes 5–7 are closely related to the previously published $(C_5Me_5)_2Sm(EPh)(THF)$ series.³⁹ For example, bond distances and angles involving the metal remain the same within error limits when the differences in ionic radii⁴⁰ are considered, and the M–E bond distances increase in a periodic order from S to Se to Te, Table 4. Once again, the smaller $(C_5Me_4H)^-$ ligand with the small scandium gives structures similar to $(C_5Me_5)^-$ complexes of the lanthanides.

 $(C_5Me_4H)_2Sc(Spy-\kappa^2-S,N)$, 8. The structures of complexes 2, 5, and 8 present an interesting opportunity to compare metallocene bonding with an X-type ligand, SPh in this case, in (a) a

Table 3. Selected Bond Distances (Å) and Angles (deg) for
$[(C_5Me_4H)_2Sc(\mu-SPh)]_2$, 2, $[(C_5Me_5)_2Y(\mu-SPh)]_2$, and
$[(C_5Me_5)_2Sm(\mu$ -SPh)] ₂ , Along with Their Eight-Coordinate
M ³⁺ Ionic Shannon Radii ⁴⁰

	Sc, 2	Y ³⁸	Sm ³⁹		
M ³⁺ ionic radius	0.870	1.019	1.079		
M(1) - S(1)	2.7114(4)	2.8931(6)	2.9341(6)		
M(1) - S(1)'	2.7335(4)	2.9031(6)	2.9388(6)		
$M(1)-Cnt^{a}$	2.202, 2.220	2.370, 2.402	2.429, 2.464		
S(1)-M(1)-S(1)'	66.778(14)	61.59(2)	61.99(2)		
M(1)-S(1)-M(1)'	113.22(1)	118.41(2)	118.01(2)		
Cnt1-M(1)-Cnt2	130.1	128.5	128.6		
^{<i>a</i>} Cnt = centroid of the cyclopentadienyl ring.					

solvate-free bridged dimer, (b) a terminal Lewis base adduct, and (c) a complex with a chelating Lewis base. In each case the metal is eight coordinate, but Table 5 shows that these variations have a significant effect on Sc-S bond distances. The (ring centroid)-Sc-(ring centroid) angles (2, 130.1°; 5, 133.5°; 8, 134.6°) suggest that 2 is the most crowded and 5 and 8 are similar. This is consistent with the fact that 2 has the longest Sc-S distances. However, this is not shown by the Sc-(ring centroid) distances, which overlap for 2 and 5. Although the chelating Lewis base adduct 8 has the smallest Sc-(ring centroid) distances, the THF adduct **5** has the shortest Sc–S bond. However, the Sc-C distance in 8 could also be effected by a contribution from a thioketone amido resonance form.⁴³ These data suggest that distances and angles are a result of a complicated interplay of steric and electronic effects even in this similar series of complexes. Crystal packing effects may also be important, but are even more difficult to evaluate.

Reactivity of $(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)$, 9, with PhEEPh (E = S, Se, Te). $(\eta^5-C_5Me_4H)_2Sc(\eta^1-C_5Me_4H)$, 9, reacts with PhEEPh reagents in a manner similar to the $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$ reactions described above. Reactions in toluene generate the same scandium metallocenes obtained from 1, namely, $[(C_5Me_4H)_2Sc(EPh)]_x$ (E = S, 2; Se, 3; Te, 4), and in this case $(C_5Me_4H)EPh$ is observed as the byproduct, eq 5. No evidence for $(C_5Me_4H)_2$, the expected byproduct of sterically induced reduction, was observed. In the reaction of 9 with PhSSPh, a longer reaction time is required (5 d) for the reaction to go to completion when compared to 1 (24 h).



DISCUSSION

The diphenyldichalcogenides, PhEEPh, readily participate in reactions with $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, which can be explained as σ bond metatheses. Scheme 2 shows a four-center intermediate that could be present for these reactions based on previous studies of σ bond metathesis.^{18,20–22} In each of the reactions with the allyl complex $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1, both in toluene and in toluene/THF, the allyl phenyl chalcogenide byproduct, $(C_3H_5)EPh$, expected from σ bond metathesis was isolated. In each of these reactions, allyl complex 1 is acting as an η^1 -alkyl

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_4H)_2Sc(SPh)(THF)$, 5, $(C_5Me_4H)_2Sc(SePh)(THF)$, 6, $(C_5Me_4H)_2Sc(TePh)(THF)$, 7, $(C_5Me_5)_2Sm(SPh)(THF)$, 10, $(C_5Me_5)_2Sm(SePh)(THF)$, 11, and $(C_5Me_5)_2Sm(TePh)(THF)$, 12

