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# Sigma bond metathesis with pentamethylcyclopentadienyl ligands in sterically crowded (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M complexes<sup>†</sup>

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To further explore the reactivity of the  $(C_3Me_5)^-$  ligand in the sterically crowded  $(C_5Me_5)_3M$  complexes, reactions with PhEEPh (E = S, Se, Te) have been examined. With M = La, Pr, Nd, Sm, and Y, PhSSPh reacts to form the expected reduction products,  $[(C_5Me_5)_2M(SPh)]_2$ , but the major organic byproduct is not the sterically induced reduction product,  $(C_5Me_5)_2$ . Instead, the sigma bond metathesis product,  $C_5Me_5SPh$ , is the major byproduct. In contrast, reactions with  $(C_5Me_5)_3Ce$  and  $(C_5Me_5)_3U$  gave a mixture of  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  as byproducts. PhSSPh reactions with the lanthanide nitrile adducts,  $(C_5Me_5)_3Ln(NCCMe_3)_2$  (Ln = La, Ce) and  $(C_5Me_5)_3Nd(NCCMe_3)$ , formed  $[(C_5Me_5)_2Ln(SPh)(NCCMe_3)]_2$  and only  $C_5Me_5SPh$  as the byproduct. PhSeSPh reactions paralleled the PhSSPh results, but reactions of PhTeTePh with  $(C_5Me_5)_3La, (C_5Me_5)_3Sm$ , and  $(C_5Me_5)_3La(NCCMe_3)_2$  gave only  $(C_5Me_5)_2$  as a byproduct.

#### Introduction

Since the isolation of the sterically crowded  $(\eta^5-C_5Me_5)_3Sm$  complex in 1991, three general modes of unexpected  $(C_5Me_5)_3Sm$  complexes depending on the substrate. The  $(C_5Me_5)_3M$  complexes depending on the substrate. The  $(C_5Me_5)_3M$  complex can act as a one electron reductant where one of the  $(C_5Me_5)^-$  ligands delivers an electron and forms half an equivalent of pentamethylcyclopentadienyl dimer,  $(C_5Me_5)_2$ ,<sup>1-3</sup> eqn (1).

$$(C_5Me_5)^- \rightarrow \frac{1}{2}(C_5Me_5)_2 + 1e^-$$
 (1)

This process, which is exemplified in eqn (2), has been called sterically induced reduction (SIR). A second type of reaction involves  $\eta^1$ -like (C<sub>5</sub>Me<sub>5</sub>)<sup>-</sup> reactivity.



These reactions include insertion of CO, CO<sub>2</sub>, and CS<sub>2</sub> into the M– $C(C_5Me_5)$  bond,<sup>1,4,5</sup> olefin polymerization,<sup>6</sup> ring-opening of THF,<sup>1</sup> and hydrogenolysis,<sup>1,7</sup> *e.g.* eqn (3).



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† Electronic supplementary information (ESI) available: experimental details. CCDC reference numbers 765768–765771. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c002654a A third type of reaction involving displacement of a pentahapto  $(\eta^5-C_5Me_5)^-$  ligand by a ligand of lower hapticity, *e.g.*  $[N(SiMe_3)_2]^-$ ,<sup>5,8</sup> is shown in eqn (4).



One additional general reaction has been found for  $(C_5Me_5)_3M$  complexes, namely the formation of base adducts  $(C_5Me_5)_3ML^{9-11}$  and  $(C_5Me_5)_3ML_2^{5,11}$  eqn (5).



Most of these reactions give single products in high yield. However, the reactions of  $(C_5Me_5)_3Sm$  with alkyl and aryl halides were found to be more complicated,<sup>1</sup> *e.g.* eqn (6). Byproducts of nucleophilic displacement and radical reactions were observed as well as  $(C_5Me_5)_2$ , the byproduct that is characteristic of SIR according to eqn (1).



We now report a reaction system for  $(C_5Me_5)_3M$  complexes in which more than one reaction pathway appears to be accessible,

namely the reactions with PhEEPh substrates (E = S, Se, Te). The PhEEPh series is frequently examined in reductive felement chemistry<sup>12-15</sup> since the (EPh)<sup>-</sup> products usually can be fully characterized by X-ray crystallography and the reduction potentials have a broad range: -1.75 V,<sup>16</sup> -1.2 V,<sup>16</sup> and  $-1.06 \text{ V}^{17}$ *vs.* SCE for E = S, Se, and Te, respectively. Examination of the reductive capacity of the (C<sub>5</sub>Me<sub>5</sub>)<sup>-</sup> ancillary ligand in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M complexes and the nitrile adducts (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M(NCCMe<sub>3</sub>)<sub>x</sub> with PhEEPh reveals a surprising variation in reactivity as a function of M, x, and E.

