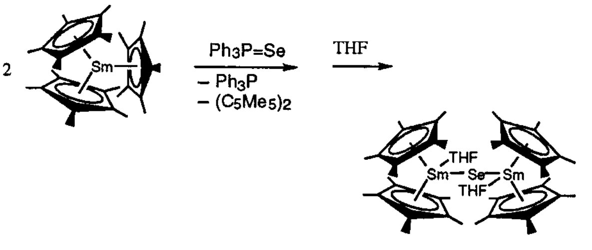
The Trivalent Neodymium Complex $[(C_5Me_5)_3Nd]$ Is a One-Electron Reductant!**

William J. Evans,* Gregory W. Nyce, Robert D. Clark, Robert J. Doedens, and Joseph W. Ziller

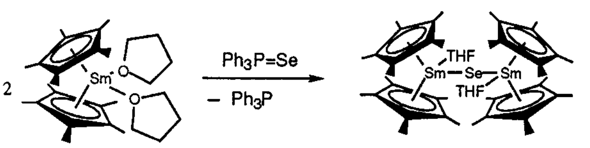
Increased selectivity in synthetic chemistry is a continuing goal of chemical research for esthetic, economic, and environmental reasons. Selectivity in metal-based chemistry can often be increased by optimizing steric factors and varying the ligand size. However, the lanthanide metals offer an additional opportunity to optimize steric factors by varying the size of the metal atom. This is possible because the limited radial extension of the 4f valence orbitals[1] makes these metals chemically similar and there are 15 choices[2] which vary gradually in size by about 0.015 Å increments.[3]

Although optimization of the size of the metal atom is possible in trivalent lanthanide chemistry, since molecular Ln^{III} compounds are known for all of the metals in the series,[4] it has not been achievable with the reductive chemistry of the divalent lanthanides, since only a few of the lanthanides form molecular compounds containing divalent metals and the reductive behavior of these metals is quite different. Hence the extensive reductive chemistry of Sm^{II}[5] can only be size-optimized by varying the ligand set and not by choosing another Ln^{II} center of better size. Eu^{II} and Yb^{II} are much weaker reductants and the recently discovered $[TmI_2(dme)_3]$ (dme = 1,2-dimethoxyethane) is much more difficult to handle.[6] As a result, the extensive one-electron reductive lanthanide chemistry found for Sm^{II} is limited to this element.

However, recently, we have shown[7] that the sterically crowded trivalent samarium complex $[(C_5Me_5)_3Sm]$[8] displays one-electron reductive chemistry which is analogous to the one-electron reductive chemistry of divalent $[(C_5Me_5)_2Sm]$.[9] For example, analogous reductions of Se=PPh$_3$ to PPh$_3$ and Se^{2-} by the trivalent[7] and divalent[10] compounds are shown in Equations (1) and (2), respectively. Since $(C_5Me_5)_2$ is a by-product of the reduction with the Sm^{III} complex, it appears that one of the $(C_5Me_5)^-$ rings in $[(C_5Me_5)_3Sm]$ is the reducing agent. This is reasonable considering the extreme steric crowding in $[(C_5Me_5)_3Sm]$: the $(C_5Me_5)^-$ rings are not close enough to the metal center to be stabilized very well and they can react by reductive pathways to form less sterically crowded products. In comparison, simple $(C_5Me_5)^-$ salts such as KC_5Me_5 and $C_5Me_5MgCl \cdot THF$ do not display this reductive reactivity with Se=PPh$_3$.



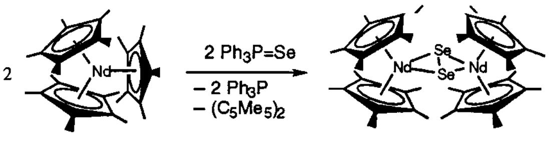
(1)



(2)

The one-electron reduction by the sterically crowded Sm^{III} complex suggested that reduction chemistry could be done with any of the lanthanides if suitably crowded trivalent lanthanide complexes could be synthesized. This would mean that the reductive chemistry of Sm^{II} could be extended to other lanthanides which have different physical properties and potentially more favorable metal sizes. To prove this, it was necessary to demonstrate a reduction reaction with a metal which did not have a readily accessible divalent state, since in the samarium system in Equation (1) there would always be a possibility that the reaction could go through an undetected Sm^{II} intermediate. Fortunately, we recently discovered a high-yield synthetic route to the second crystallographically characterized $[(C_5Me_5)_3Ln]$ complex, $[(C_5Me_5)_3Nd]$ (**1**),[11] which allows us to test this concept. It should be noted that Nd^{II} has been reported in solid-state halide systems[12] and is presumed to form upon potassium reduction,[13] but no $[(C_5Me_5)_2Nd]$ complex is formed as readily as $[(C_5Me_5)_2Sm]$.

