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[4] Calculations were performed on an IBM RS 6000 workstation running Insight II Discover 98.0 (MSI, San Diego). The structures were energy minimized with the force field cvff.frc. and the minimization algorithm VA09A: diastereomer 7*R*,9*R*: 39.2 kcal mol^{-1}; 7*S*,9*R*: 40.0 kcal mol^{-1}; 7*S*,9*S*: 42.0 kcal mol^{-1}; 7*R*,9*S*: 44.3 kcal mol^{-1}.

[5] Early installation of the C1 hydroxyl group by starting from a 3,4-dimethylcyclohex-2-enol derivative was not attempted because of the anticipated difficulties in the cycloaddition. See: R. Malherbe, G. Rist, D. Bellus, *J. Org. Chem.* **1983**, *48*, 860 – 869; E. Vedejs, R. A. Buchanan, *J. Org. Chem.* **1984**, *49*, 1840 – 1841, and references therein.

[6] Yields are for purified, chromatographically homogeneous substances. The NMR, IR, and mass spectra are in full accord with the proposed structures and satisfactory combustion analyses and/or high resolution mass spectral data have been obtained for all new compounds. **5**: m.p. 71 – 71.5 °C (diethyl ether/hexane); $[\alpha]_D^{20} = +426$ ($c = 1.2$ in $CHCl_3$). **7**: $[\alpha]_D^{20} = +62.9$ ($c = 1.8$ in $CHCl_3$). **8a**: m.p. 145 – 146 °C (ethyl acetate/hexane); $[\alpha]_D^{20} = -1.1$ ($c = 2.5$ in $CHCl_3$). **8b**: m.p. 145 – 146 °C (diethyl ether/hexane); $[\alpha]_D^{20} = +50.1$ ($c = 1.6$ in $CHCl_3$). **9a**: $[\alpha]_D^{20} = +32.0$ ($c = 4.1$ in $CHCl_3$). **9b**: m.p. 166.5 – 167 °C (chloroform/hexane); $[\alpha]_D^{20} = -91.2$ ($c = 1.3$ in $CHCl_3$). **10**: m.p. 131 – 131.5 °C (dichloromethane/hexane); $[\alpha]_D^{20} = +100.0$ ($c = 1.4$ in $CHCl_3$). **1**: m.p. 177 – 178 °C (dichloromethane/hexane); $[\alpha]_D^{20} = -71.7$ ($c = 1.0$ in $CHCl_3$), $[\alpha]_D^{22} = -79.7$ ($c = 1.0$ in CH_3OH). **2**: m.p. 165 – 165.5 °C (dichloromethane); $[\alpha]_D^{20} = -76.2$ ($c = 0.8$ in $CHCl_3$), $[\alpha]_D^{22} = -156.1$ ($c = 0.7$ in CH_3OH). **3**: m.p. 101.5 – 102 °C; $[\alpha]_D^{22} = -118.1$ ($c = 0.8$ in $CHCl_3$), $[\alpha]_D^{22} = -149.3$ ($c = 1.1$ in CH_3OH). **4**: m.p. 130 – 130.5 °C (diethyl ether/hexane); $[\alpha]_D^{20} = -105.6$ ($c = 1.0$ in $CHCl_3$), $[\alpha]_D^{22} = -124.5$ ($c = 1.1$ in CH_3OH).

[7] C. Mottet, O. Hamelin, G. Garavel, J.-P. Deprés, A. E. Greene, *J. Org. Chem.* **1999**, *64*, 1380 – 1382.

[8] For a review, see H. J. Reich, S. Wollowitz, *Org. React.* **1993**, *44*, 1 – 296.

[9] J.-L. Luche, *J. Am. Chem. Soc.* **1978**, *100*, 2226 – 2227; J.-L. Luche, L. Rodriguez-Hahn, P. Crabbé, *J. Chem. Soc. Chem. Commun.* **1978**, 601 – 602.

[10] This stereochemical assignment was initially based on literature precedent[3b, i] for an A-ring β-face approach in bakkane derivatives and was later confirmed indirectly by X-ray diffraction analysis of diol **10**. NOSEY experiments on **8b** proved inconclusive.

[11] T. Itoh, K. Jitsukawa, K. Kaneda, S. Teranishi, *J. Am. Chem. Soc.* **1979**, *101*, 159 – 169; for reviews, see K. B. Sharpless, T. R. Verhoeven, *Aldrichim. Acta* **1979**, *12*, 63 – 74; K. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431 – 458.