#### Experimental

The syntheses and manipulations described below were conducted under nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents were dried over sodium-potassium alloy, degassed, and vacuum transferred prior to use. PhSSPh, PhSeSePh, and PhTeTePh were purchased from Aldrich and sublimed prior to use. The  $(C_5Me_5)_3M$  complexes  $(M = La^{18} Ce^1 Pr^1 Nd^{19})_3M$ Sm,<sup>20</sup> Y,<sup>21</sup> and U<sup>6</sup>),  $(C_5Me_5)_3M(NCCMe_3)_2$  (M = La,<sup>5</sup> Ce<sup>11</sup>), and  $(C_5Me_5)_3M(NCCMe_3)$  (M = Nd,<sup>11</sup> U<sup>11</sup>) were prepared as previously described. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer at 25 °C. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR system. Elemental analyses were performed on a Perkin Elmer 2400 Series II CHNS analyzer. Mass spectrometry analysis was performed on a Thermo Trace MS+ GCMS.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(SPh)]<sub>2</sub>, 1a

PhSSPh (10 mg, 0.046 mmol) was added to a stirred solution of  $(C_5Me_5)_3La$  (25 mg, 0.046 mmol) in 5 mL of toluene. After stirring for 12 h, the solvent was removed under reduced pressure to yield a tacky yellow solid which was washed with hexane to yield the previously characterized  $[(C_5Me_5)_2La(SPh)]_2^{13e}$  in quantitative yield. The hexane wash was dried under reduced pressure to yield the previously characterized byproducts  $C_5Me_5SPh^{22}$  and  $(C_5Me_5)_2^{23}$  which were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (17:1 ratio).

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(SePh)]<sub>2</sub>, 1b

Following the procedure for **1a**, PhSeSePh (57 mg, 0.18 mmol) was reacted with  $(C_5Me_5)_3La$  (98 mg, 0.18 mmol) in 10 mL of toluene.  $[(C_5Me_5)_2La(SePh)]_2$  was isolated as a pale yellow solid (78 mg, 77% crystalline yield). Pale yellow X-ray quality crystals were grown from a concentrated toluene solution at -35 °C and the structure was determined (see below). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.53 (m, 2 H, Se*Ph*), 7.09 (m, 2 H, Se*Ph*), 7.01 (m, 1 H, Se*Ph*), 2.21 (s, 30 H,  $C_5Me_5$ ). <sup>13</sup>C NMR ( $C_6D_6$ ):  $\delta$  134.9 (Se*Ph*), 129.5 (Se*Ph*), 125.3 (Se*Ph*), 123.1 ( $C_5Me_5$ ), 12.6 ( $C_5Me_5$ ). IR: 3053w, 2960 m, 2905 s, 2856 s, 2726w, 2214w, 1575 s, 1529w, 1471 s, 1434 s, 1380 m, 1068 m, 1020 m, 999w, 803w, 733 s, 691 s, 667 m, 611w, 570w cm<sup>-1</sup>. Anal. Calcd for  $C_{52}H_{70}La_2Se_2$ : C, 55.23; H, 6.24. Found: C, 55.34; H, 6.24. The byproducts  $C_5Me_5SePh^{24}$  and ( $C_5Me_5$ )<sub>2</sub> were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (22 : 1 ratio).

Following the procedure for **1a**, PhTeTePh (51 mg, 0.12 mmol) was reacted with  $(C_5Me_5)_3La$  (67 mg, 0.12 mmol) in 5 mL of toluene.  $[(C_5Me_5)_2La(TePh)]_2$  was isolated as a yellow solid (44 mg, 76% crystalline yield). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  7.88 (m, 2 H, Te*Ph*), 7.01 (m, 3 H, Te*Ph*), 2.25 (s, 30 H,  $C_5Me_5$ ). Anal. Calcd for  $C_{52}H_{70}La_2Te_2$ : C, 50.85; H, 5.75. Found: C, 50.99; H, 5.74.  $(C_5Me_5)_2$  was isolated as the only byproduct along with unreacted PhTeTePh.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(SPh)(NCCMe<sub>3</sub>)]<sub>2</sub>, 2a

Following the procedure for **1a**, PhSSPh (29 mg, 0.13 mmol) was reacted with  $(C_5Me_5)_3La(NCCMe_3)_2$  (95 mg, 0.13 mmol) in 10 mL of toluene.  $[(C_5Me_5)_2La(SPh)(NCCMe_3)]_2$  was isolated as a colorless solid (52 mg, 65% crystalline yield). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.52 (m, 2 H, *SPh*), 7.05 (m, 3 H, *SPh*), 2.11 (s, 30 H,  $C_5Me_5$ ), 0.82 (s, 9H,  $Me_3CCN$ ). Anal. Calcd for  $C_{62}H_{88}La_2N_2S_2$ : C, 61.88; H, 7.37; N, 2.33. Found: C, 61.83; H, 7.83; N, 2.29.  $C_5Me_5SPh$  was isolated as the only observed byproduct.