The reaction analogous to that in Equation 1 was examined with neodymium and it was found that $[(C_5Me_5)_3Nd]$ does indeed function as a one-electron reductant: Se=PPh$_3$ is reduced to Ph$_3$P and $[\{(C_5Me_5)_2Nd\}_2(\mu{:}\eta^2{:}\eta^2\text{-}Se_2)]$. The $(C_5Me_5)_2$ by-product is consistent with reduction by $(C_5Me_5)^-$. Interestingly, the product of this 2:1 $(C_5Me_5)_3Nd$:Se=PPh$_3$ reduction is a Se_2^{2-} rather than a Se^{2-} complex as found in Equation 1 and residual $[(C_5Me_5)_3Nd]$ remains at the end of the 2:1 reaction. Accordingly a 1:1 reaction was examined and found to give **2** cleanly in high yield [Eq. (3)].



1 **2**

(3)

Complex **2** was characterized by elemental and chemical analysis, NMR and IR spectroscopy, and X-ray crystallography (Figure 1).[14] The Se–Se distance (2.389(2) Å) is comparable to the range of Se–Se single bond lengths (2.256(6)–2.383(7) Å),[15] and all the other distances are normal for Nd^{III} metallocenes.[16]

After complex **2** was isolated, the analogous 1:1 $[(C_5Me_5)_3Ln]$:Se=PPh$_3$ reaction was attempted with samarium and the analogous isostructural and isomorphous complex **3** [17] was obtained. Hence $[(C_5Me_5)_3Sm]$ can convert Se=PPh$_3$ to both Se_2^{2-} and Se^{2-} depending upon the stoichiometry. To confirm this, the reaction of **3** with $[(C_5Me_5)_3Sm]$ was examined and

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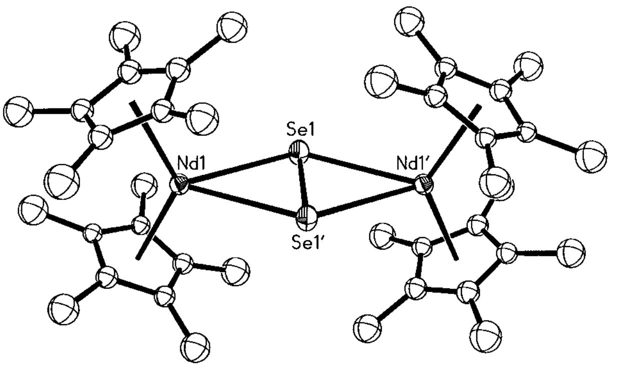
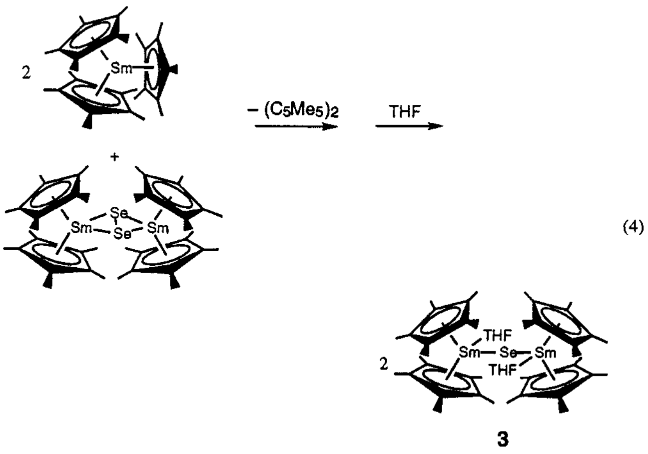


Figure 1. Molecular structure of $[\{(C_5Me_5)_2Nd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)]$ (**2**) with the thermal ellipsoid plot drawn at the 50% probability level.

found to form the Se^{2-} product, $[\{(C_5Me_5)_2Sm(thf)\}_2(Se)]$, as expected [Eq. (4)]. Since $[(C_5Me_5)_3Sm]$ appears to be a stronger reductant than $[(C_5Me_5)_3Nd]$, this suggests that the reductive reactivity of $[(C_5Me_5)_3Ln]$ complexes can be tunable on the basis of metal size.