[12] For a review, see G. A. Molander, *Org. React.* **1994**, *46*, 211 – 367. This type of double reduction with SmI_2 is apparently unprecedented; however, the less chemoselective Li-NH_3-NH_4Cl system has been used for this purpose. See: A. A. Devreese, M. Demuynck, P. J. De Clercq, M. Vandewalle, *Tetrahedron* **1983**, *39*, 3039 – 3048; C. S. Swindell, S. J. deSolms, *Tetrahedron Lett.* **1984**, *25*, 3801 – 3804. The *cis* ring fusion was anticipated based on precedent;[3b,i] the C9β isomer was expected to result since SmI_2 is known to deliver in general the more stable isomer ($\Delta E_{9\beta\text{-}9\alpha} = -2.0$ kcal mol^{-1}[4]). The configuration at C9 in **10**, however, is irrelevant in that it too is subjected to equilibration in the retroaldol – aldol reaction.

[13] Crystal data for (±)-**10** (from parallel studies):[17] $C_{15}H_{22}O_4$, tetragonal, $I4_1/a$, $a = 20.220(7)$, $c = 13.427(7)$ Å, $V = 5490(3)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.289$ Mg m^{-3}, $F(000) = 2304$, $\theta = 2.0 - 30°$, 5466 measured reflections, 5274 (R(int) = 0.017) independent reflections, $R(F)$ ($F > 2\sigma(F)$) = 0.0487, wR (all data) = 0.0512, GOF = 1.965.

[14] See: J. D. White, N. S. Cutshall, T.-S. Kim, H. Shin, *J. Am. Chem. Soc.* **1995**, *117*, 9780 – 9781 and ref. [3n)].

[15] Crystal data for (±)-**1** (from parallel studies):[17] $C_{15}H_{22}O_4$, monoclinic, $P2_1/c$, $a = 13.261(3)$, $b = 7.267(6)$, $c = 15.454(5)$ Å, $\beta = 110.36(2)°$, $V = 1396(1)$ Å^3, $Z = 14$, $\rho_{calcd} = 1.267$ Mg m^{-3}, $F(000) = 576$, $\theta = 2.50 - 30°$, 4449 measured reflections, 4305 (R(int) = 0.011) independent reflections, $R(F)$ ($F > 1\sigma(F)$) = 0.0452, wR (all data) = 0.0584, GOF = 2.011.

[16] B. Hartmann, A. Kanazawa, J.-P. Deprés, A. E. Greene, *Tetrahedron Lett.* **1991**, *32*, 5077 – 5081.

[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147277 (±-**1**) and -147278 (±-**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

A Tandem Sulfur Transfer/Reduction/Michael Addition Mediated by Benzyltriethylammonium Tetrathiomolybdate**

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Disulfides and sulfur containing organic compounds are important functional groups widely present in nature and have commercial significance.[1] Therefore, the synthesis of disulfides, sulfides, and ω-thioketones is not only attractive but also finds numerous applications.[2] Studies directed

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towards the cleavage of disulfide bonds in proteins are an important determinant in understanding the structural activity and structural domains of proteins, this helps in the design and development of new therapeutic agents and the conversion of large proteins into smaller fragments that are more amenable for sequencing.[3] The sulfur–sulfur bond in organic disulfides may be cleaved by nucleophilic, electrophilic, and radical processes. Several transition metal complexes have also been shown to cleave sulfur–sulfur bonds in organic disulfides.[4]

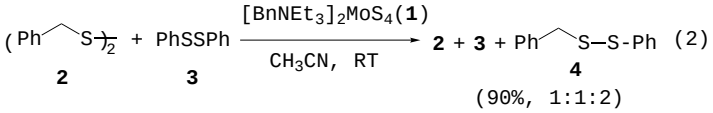
We have reported the usefulness of benzyltriethylammonium tetrathiomolybdate (**1**) as an efficient sulfur transfer reagent in organic synthesis.[5] Further work revealed that the tetrathiomolybdate **1** mediates reductive dimerization of organic thiocyanates and selenocyanates to the corresponding disulfides and diselenides.[6]

In continuing our quest to exploit the redox chemistry associated with Mo–S systems we find that **1** can mediate not only the formation of the disulfide bond but can also cleave the disulfide bond under appropriate reaction conditions. Herein, we present our findings that **1** can mediate disulfide interchange reactions and that the intermediate generated in situ in the cleavage of the disulfide bond undergoes a facile conjugate addition to suitable Michael acceptors.