 $[(C_5Me_5)_2La(SPh)(NCCMe_3)]_2$  was also produced in quantitative yield from the reaction of  $[(C_5Me_5)_2La(SPh)]_2$ , **1b**, (13 mg, 0.013 mmol) with Me<sub>3</sub>CCN (3  $\mu$ L, 0.027 mmol) in C<sub>6</sub>D<sub>6</sub>.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(SePh)(NCCMe<sub>3</sub>)]<sub>2</sub>, 2b

Following the procedure for **1a**, PhSeSePh (33 mg, 0.11 mmol) was reacted with  $(C_5Me_5)_3La(NCCMe_3)_2$  (75 mg, 0.11 mmol) in 10 mL of toluene.  $[(C_5Me_5)_2La(SePh)(NCCMe_3)]_2$  was isolated as a pale yellow solid (39 mg, 57% crystalline yield). Pale yellow X-ray quality crystals were grown from a concentrated toluene solution at -35 °C and identified by X-ray diffraction. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.81 (m, 2 H, SePh), 6.99 (m, 3 H, SePh), 2.16 (s, 30 H,  $C_5Me_5$ ), 0.80 (s, 9H,  $Me_3$ CCN). Anal. Calcd for  $C_{62}H_{88}La_2N_2Se_2$ : C, 57.41; H, 6.84; N, 2.16. Found: C, 57.20; H, 6.52; N, 2.02.  $C_5Me_5$ SePh was isolated as the only byproduct.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(TePh)(NCCMe<sub>3</sub>)]<sub>2</sub>, 2c

Following the procedure for **1a**, PhTeTePh (44 mg, 0.11 mmol) was reacted with  $(C_5Me_5)_3La(NCCMe_3)_2$  (76 mg, 0.11 mmol) in 10 mL of toluene.  $[(C_5Me_5)_2La(TePh)(NCCMe_3)]_2$  was isolated as a pale yellow solid (27 mg, 19% crystalline yield). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  8.15 (m, 2 H, TePh), 7.00 (m, 3 H, TePh), 2.24 (s, 30 H,  $C_5Me_5$ ), 0.74 (s, 9H,  $Me_3CCN$ ).  $(C_5Me_5)_2$  was isolated as the only byproduct along with unreacted PhTeTePh.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ce(SPh)]<sub>2</sub>, 3

Following the procedure for **1a**, PhSSPh (24 mg, 0.11 mmol) was reacted with  $(C_5Me_5)_3Ce$  (52 mg, 0.095 mmol) in 8 mL of toluene.  $[(C_5Me_5)_2Ce(SPh)]_2$  was isolated as a dark purple solid (35 mg, 65% crystalline yield). Purple X-ray quality crystals were grown from a concentrated toluene solution at -35 °C and structurally characterized. <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  5.26 (s, 30 H,  $C_5Me_5$ ). The phenyl resonances were not observed. Anal. Calcd for  $C_{52}H_{70}Ce_2S_2$ : C, 60.08; H, 6.79. Found: C, 59.72; H, 6.83. The byproducts  $C_5Me_5$ SPh and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (2:1 ratio) along with unreacted PhSSPh.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ce(SPh)(NCCMe<sub>3</sub>)]<sub>2</sub>, 4

Following the procedure for **1a**, PhSSPh (36 mg, 0.16 mmol) was reacted with  $(C_5Me_5)_3Ce(NCCMe_3)_2$  (116 mg, 0.16 mmol) in 10 mL of toluene.  $[(C_5Me_5)_2Ce(SPh)(NCCMe_3)]_2$  was isolated as a bright orange solid (59 mg, 60% crystalline yield). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  4.56 (s, 30 H,  $C_5Me_5$ ), (1.50 s, 2 H, SPh), -0.04 (s, 3 H, SPh), -4.50 (s, 9H, Me\_3CCN). Anal. Calcd for  $C_{62}H_{88}Ce_2N_2S_2$ : C, 61.76; H, 7.36; N, 2.32. Found: C, 61.74; H, 7.74; N, 2.31.  $C_5Me_5$ SPh was isolated as the only observed byproduct.

