Evidence for Concerted Extrusion of TeR_2 From Permethylscandocene Tellurolates

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Use of stereochemical probes shows that both the formation of permethylscandocene tellurolates (*via* tellurium insertion into Sc–C bonds) and the decomposition of permethylscandocene tellurolates (*via* extrusion of TeR_2) proceed with retention of configuration in the probe, implying concerted transition states for both reactions.

The thermal decomposition of molecular metal tellurolate derivatives to binary metal tellurides represents a promising low-temperature route to these materials under controlled conditions. Homoleptic lanthanide,[1] early metal[2] and group 12 metal[3] tellurolates have been found to decompose *via* the stoichiometry shown in eqn. (1) but relatively little is known concerning the intimate mechanism of this reaction. We recently reported the decay of permethyl scandocene tellurolate derivatives as in eqn. (1),[4] a useful model for

$$[M(ER)_2]_n \xrightarrow{\text{Heat}} [ME]_n + n\,ER_2 \qquad (1)$$

the decomposition of homoleptic metal tellurolate derivatives. Using well known 1,2-$[^2H_2]$-neohexyl stereochemical probes, we now report results which indicate that the extrusion of TeR_2 from metal tellurolates proceeds *via* a concerted transition state.

The experiments reported herein are depicted in Fig. 1. In analogous reactivity patterns to those established for the insertion of olefins into the Zr–H bond of Schwartz's reagent, $[(C_5H_5)_2ZrHCl]_n$,[5] insertion of (*E*)-CH(D)=CHBu^t into the Sc–D bond of $[(C_5Me_5)_2ScD]$[7] results in diastereomerically pure *erythro*-$[(C_5Me_5)_2ScCH(D)CH(D)Bu^t]$, *erythro*-$[^2H_2]$-**1**,† as determined by $^1H\{^2H\}$ NMR spectroscopy ($^3J_{HH}$ = 15.1 Hz). Although reversible β-elimination is likely occurring[8] and represents an epimerization process, it fortunately is not

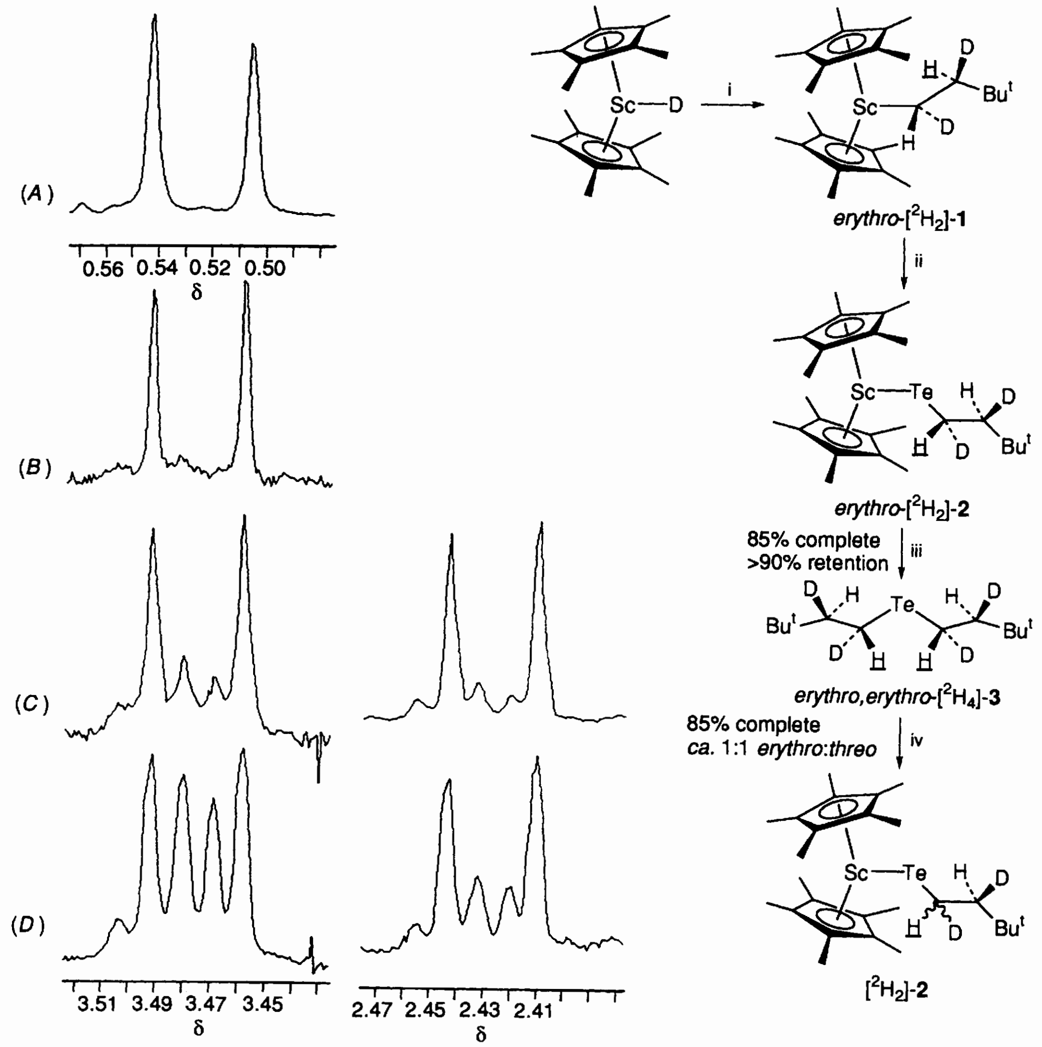
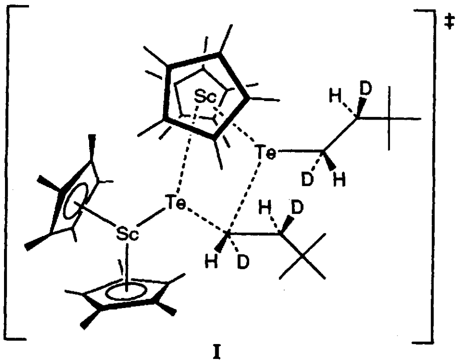