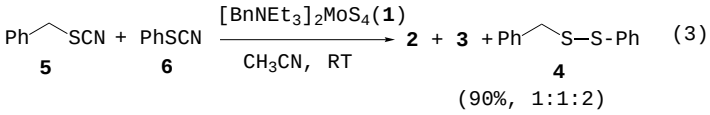
In work on induced redox reactions of ammonium tetrathiomolybdate Stiefel and co-workers[7] demonstrated that under forcing conditions (DMF, 90 °C) alkyl and aryl disulfides undergo cleavage to produce thiolates and $Mo_2S_8^{2-}$ [Eq. (1)]. Since we have reported that **1** effects sulfur transfer to alkyl halides to form disulfide bonds very efficiently, and in light of Stiefel's observations, it was of interest to find out whether **1** would effect an exchange reaction of a mixture of disulfides.

$$2(NH_4)_2MoS_4 + RSSR \xrightarrow[\Delta]{DMF} (NH_4)_2Mo_2S_8 + 2NH_4RS \qquad (1)$$

A 1:1 mixture of dibenzyl disulfide (**2**) and diphenyl disulfide (**3**) in CH_3CN was reacted with **1** (2 equiv) at room temperature for 15 h. Interestingly, the unsymmetrical disulfide, benzylphenyl disulfide (**4**) was obtained as the major product along with the symmetrical disulfides **2** and **3** in the ratio of 2:1:1 (90%, [Eq (2)]. This reaction clearly indicates that **1** is mediating an exchange reaction of disulfides which must involve cleavage of the disulfide bond.



As tetrathiomolybdate **1** converts alkyl halides and organic thiocyanates to disulfides,[5, 6a] it was decided to find out whether two disulfide precursors (like two alkyl halides or thiocyanates) in the presence of excess of **1** would also lead to unsymmetrical disulfides in an exchange reaction. Thus, a mixture of benzyl thiocyanate (**5**; 1 equiv) and phenyl thiocyanate (**6**; 1 equiv) was treated with **1** (2 equiv) [Eq (3)]. As expected, the unsymmetrical disulfide **4** was isolated as the major product (90%) along with **2** and **3** in the ratio 2:1:1.



These results clearly suggest that disulfides undergo cleavage of the disulfide bond with an excess of **1** and undergo exchange reactions to produce unsymmetrical disulfides. Encouraged by these findings, we were interested to find out whether alkyl and aryl disulfides in the presence of **1** would undergo 1,4-addition to suitable Michael acceptors. If this were successful, it would avoid the use of free thiols in the Michael reactions.

In the initial experiments diphenyl disulfide (**3**) was treated with **1** in the presence of a number of Michael acceptors and as anticipated the corresponding Michael adducts were formed in very good yields (Table 1). Thus, in the reaction of **3** (0.5 equiv) and methyl vinyl ketone (**7**) (1 equiv) with **1** (1.1 equiv), the β-ketosulfide **8**[8] was isolated in 85% yield. Similarly, the reaction of **1** with **3** in the presence of either ethyl acrylate (**9**) or acrylonitrile (**11**) or 2-cyclohexenone (**13**) resulted in the formation of the corresponding Michael adducts **10**,[8] **12**,[9] **14**[10] respectively in very good yields (Table 1). In the reaction of **2** and methyl vinyl ketone **7** in the presence of **1**, the ketosulfide **15** was obtained as the exclusive product.[11] When *p*-nitrobenzyl disulfide **16** was treated with **7** in the presence of **1** the corresponding product **17** was isolated in good yield (Table 1). This appears to be a general reaction with wide applications.

Having successfully executed the one-pot reduction of disulfide followed by Michael reaction the stage was set for effecting a three-step tandem reaction starting from an alkyl halide, wherein the first step is the sulfur transfer reaction mediated by **1**. Thus, when benzyl bromide (**18**) was allowed to react with **1** (2 equiv) and **7**, the corresponding ketosulfide **15** was isolated in 86% yield (Table 2). Clearly in one pot we have been able to effect sulfur transfer, reduction of disulfide, and conjugate addition of thiolate to **7**. A similar reaction of *p*-nitrobenzyl bromide **19** with two equivalents of **1** and an equivalent of **7** led to the formation of the corresponding ketosulfide **17** in 91% yield (Table 2).

Having found that the tandem reactions work well, it was then decided to apply this one pot methodology to intramolecular reactions (Table 2). When the chloroenone **20** (1 equiv) was treated with **1** (2 equiv) the corresponding spiro compound, **21**[12] was isolated in 80% yield, while the bromoenone **22** under similar conditions afforded the corresponding β-ketosulfide **23**.