#### $[(C_5Me_5)_2Pr(SPh)]_2, 5$

Following the procedure for **1a**, PhSSPh (14 mg, 0.064 mmol) was reacted with  $(C_5Me_5)_3Pr$  (33 mg, 0.060 mmol) in 5 mL of toluene.  $[(C_5Me_5)_2Pr(SPh)]_2$  was isolated as a bright yellow solid (55 mg, 79% crystalline yield). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  11.49 (s, 30 H,  $C_5Me_5$ ). The phenyl resonances were not observed. Anal. Calcd for  $C_{52}H_{70}Pr_2S_2$ : C, 59.99; H, 6.78. Found: C, 60.11; H, 7.41. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (13:1 ratio).

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Nd(SPh)]<sub>2</sub>, 6

Following the procedure for **1a**, PhSSPh (20 mg, 0.096 mmol) was reacted with  $(C_5Me_5)_3Nd$  (51 mg, 0.092 mmol) in 5 mL of toluene.  $[(C_5Me_5)_2Nd(SPh)]_2$  was isolated as a pale green solid (45 mg, 87% crystalline yield). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  11.70 (s, 30 H,  $C_5Me_5$ ). The phenyl resonances were not observed. Anal. Calcd for  $C_{52}H_{70}Nd_2S_2$ : C, 59.61; H, 6.73. Found: C, 59.07; H, 6.57. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (32:1 ratio).

#### $[(C_5Me_5)_2Nd(SPh)(NCCMe_3)]_2, 7$

Following the procedure for **1a**, PhSSPh (16 mg, 0.073 mmol) was reacted with  $(C_5Me_5)_3Nd(NCCMe_3)$  (46 mg, 0.073 mmol) in 5 mL of toluene.  $[(C_5Me_5)_2Nd(SPh)(NCCMe_3)]_2$  was isolated as a blue green solid (31 mg, 70% crystalline yield). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  9.36 (s, 30 H,  $C_5Me_5$ ), -8.80 (s, 9H,  $Me_3CCN$ ). The phenyl resonances were not observed. Anal. Calcd for  $C_{62}H_{88}Nd_2N_2S_2$ : C, 61.34; H, 7.31; N, 2.31. Found: C, 61.01; H, 7.23; N, 2.23.  $C_5Me_5SPh$  was isolated as the only byproduct.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(SPh)]<sub>2</sub>, 8a

Following the procedure for **1a**, PhSSPh (17 mg, 0.078 mmol) was reacted with  $(C_5Me_5)_3Sm$  (42 mg, 0.076 mmol) in 5 mL of toluene. Quantitative conversion to the previously characterized  $[(C_5Me_5)_2Sm(SPh)]_2^{15a}$  was observed by <sup>1</sup>H NMR spectroscopy. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (15:1 ratio).

#### $[(C_5Me_5)_2Sm(SePh)]_2, 8b$

Following the procedure for **1a**, PhSeSePh (14 mg, 0.045 mmol) was reacted with  $(C_5Me_5)_3Sm$  (25 mg, 0.045 mmol) in 5 mL of toluene. Quantitative conversion to the previously characterized  $[(C_5Me_5)_2Sm(SePh)]_2^{15a}$  was observed by <sup>1</sup>H NMR spectroscopy.  $C_5Me_5SePh$  was isolated as the only byproduct.

Following the procedure for **1a**, PhTeTePh (10 mg, 0.024 mmol) was reacted with  $(C_5Me_5)_3Sm$  (13 mg, 0.023 mmol) in 2 mL of toluene. Quantitative conversion to the previously characterized  $[(C_5Me_5)_2Sm(TePh)]_2^{15a}$  was observed by <sup>1</sup>H NMR spectroscopy.  $(C_5Me_5)_2$  was isolated as the only byproduct along with unreacted PhTeTePh.

#### [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(SPh)]<sub>2</sub>, 9

Following the procedure for **1a**, PhSSPh (12 mg, 0.055 mmol) was reacted with  $(C_5Me_5)_3Y$  (27 mg, 0.054 mmol) in 5 mL of methylcyclohexane. Quantitative conversion to the previously characterized  $[(C_5Me_5)_2Y(SPh)]_2^{13e}$  was observed by <sup>1</sup>H NMR spectroscopy. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (13:1 ratio).