These results show that one-electron reduction reactions can be done not only with sterically crowded Sm^{III} complexes, but also with sterically crowded complexes of metals which do not have readily accessible divalent states. It is anticipated that one-electron reduction chemistry can be extended to all of the lanthanides as syntheses of appropriately sterically crowded complexes are developed. This should allow the reductive chemistry previously limited to samarium to be generalized to the rest of the lanthanide series and it should allow optimization of this lanthanide reduction chemistry on the basis of metal size. We also anticipate that investigation of the reductive chemistry of other $[(C_5Me_5)_3Ln]$ complexes will lead to new lanthanide metallocene complexes as demonstrated by the synthesis of **2**. Examination of the reductive chemistry of a range of sterically crowded molecules is clearly warranted to determine the importance of the $(C_5Me_5)^-$ ligand to this chemistry.

Experimental Section

2: In a THF-free glovebox, toluene (10 mL) was added to $[(C_5Me_5)_3Nd]$ (150 mg, 0.272 mmol) and $Ph_3P{=}Se$ (93 mg, 0.272 mmol) and the reaction mixture was stirred to form an olive green solution. Within 30 min, the solution turned cherry red and gradually a red precipitate appeared. After the reaction was stirred at ambient temperature for 22 h, the solvent was removed under reduced pressure and the red precipitate was washed with toluene (2 × 5 mL). The ^1H NMR spectrum of the light green toluene wash contained resonances for Ph_3P and $(C_5Me_5)_2$. The red precipitate was crystallized from hot toluene to yield $[\{(C_5Me_5)_2Nd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)]$ (**2**) (91 mg, 68%, m.p. >260 °C) as dark burgundy crystals. The ^1H NMR spectrum of the crystals was taken at 57 °C to enhance solubility. ^1H NMR (400 Hz,[D_6] benzene, 57 °C): $\delta = 8.64$ (br.s, C_5Me_5); IR (KBr): $\tilde{\nu} = 2966$ s, 2907 s, 2849 s, 2719 m, 1437 m, 1372 m, 1084 w, 1055 w, 1020 cm $^{-1}$; C,H analysis (%): Calcd for $C_{40}H_{60}Nd_2Se_2$: C 48.66, H 6.13; found: C 48.40, H 5.97.

3: $[(C_5Me_5)_3Sm]$ (154 mg, 0.277 mmol) was treated with $Ph_3P{=}Se$ (101 mg, 0.296 mmol) in toluene (10 mL) as described above. The mixture was initially dark brown and turned clear red after 2 h. After the reaction was stirred overnight, dark red solids were separated by centrifugation, washed with hexanes (5 mL), and dried under vacuum to yield $[\{(C_5Me_5)_2Sm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)]$ (**3**) (45 mg, 33%, m.p. >260 °C). The ^1H NMR spectrum of the crystals was taken at 100 °C to enhance solubility. ^1H NMR (400 MHz, [D_8] toluene, 100 °C): $\delta = 1.10$ (s, C_5Me_5); IR (KBr): $\tilde{\nu} = 2962$ s, 2906 s, 2851 s, 2720 w, 1453 m, 1372 m, 1093 w, 1025 w cm^{-1}; C,H analysis (%): Calcd for $C_{40}H_{60}Sm_2Se_2$: C 48.06, H 6.05; found: C 47.86, H 5.89. Crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from boiling toluene.

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[14] Crystal data for **2** at 168 K: $C_{40}H_{60}Nd_2Se_2$, monoclinic, $P2_1/n$, $a=8.5323(8)$, $b=20.5232(11)$, $c=11.6385(7)$ Å, $\beta=103.329(5)^\circ$, $V=1983.1(2)$ Å^3, $Z=2$. At convergence, $wR2=0.1261$ and $GOF=1.371$ for 182 variables refined against all 4559 unique data (as a comparison for refinement on F, $R1=0.0505$ for those 4068 data with ($F>4\sigma(F)$).