The same methodology was then extended to the synthesis of bicyclo[3.3.1]nonane skeletons. In the reaction of bromoenones[13] **24** and **26** with **1** (2.2 equiv), the corresponding bicyclic adducts **25** and **27** were obtained in near quantitative yields.

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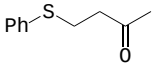
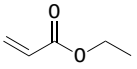
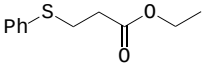
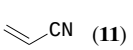
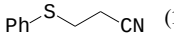
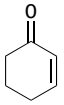
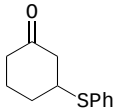
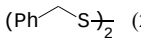
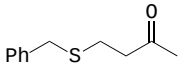
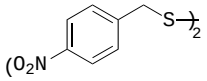
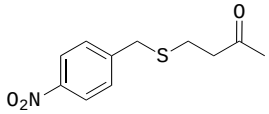
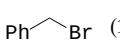
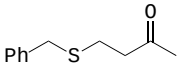
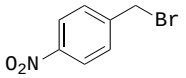
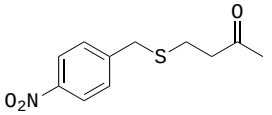
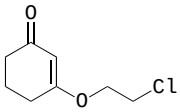
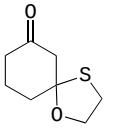
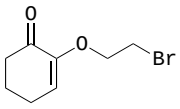
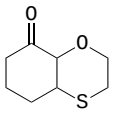
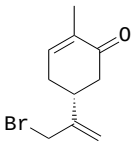
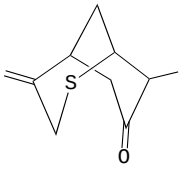
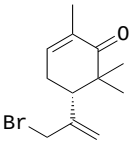
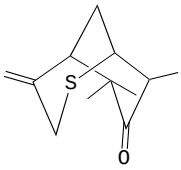
Table 1. Cleavage of disulfides and conjugate addition to a Michael acceptor in the presence of **1**.

Substrate/s		Time [h]	Product	Yield [%][a]
PhSSPh (**3**)	 (**7**)	5	 (**8**)	85
3	 (**9**)	8	 (**10**)	81
3	 (**11**)	5	 (**12**)	86
3	 (**13**)	5	 (**14**)	80
 (**2**)	**7**	6	 (**15**)	88
 (**16**)	**7**	4	 (**17**)	82

[a] Yield refers to pure, isolated products.

Table 2. Tandem sulfur transfer/reduction/Michael addition in one pot.

Substrate/s	Time [h]	Product	Yield [%][a]
 (**18**) + **7**	10	 (**15**)	86
 (**19**) + **7**	8	 (**17**)	91
 (**20**)	10	 (**21**)	80
 (**22**)	8	 (**23**)	75
 (**24**)	8	 (**25**)	94
 (**26**)	6	 (**27**)	98

[a] Yield refers to pure, isolated products.

The chemistry described herein demonstrates that the tandem sulfur transfer/reduction/Michael addition strategy mediated by tetrathiomolybdate **1** is very efficient in the synthesis of variety of useful synthetic intermediates. The highlights of this methodology are the one-pot reactions, and that there is no free thiol involved in the reaction.

Experimental Section

Typical experimental procedure for the tandem sulfur transfer reduction Michael addition: Benzyl triethylammonium tetrathiomolybdate **1** (1.135 g, 1.86 mmol) was added to a solution of bromoenone **26** (0.200 g, 0.85 mmol) in acetonitrile (3 mL) and stirred at room temperature (25 °C) for 6 h. The solvent was evaporated under reduced pressure, the black residue was extracted with dichloromethane:diethyl ether (1:5, 25 mL × 5), and filtered through a Celite pad. The filtrate was concentrated and purification on a silica gel column eluting with ethyl acetate:hexane (1:10) furnished the pure compound **27** as a white solid (0.175 g, 98 %); m.p. 84–86 °C; IR (nujol): $\tilde{\nu}$ = 2980, 2900, 1680, 1630, 1440, 1400, 1380, 1360, 1320, 1280 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.75 (s, 1H), 4.71 (s, 1H), 3.14 (d, J = 14 Hz, 1H), 3.05–2.99 (m, 2H), 2.8 (dt, J = 13.6, 3.4 Hz, 1H), 2.65 (d, J = 14.4 Hz, 1H), 2.50 (s, 1H), 2.34 (d, J = 13.6 Hz, 1H), 1,25 (s, 6H), 1.19 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = : 216.3, 145.5, 111.0, 53.10, 44.83, 44.6, 35.7, 28.0, 27.9, 23.21, 13.3; low resolution MS m/z: 210 [M^+], 195, 182, 177, 163, 149, 140, 124, 111, 93; high resolution MS: calcd for $C_{12}H_{18}OS$. 210.1078; found 210.1080; $[\alpha]_D^{25}$ = 211° (c = 0.010 g in CH_2Cl_2).