#### (C5Me5)2U(SPh)2, 10

Following the procedure for **1a**, PhSSPh (30 mg, 0.14 mmol) was reacted with  $(C_5Me_5)_3U$  (44 mg, 0.068 mmol) in 5 mL of toluene. Quantitative conversion to the previously characterized  $(C_5Me_5)_2U(SPh)_2^{25}$  was observed by <sup>1</sup>H NMR spectroscopy. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (1:4 ratio) along with unreacted PhSSPh.

#### 10 from (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U(NCCMe<sub>3</sub>) with PhSSPh

Following the procedure for **1a**, PhSSPh (36 mg, 0.16 mmol) was reacted with  $(C_5Me_5)_3U(NCCMe_3)$  (60 mg, 0.083 mmol) in 5 mL of toluene. Quantitative conversion to the previously characterized  $(C_5Me_5)_2U(SPh)_2^{25}$  was observed by <sup>1</sup>H NMR spectroscopy. The byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy (1:3 ratio) along with unreacted PhSSPh.

#### C5Me5. with PhSSPh

 $(C_5Me_5)_2$  (12 mg, 0.044 mmol) and PhSSPh (10 mg, 0.046 mmol) were dissolved in 1 mL of  $C_6D_6$  and transferred to a J-Young tube which was subsequently evacuated to the vapor pressure of the solvent and heated to 90 °C. After 12 h, the solution turned bright yellow. The <sup>1</sup>H NMR spectrum showed the complete conversion of  $(C_5Me_5)_2$  to  $C_5Me_5H$  and tetramethylfulvene along with unreacted PhSSPh. No evidence was observed for  $C_5Me_5SPh$ .

# X-ray data collection, structure determination, and refinement for 1b, 2b, 3, and 5

Complexes  $[(C_5Me_5)_2La(SePh)]_2$ , **1b**, Fig. 1,  $[(C_5Me_5)_2Ce(SPh)]_2$ , **3**, and  $[(C_5Me_5)_2Pr(SPh)]_2$ , **5**, are isomorphous and analogous to those of the previously characterized  $[(C_5Me_5)_2M(SPh)]_2$  (M = La,<sup>15e</sup> Sm,<sup>15a</sup> Y<sup>15e</sup>) and display no unusual bond distances or angles. The structure of  $[(C_5Me_5)_2La(SePh)(NCCMe_3)_2]_2$ , **2b**, Fig. 2, is similar to that of **1b** with one *tert*-butyl nitrile coordinated to each metal center. Detailed X-ray data information is available in the supporting information.<sup>†</sup>



**Fig. 1** Thermal ellipsoid plot of  $[(C_3Me_5)_2La(SePh)]_2$ , **1b**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



**Fig. 2** Thermal ellipsoid plot of  $[(C_5Me_3)_2La(SePh)(NCCMe_3)]_2$ , **2b**, drawn at the 50% probability level. There are two independent molecules of **2b** in the crystal structure each lying about independent inversion centers. The second independent molecule of **2b**, hydrogen atoms and benzene solvent molecules have been omitted for clarity.

#### Results

The reaction of  $(C_5Me_5)_3La$  with 1 equiv of PhEEPh yielded the  $[(C_5Me_5)_2La(EPh)]_2$  organometallic products (E = S, 1a; Se, 1b; Te, 1c) expected on the basis of previous reductions of PhEEPh with divalent lanthanide complexes, eqn (7).<sup>15a</sup>



In a sterically induced reduction reaction, this would produce  $(C_5Me_5)_2$  as the byproduct from the half-reactions shown in

Scheme 1. Indeed, the reaction with E = Te formed  $(C_5Me_5)_2$  as the only observed byproduct, eqn (8).



Scheme 1

However, in the  $(C_5Me_5)_3La$  reactions with PhEEPh where E = Sand Se, the major byproduct of the reaction was the corresponding  $C_5Me_5EPh$ .  $(C_5Me_5)_2$  was observed only as a minor byproduct with  $C_5Me_5EPh$ :  $(C_5Me_5)_2$  ratios of roughly 20:1, eqn (9).



The formation of C<sub>5</sub>Me<sub>5</sub>EPh in these reactions could be explained by a sigma bond metathesis (SBM)<sup>26</sup> involving an ( $\eta^1$ -C<sub>5</sub>Me<sub>5</sub>)<sup>-</sup> ligand, Scheme 2. This type of SBM was previously observed in the reaction of [(C<sub>5</sub>H<sub>4</sub>CMe<sub>3</sub>)<sub>2</sub>Ln( $\mu$ -Me)]<sub>2</sub> (Ln = Y, Lu) with REER (E = S, Se; R = Ph, "Bu, 'Bu, CH<sub>2</sub>Ph) that forms MeER and [(C<sub>5</sub>H<sub>4</sub>CMe<sub>3</sub>)<sub>2</sub>Ln( $\mu$ -ER)]<sub>2</sub>.<sup>27</sup>