Fig. 1 *Reagents*: i, *E*-CH(D)=CHBu^t, 1 equiv.; ii, Te=PBu$^n_3$, 1 equiv.; iii, 90 °C, 24 h; iv, *hν*, 10 min. Spectrum (*A*): β-C*H*(D) resonance for *erythro*-$[^2H_2]$-**1**; spectrum (*B*): α-C*H*(D) resonance for *erythro*-$[^2H_2]$-**2**; spectra (*C*) and (*D*): α-C*H*(D) resonances for *erythro*-$[^2H_2]$-**2** (left trace) and *erythro,erythro*-$[^2H_4]$-**3**- (right trace) after heating and irradiation, respectively. The intensities of the peaks have been adjusted to the same vertical scale and do not reflect relative amounts of the two species in solution.



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kinetically significant over the course of the several minutes necessary to perform subsequent manipulations. Insertion of tellurium into the Sc–C bond of *erythro*-[$^{2}H_{2}$]-**1** using Te=PBu$^{n}_{3}$ as a tellurium transfer agent occurs rapidly and quantitatively with retention of stereochemistry to afford the tellurolate *erythro*-[$(C_5Me_5)_2ScTeCH(D)CH(D)Bu^t$], *erythro*-[$^{2}H_{2}$]-**2**, ($^{3}J_{HH}$ 13.6 Hz).† Tellurium insertion with retention is not surprising in view of the fact that the majority of insertion reactions take place *via* concerted transition states.[9] However, this result conveniently allowed us to examine the stereochemistry associated with the more fundamentally interesting dialkyl telluride extrusion process leading to metal tellurides.

As indicated in Fig. 1, thermolysis of solutions of *erythro*-[$^{2}H_{2}$]-**2** in the dark resulted in concerted elimination of the diastereoisomers of *erythro,erythro*-Te[$CH(D)CH(D)Bu^t$]$_2$, (*erythro,erythro*-[$^{2}H_{4}$]-**3**), with greater than 90% diastereoselectivity ($^{3}J_{HH}$ = 13.4 Hz)† and concomitant production of the known telluride bridged dimer [$(C_5Me_5)_2ScTeSc(C_5Me_5)_2$] **4**.[4] The *meso*- and *rac*-diastereoisomers of *erythro,erythro*-[$^{2}H_{4}$]-**3** were not distinguishable spectroscopically and the identity of this product was confirmed by independent synthesis of [$^{2}H_{0}$]-**3**.[10] Although mechanisms involving initial homo- or hetero-lysis of the Te–C bond in *erythro*-[$^{2}H_{2}$]-**2** are certainly plausible, our results suggest that the major pathway involves a bimolecular‡ concerted transition state leading to retention of configuration in *erythro, erythro*-[$^{2}H_{4}$]-**3** such as that depicted in **I**.

We have previously shown that the extrusion reaction is reversed in a very facile photochemical reaction.[4] When samples containing *erythro,erythro*-[$^{2}H_{4}$]-**3** and **4** generated as described above were irradiated with UV light through a Pyrex filter for 10 minutes, almost complete conversion back to [$^{2}H_{2}$]-**2** was observed. After this treatment, however, a 1 : 1 mixture of *erythro*- and *threo*-[$^{2}H_{2}$]-**2** was found (Fig. 1). Notably, some epimerization was also seen in *erythro,erythro*-[$^{2}H_{2}$]-**3** but not to the extent observed in [$^{2}H_{2}$]-**2**. These data can be explained by either some epimerization process likely involving radicals or (since only one of the two Te–C bonds in *erythro,erythro*-[$^{2}H_{4}$]-**3** is involved in the reaction with **4**) a concerted process involving inversion at carbon. We are currently designing experiments to distinguish between these two mechanisms.

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Footnotes

† $^{1}H\{^{2}H\}$ NMR data for new compounds (400 MHz, C_6D_6, δ in ppm). *erythro*-[$^{2}H_{2}$]-**1**: [$^{2}H_{2}$]-**2** C_5Me_5, δ 1.86; CMe_3, 1.19; α-CH(D) 1.08; β-CH(D) 0.52, $^{3}J_{HH}$ = 15.1 Hz. *erythro*-[$^{2}H_{2}$]-**2**: C_5Me_5, δ 1.94; CMe_3, 0.99; α-CH(D) 3.45; β-CH(D) obscured by residual PBu$^{n}_{3}$ resonances, $^{3}J_{HH}$ = 13.6 Hz. *erythro,erythro*-[$^{2}H_{4}$]-**3**: CMe_3, δ 0.78; α-CH(D) 2.43; β-CH(D) 1.64, $^{3}J_{HH}$ = 13.4 Hz. $^{13}C\{^{1}H\}$ NMR data for [$^{2}H_{0}$]-**3** (50 MHz, C_6D_6, δ in ppm): $TeCH_2CH_2$, δ 47.9; $TeCH_2CH_2$, −3.7; CMe_3, 28.8; CMe_3, 32.6.

‡ X-Ray structural analysis of the benzyl tellurolate derivative $(C_5Me_5)_2ScTeCH_2Ph$ showed a mononuclear structure in the solid state.[11]

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