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Transition Metal Complexes as Photosensitizers for Near-Infrared Lanthanide Luminescence**

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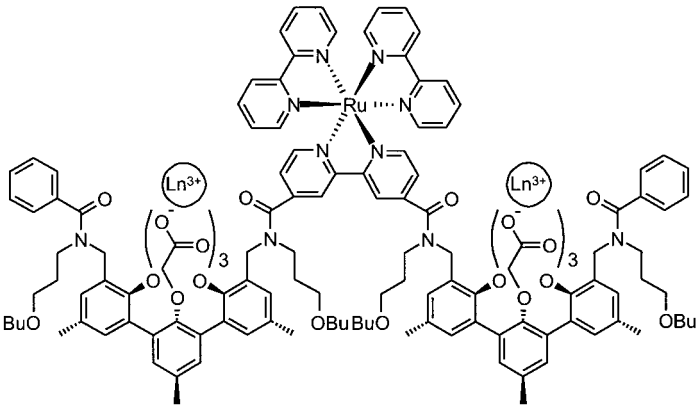
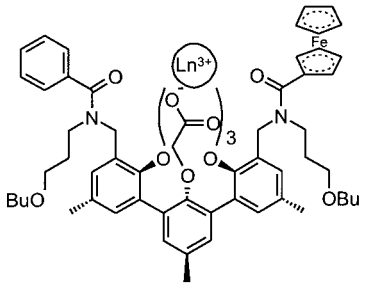
The design of sensitizer-functionalized lanthanide complexes that exhibit efficient luminescence in the near-infrared (NIR) region is currently of interest because of potential applications in fluoroimmuno-assays,[1] in laser systems,[2] and in polymer-based optical signal amplifiers.[3, 4] NIR luminescence of complexes of the lanthanide ions erbium(III), neodymium(III), and ytterbium(III) is readily observed in solution at room temperature, only when the ions are excited *indirectly* by energy transfer from the triplet state[5] of an incorporated organic chromophore (the antenna or sensitizer). Direct excitation is more demanding because of the forbidden optical transitions within the 4f subshells of lanthanide ions. As a result, the absorption coefficients are very low (typically $1-10\,M^{-1}cm^{-1}$) and the lifetimes of the excited states are relatively long (microseconds to milliseconds).

Herein, we report the first example of Nd^{III} and Yb^{III} luminescence sensitized by the transition metal complexes ruthenium(II) tris(bipyridine) ($[Ru(bpy)_3]^{2+}$) and ferrocene. Investigations of sensitizers for NIR lanthanide luminescence have focused on conjugated organic molecules, nevertheless, there are only a few examples of sensitizers that enable visible light excitation instead of near-UV excitation.[1, 4, 6, 7] The $[Ru(bpy)_3]^{2+}$ complex not only has an intersystem-crossing quantum yield near unity, but it should enable excitation of Nd^{III} and Yb^{III} with visible light of up to 500 nm. Compared to $[Ru(bpy)_3]^{2+}$, ferrocene has weaker absorption bands in the visible region,[8] but its low-lying triplet state ($E_T = 13300\,cm^{-1}$)[9] closely matches the receiving luminescent states of Nd^{III} ($11300\,cm^{-1}$) and Yb^{III} ($10250\,cm^{-1}$).

Our systems $[(Ln_2\text{-}Ru)\mathbf{1}]^{2+}$ and (Ln)**2** are based on *m*-terphenyl-based lanthanide (Ln) complexes[10–12] that are covalently linked to the transition metal complexes. Experimental and physical data can be found in the Supporting Information.



$[(Ln_2\text{-}Ru)\mathbf{1}]^{2+}$



(Ln)**2**

Excitation of the $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ and $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ complexes in deoxygenated $[D_6]$DMSO (10^{-5} M) with visible light resulted in Ln^{III}-centered NIR luminescence. Figure 1 shows the emission bands of $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ at 1060 and 1330 nm corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4I_{13/2}$ transitions of Nd^{III}, respectively, and the emission band of $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ at

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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