Alternatively,  $C_5Me_5EPh$  could form in a process in which the  $C_5Me_5$ · radical, formed when a  $(C_5Me_5)^-$  ligand gives up one electron, *e.g.* eqn (1),<sup>1,2,3,21,28</sup> is trapped by PhSSPh, a known radical trapping reagent,<sup>29</sup> Scheme 3. To test the possibility in Scheme 3, a solution of  $(C_5Me_5)_2$  was heated in the presence of PhSSPh. It has previously been shown that heat will crack  $(C_5Me_5)_2$  to produce two  $C_5Me_5$ · radicals.<sup>30</sup> However, no evidence was observed for  $C_5Me_5Ph$ . Only the  $(C_5Me_5)_2$  disproportionation products,  $C_5Me_5H$  and tetramethylfulvene, were observed along

$$(C_5Me_5)^- \longrightarrow C_5Me_5 \bullet + 1 e^-$$
  
 $C_5Me_5 \bullet + 1/_2 PhEEPh \longrightarrow C_5Me_5EPh$ 

Scheme 3

	C <sub>5</sub> Me <sub>5</sub> SPh	$(C_5Me_5)_2$	
$(C_sMe_s)_sLa$	94	6	
$(C_5Me_5)_3La(NCCMe_3)_2$	100	0	
$(C_5Me_5)_3Ce$	67	33	
$(C_5Me_5)_3Ce(NCCMe_3)_2$	100	0	
$(C_5Me_5)_3Pr$	93	7	
$(C_5Me_5)_3Nd$	97	3	
$(C_5Me_5)_3Nd(NCCMe_3)$	100	0	
$(C_5Me_5)_3Sm$	94	6	
$(C_5Me_5)_3Y$	93	7	
$(C_5Me_5)_3U$	20	80	
$(C_5Me_5)_3U(NCCMe_3)$	25	75	

with unreacted PhSSPh. A control reaction was run by heating an isolated sample of  $C_5Me_5SPh$  to 110 °C in toluene: no decomposition was observed. Hence, the formation of  $C_5Me_5EPh$ is most consistent with sigma bond metathesis.

The formation of  $(C_5Me_5)_2$  in the E = Te reaction is consistent with SIR. However, it would be possible for  $C_5Me_5$  TePh to form *via* SBM and then decompose to  $(C_5Me_5)_2$  and PhTeTePh, eqn (10). To test this possibility, a procedure analogous to the synthesis used to produce  $C_5Me_5$ SPh<sup>22</sup> was attempted with PhTeTePh. However, no reaction was observed between LiC<sub>5</sub>Me<sub>5</sub> and PhTeTePh.

$$2C_5Me_5TePh \xrightarrow{?} (C_5Me_5)_2 + PhTeTePh$$
 (10)

#### Reactions with $(C_5Me_5)_3M$ complexes (M = Ce, Pr, Nd, Sm, Y, U)

The reactions of PhSSPh with the more sterically crowded  $(C_5Me_5)_3M$  complexes of the smaller metals, Pr, Nd, Sm, and Y, also produced the expected organometallic reduction products,  $[(C_5Me_5)_2M(SPh)]_2$  (M = Pr, 5; Nd, 6; Sm, 8a; Y, 9) along with the byproducts  $C_5Me_5SPh$  and  $(C_5Me_5)_2$ , in this case in an approximately 15:1 ratio. The percentage of each byproduct,  $C_5Me_5SPh$  and  $(C_5Me_5)_2$ , for each reaction, is shown in Table 1.

The reactions of PhSSPh with  $(C_5Me_5)_3M$  (M = Ce, U) gave the analogous metal-containing products,  $[(C_5Me_5)_2Ce(SPh)]_2$ , **3**, and  $(C_5Me_5)_2U(SPh)_2$ , **10**, eqn (11), respectively. However, much different, yet reproducible  $C_5Me_5SPh$  to  $(C_5Me_5)_2$  ratios were observed: 2:1 for cerium and 1:4 for uranium, Table 1.



#### Reactions with (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Ln(NCCMe<sub>3</sub>)<sub>x</sub>

To further assess the effects of coordination environment on this system, reactions of the nitrile adducts  $(C_5Me_5)_3Ln(NCCMe_3)_x$ (Ln = La, x = 2; Ce, x = 2; Nd, x = 1) with PhSSPh were examined. These yielded nitrile adducts of the organometallic reduction products found above,  $[(C_5Me_5)_2Ln(SPh)(NCCMe_3)]_2$ , **2a**, **4**, and **7**, respectively, eqn (12).