	E, complex					
	S, 5	Se, 6	Te, 7 ^{<i>a</i>}	S, 10 ³⁹	Se, 11 ³⁹	Te, 12 ³⁹
M(1)-O(1)	2.2425(9)	2.240(1)	2.241(1)	2.445(3)	2.443(3)	2.449(2)
M(1)-E(1)	2.5222(4)	2.6836(3)	2.9393(3)	2.761(1)	2.8837(6)	3.1279(3)
$M(1)-Cnt^b$	2.244, 2.217	2.234, 2.217	2.230, 2.213	2.442, 2.452	2.448, 2.445	2.448, 2.445
$E(1) - C(19)^{c}$	1.769(1)	1.916(1)	2.129(2)			
$E(1) - C(21)^{c}$				1.759(5)	1.913(4)	2.127(2)
Cnt1-M(1)-Cnt2	133.5	134.1	134.2	133.7	134.1	135.2
C(19)-E(1)-M(1)	119.93(4)	117.72(4)	112.54(4)			
C(21)-E(1)-M(1)				120.8(2)	118.5(1)	112.49(6)
O(1) - M(1) - E(1)	92.16(3)	93.44(3)	94.46(3)	89.72(9)	89.35(8)	92.51(4)

^{*a*} There are two independent molecules of 7 in the unit cell. The distances and angles of the second independent molecule of 7 are omitted for clarity. ^{*b*} Cnt = centroid of the cyclopentadienyl ring. ^{*c*} Ipso carbon atom of the phenyl ring.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_4H)_2Sc(SPh)]_2$, 2, $(C_5Me_4H)_2Sc(SPh)(THF)$, 5, and $(C_5Me_4H)_2Sc(Spy-\kappa^2-S,N)$, 8

	2	5	8
$Sc(1)-Cnt^{a}$	2.220, 2.202	2.244, 2.217	2.179, 2.181
Sc(1) - S(1)	2.7114(4)	2.5222(4)	2.6158(4)
Sc(1)-S(1)'	2.7335(4)		
Sc(1) - N(1)			2.249(1)
$Sc(1) - C(19)^{b}$			2.828(1)
Cnt1-Sc(1)-Cnt2	130.1	133.5	134.6
Cnt-Sc(1)-S(1)	111.9, 109.9	100.7, 110.7	109.3, 110.2
Cnt-Sc(1)-S(1)'	112.6, 108.0		
Cnt-Sc(1)-O(1)		104.8, 107.2	
Cnt-Sc(1)-N(1)			108.3, 107.9
^{<i>a</i>} Cnt = centroid of the	cyclopentadieny	d ring. ^b Ipso carl	oon atom of the
phenyl ring.			

Scheme 2. Proposed Four-Center Intermediate for the Reactions of $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1, with PhEEPh



ligand. Hence, the diphenyldichalcogenide reaction is another example of accessing Sc-C bond reactivity via allyl ligands in rare earth complexes.^{27–32}

Examination of the reactions of PhEEPh with $(\eta^{5}-C_{5}Me_{4}H)_{2}Sc(\eta^{1}-C_{5}Me_{4}H)$, 9, gave the same organometallic products, $[(C_{5}Me_{4}H)_{2}Sc(EPh)]_{x}$, as observed with 1 along with the σ bond metathesis byproduct, $(C_{5}Me_{4}H)EPh$. Hence, 9 reacts like an η^{1} -alkyl complex, and the η^{1} -structure delivers pseudoalkyl reactivity. This is quite reasonable, but it had not previously been demonstrated with a tris(poly-alkylcyclopentadienyl) complex that had an η^{1} -cyclopentadienyl structure characterized by X-ray crystallography.

CONCLUSION

The allyl complex $(C_5Me_4H)_2Sc(\eta^3-C_3H_5)$, 1, demonstrates Sc-C bond reactivity in σ bond metathesis reactions with PhEEPh (E = S, Se, Te) reagents. Reactions occur in good yield in both toluene and toluene/THF to form (C3H5)EPh and the $[(C_5Me_4H)_2Sc(EPh)]_x$ and $(C_5Me_4H)_2Sc(EPh)(THF)$ complexes, respectively. The bis(tetramethylcyclopentadienyl) scandium reaction products show structural similarity to pentamethylcyclopentadienyl yttrium and lanthanide metallocenes and demonstrate a correlation in structure between Sc^{3+} with $(C_5Me_4H)^$ ligands and the larger rare earths with $(C_5Me_5)^-$ ligands. The chelated Lewis base complex $(C_5Me_4H)_2Sc(Spy-\kappa^2-S_N)$ forms similarly from pySSpy and allows structural comparisons with $[(C_5Me_4H)_2Sc(SPh)]_2$ and $(C_5Me_4H)_2Sc(SPh)(THF)$ that show the flexibility of metallocene coordination environments with varying Lewis bases. The tris(polyalkylcyclopentadienyl) complex, $(\eta^{5}-C_{5}Me_{4}H)_{2}Sc(\eta^{1}-C_{5}Me_{4}H)$, also reacts with PhEEPh reagents by σ bond metathesis, indicating that the η^1 -structure found in the solid state translates into clean σ bond metathesis reactivity.

ASSOCIATED CONTENT

Supporting Information. X-ray data collection, structure solution, and refinement (PDF) and X-ray diffraction details of compounds 2–8 (CIF, CCDC Nos. 814911–814917). This material is available free of charge via the Internet at http://pubs.acs.org.

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