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[17] a) Crystal data for **3** at 168 K: $C_{40}H_{60}Sm_2Se_2$, monoclinic, $P2_1/n$, $a=8.5307(4)$, $b=20.4855(10)$, $c=11.5805(5)$ Å, $\beta=103.762(1)^\circ$, $V=1967.7(2)$ Å^3, $Z=2$. At convergence, $wR2=0.1530$ and $GOF=1.324$ for 181 variables refined against all 4778 unique data (as a comparison for refinement on F, $R1=0.0510$ for those 4574 data with ($F>4\sigma(F)$). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112873 and CCDC-112874. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Regio- and Stereoselective Synthesis of γ-Alkylidenebutenolides by Cyclization of Dilithiated 1,3-Dicarbonyl Compounds with *N,N'*-Dimethoxy-*N,N'*-dimethylethanediamide[**]

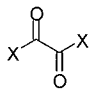
Peter Langer[*] and Martin Stoll

Dedicated to Professor Armin de Meijere
on the occasion of his 60th birthday

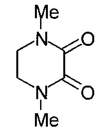
Numerous natural products, including prominent compounds such as dihydroxerulin, tetrenolin, freelingyne, or pulvinic acid, belong to the pharmacologically important category of γ-alkylidenebutenolides.[1] Dihydroxerulin, for instance, has proven to be an important nontoxic inhibitor in the biosynthesis of cholesterol,[2] while tetrenolin exhibits antibiotic activity against gram-positive bacteria.[3] α-Hydroxy-γ-alkylidenebutenolides are particularly suitable building blocks for natural product synthesis (by means of transition metal-catalyzed coupling and reduction reactions of the corresponding enol triflates). However, it was only recently that an efficient stereoselective route was introduced to obtain a specific member of this class, 5-(2-hydroxyethylidene)-2(5*H*)-furanone, by stereospecific elimination of L- and D-gulono-1,4-lactone.[4] Since a carbohydrate derivative is used as the substrate for this reaction, this method cannot be used to synthesize other substituted butenolides. Previously reported β-eliminations for the synthesis of α-alkyl-substituted or unsubstituted γ-alkylidenebutenolides proceed with low[5] stereoselectivity or no stereoselectivity at all.[6] Wittig reactions of suitable phosphorylides with methoxymaleic anhydrides proceed with undesired regiochemistry and generally unsatisfactory stereoselectivity.[7] Wittig reactions of alkyl-substituted maleic anhydrides[8] or other methods[9] lead only to *E*/*Z* mixtures of α-alkyl-substituted or unsubstituted γ-alkylidenebutenolides. To our knowledge, no method exists which provides a direct and stereoselective approach to γ-alkylidenebutenolides with a wide range of substitution patterns.

To fill this gap, we investigated the concept of direct cyclization of 1,3-dicarbonyl compounds with the oxalic acid dielectrophiles **2**. Despite the simplicity of this idea, the cyclization of 1,3-dicarbonyl compounds containing a terminal hydrogen atom (e.g. acetylacetone) with oxalyl chloride in the presence of Lewis acids was not successfully carried out until 1990.[10] The cyclization in this case proceeds through the *central* carbon atom and an oxygen atom of the 1,3-diketone under formation of 4-acyl-5-alkyl-2,3-dioxo-2,3-dihydrofurans. To the best of our knowledge, we present herein the first cyclizations of 1,3-dicarbonyl compounds with oxalic acid dielectrophiles which proceed by attack of a *terminal* carbon atom of the nucleophile. This method allows for a simple regio- and stereoselective route to a series of γ-alkylidenebutenolides. To achieve the desired regioselectivity, the 1,3-dicarbonyl compounds are used in the corresponding ambident dianionic form.[11, 12]

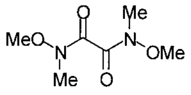
Initial experiments showed that reactions of the dianion of ethyl acetoacetate (**1a**) with diethyl oxalate (**2a**) or oxalyl chloride (**2b**) led to the formation of complex, inseparable mixtures (owing to overaddition, polymerization, or decomposition; Table 1). The reaction of the dianion of **1a** with 1,4-dimethylpiperazine-2,3-dione (**2c**)[13] also remained unsuccessful, although **2c** had previously been reported to undergo condensation reactions with two equivalents of monofunctional organolithium compounds. Fortunately, the problem could be solved with the use of the Weinreb amide[14] *N,N'*-dimethoxy-*N,N'*-dimethylethanediamide (**2d**), which was reported in 1995 and which until now has been used only in condensation reactions with simple monolithium compounds such as phenyllithium.[14a] Exposure of this Weinreb oxalic amide to the dianion of **1a** induced a cyclization reaction, and the γ-alkylidenebutenolide **3a** was obtained in 75% yield (Scheme 1). The product was formed both regioselectively (by cyclization of the terminal carbon and the neighboring oxygen atom of the dianion) and with complete stereoselectivity. The *E* configuration of the semicyclic double bond was unequivocally proven with NOE NMR studies of the γ-alkylidenebutenolide **3b**, which was obtained in 73% yield from the



2a (X = OEt)
2b (X = Cl)



2c



2d

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