However, even with Ln = Ce, the only observed byproduct was  $C_5Me_5SPh$ . Analogous results were obtained from the reaction of  $(C_5Me_5)_3La(NCCMe_3)_2$  with PhSeSePh that formed  $[(C_5Me_5)_2La(SePh)(NCCMe_3)]_2$ , **2b**, and  $C_5Me_5SePh$  as the only observed byproduct. Although these nitrile reactions with PhSSPh and PhSeSePh favored formation of  $C_5Me_5EPh$ , the reaction of  $(C_5Me_5)_3La(NCCMe_3)_2$  with PhTeTePh formed  $[(C_5Me_5)_2La(TePh)(NCCMe_3)]_2$ , **2c**, and only  $(C_5Me_5)_2$  as a byproduct.

In contrast to the lanthanide nitrile adducts, the presence of nitrile did not significantly affect the byproduct ratio in the analogous uranium reaction. Hence,  $(C_5Me_5)_3U(NCCMe_3)$  reacts with PhSSPh to form  $(C_5Me_5)_2U(SPh)_2$ , **10**, with a 1:3 ratio of  $C_5Me_5SPh$  and  $(C_5Me_5)_2$  byproducts that is similar to the 1:4 ratio observed in the reaction of  $(C_5Me_5)_3U$  with PhSSPh.

#### Discussion

The results show that at least two reaction pathways are possible in reactions of  $(C_5Me_5)^-$  ligands in sterically crowded  $(C_5Me_5)_3M$ complexes with PhEEPh which form  $[(C_5Me_5)_2M(EPh)]_2$  products in high yield. One of these is SIR, eqn (1), which should form only  $(C_5Me_5)_2$  as a byproduct. This type of reaction has been extensively demonstrated with a variety of substrates.<sup>1</sup> Another possible reaction pathway is sigma bond metathesis that should form  $C_5Me_5EPh$ . Sigma bond metathesis is not a commonly encountered reaction for  $(C_5Me_5)_3M$  complexes and has only been observed previously with H<sub>2</sub> in the hydrogenolysis shown in eqn (3).<sup>6</sup> The fact that thermolysis of  $(C_5Me_5)_2$  in the presence of PhEEPh does not form  $C_5Me_5EPh$  suggests that a third possible reaction pathway involving a SIR process in which a  $C_5Me_5$ · is trapped by PhEEPh is less likely.

The formation of some  $(C_5Me_5)_2$  byproduct in the E = S and Se reactions is consistent only with a SIR reaction. The implications of the formation of  $(C_5Me_5)_2$  in the E = Te reactions are less clear with respect to SIR since  $C_5Me_5$ TePh is not known. It is possible that  $C_5Me_5$ TePh may have been produced by SBM followed by a decomposition to  $(C_5Me_5)_2$  and PhTeTePh, eqn (10). Since  $C_5Me_5$ TePh could not be generated from the reaction of LiC<sub>5</sub>Me<sub>5</sub> with PhTeTePh, it was not possible to test this decomposition.

The exclusive formation of  $(C_5Me_5)_2$  in reductions of PhTeTePh may be related to the fact that PhTeTePh is more easily reduced  $(-1.06 \text{ V } vs. \text{ SCE})^{17}$  than PhSeSePh  $(-1.2 \text{ V } vs. \text{ SCE})^{16}$  and PhSSPh (-1.75 V vs. SCE).<sup>16</sup> It is conceivable that with this easily reduced substrate, SIR is the predominant reaction channel. With PhSeSePh and PhSSPh, sigma bond metathesis may have the lowest activation energy.

To examine if the ratio of  $(C_5Me_5)_2$  SIR byproducts to  $C_5Me_5EPh$  SBM products was influenced by the reduction

**Table 2** Percentages of the byproducts,  $C_5Me_5EPh$  and  $(C_5Me_5)_2$ , formed in the reactions of  $(C_5Me_5)_3La$  and  $(C_5Me_5)_3Sm$  with PhEEPh

$(C_5Me_5)_3La$		$(C_5Me_5)_3Sm$			
E	C <sub>5</sub> Me <sub>5</sub> EPh	$(C_5Me_5)_2$	E	$C_5Me_5EPh$	$(C_5Me_5)_2$
s	94	6	S	94	6
Se	96	4	Se	100	0
Te	0	100	Te	0	100

potentials of the substrates and the reducing capacity of the  $(C_5Me_5)_3M$  complexes, the reactions of  $(C_5Me_5)_3La$  with PhSSPh and PhSeSePh were compared to reactions with the stronger reducing agent,<sup>1</sup>  $(C_5Me_5)_3Sm$ .  $(C_5Me_5)_3Sm$  was selected as it has previously been shown to reduce cyclooctatetraene (-1.86 V *vs.* SCE)<sup>31</sup> in a SIR process.<sup>7</sup> As shown in Table 2, the greater reducing power of  $(C_5Me_5)_3Sm$  made little difference in the ratios of byproducts observed in these reactions and the more easily reduced PhSeSePh has a higher ratio of  $C_5Me_5Ph$  to  $(C_5Me_5)_2$  than that observed in the PhSSPh reactions. This higher ratio of  $C_5Me_5SePh$  to  $(C_5Me_5)_2$  is consistent with a SBM mechanism in which the weaker Se–Se bond in PhSeSePh is easier to break.

The reactions of the lanthanide nitrile adducts,  $(C_5Me_5)_3Ln(NCCMe_3)_x$ , with PhSSPh that yield  $C_5Me_5SPh$  as the only byproduct, with no evidence for  $(C_5Me_5)_2$ , are also consistent with a SBM reaction pathway. The nitrile adducts are more sterically crowded and have  $Ln-C(C_5Me_5)$  bonds that are approximately 0.1 Å longer than observed in the  $(C_5Me_5)_3Ln$  complexes.<sup>5,11</sup> This increased steric crowding could increase the possibility of an  $\eta^1$ - $C_5Me_5$  intermediate that would be crucial to the SBM reaction pathway. However, it should be noted that the change in radial size of the metal in the  $(C_5Me_5)_3Ln$  reactions with PhSSPh for Ln = La, Pr, Nd, Sm, and Y does not affect the  $C_5Me_5Ph$  to  $(C_5Me_5)_2$  ratio.

The very different byproduct ratios for  $(C_5Me_5)_3Ce$  and  $(C_5Me_5)_3U$  are also difficult to explain. The main factor that would differentiate  $(C_5Me_5)_3Ce$  from the other lanthanides is that  $Ce^{4+}$  is more accessible than  $Ln^{4+}$  ions for the other lanthanides.<sup>32</sup> However, an oxidative mechanism involving  $Ce^{4+}$  seems unlikely since the PhEPh compounds are not strong oxidants. The fact that  $(C_5Me_5)_3Ce$  displays a much different byproduct ratio from  $(C_5Me_5)_3Ce(NCCMe_3)_2$  suggests that variation of the lanthanide coordination environment is more important in determining the pathway of the reaction for this metal.

The uranium reaction, eqn (11), is somewhat different in that a U<sup>4+</sup> product is formed and the reaction involves a U<sup>3+</sup> to U<sup>4+</sup> redox transformation as well as a process involving the  $(C_5Me_5)^$ ligands. Significant differences in  $(C_5Me_5)_3Ln$  and  $(C_5Me_5)_3U$ reactions have previously been observed with CO,<sup>4,10</sup> N<sub>2</sub>,<sup>9</sup> PhCl,<sup>1,33</sup> and Me<sub>3</sub>CNC.<sup>11</sup> Interestingly, in the reactions of  $(C_5Me_5)_3U$  and  $(C_5Me_5)_3U$ (NCCMe<sub>3</sub>) with PhSSPh, the addition of the nitrile ligand to the coordination environment does not have a great effect on the reaction byproducts.

#### Conclusion

Isolation of both  $C_5Me_5EPh$  and  $(C_5Me_5)_2$  as byproducts from reactions of  $(C_5Me_5)_3M$  and  $(C_5Me_5)_3M(NCCMe_3)_x$  complexes with PhEEPh (E = S, Se, Te) shows that with the appropriate

substrates, more than one reaction pathway is accessible with these sterically crowded complexes. In previous studies, one single type of byproduct is normally observed. These studies also show that sigma bond metathesis may be much more prevalent for  $(C_5Me_5)_3M$  complexes than previously thought. The PhTeTePh reactions suggest that SIR will be favored when the substrate is easily reduced. The  $(C_5Me_5)_3Ln(NCCMe_3)_x$  reactions suggest that adding ligands to  $(C_5Me_5)_3Ln$  complexes will favor SBM over SIR. The reaction of  $(C_5Me_5)_3Ce$  with PhSSPh indicates that cerium can have a reaction profile different from other  $(C_5Me_5)_3Ln$  complexes, a feature previously not observed in  $(C_5Me_5)_3Ln$  reactivity. The implications of these conclusions on other  $(C_5Me_5)_3M$  reactions are under study.

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