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The Availability of Dysprosium Diiodide as a Powerful Reducing Agent in Organic Synthesis: Reactivity Studies and Structural Analysis of DyI$_2$((DME)$_3$ and Its Naphthalene Reduction Product[1]

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Metal-based reduction chemistry in organic synthesis may be divided into two general regimes based on available reagents and their reduction potentials.[2] One class of reductants consists of the extremely powerful reagents that allow Birch reductions,[3] for example, the alkali metals in liquid ammonia, NaK and Na(Hg) alloys, and molten alkali metals. These are rather intolerant of functional group diversity. Another class of reducing systems involves SmI$_2$(THF)$_x$, which accommodates a wide range of functional groups, but is less reducing.[4] A variety of methods have been used to increase the reduction potential of SmI$_2$(THF)$_x$,[5,6] the most common being the addition of hexamethylphosphoramide (HMPA). In addition, a new divalent lanthanide reagent, TmI$_2$(THF)$_x$,[7] has recently been reported which partially narrows the gap between the Birch reductions and SmI$_2$, since Tm(II) is 0.8 V more reducing than Sm(II).[8] Tm(II) reagents were not considered earlier since it was only in 1997 that the first molecular complex of this highly reactive ion was definitively identified.[9] The isolation of that complex, TmI$_2$(DME)$_3$, led to the development of Tm(II) chemistry which now includes facile in situ synthesis of TmI$_2$(THF)$_X$ [7] analogous to the commonly used SmI$_2$(THF)$_2$.[4]

To further narrow the gap between the Birch-type reductants and the Sm(II)/Tm(II) reagents using lanthanide metals would require access to Ln(II) ions significantly more difficult to isolate than Tm(II). Although divalent ions of most of the lanthanides have been reported to form under extreme conditions in solid-state lattices,[10] isolation of easily accessible, soluble forms that would be used in organic synthesis seemed unlikely. However, Bochkarev and co-workers have recently reported that a soluble Dy(II) complex can be obtained from Dy/I$_2$ reactions which occur at temperatures up to 1500 °C.[11] Although the analytical and spectroscopic data were consistent with Dy(II), the existence of this ion could not be established by magnetic data since the Dy(II) and Dy(III) ions coincidentally have the same magnetic moment and definitive structural data were elusive. Since several incorrect claims of unusual oxidation states of f element complexes have been made in the past based only on spectroscopy, we wanted crystallographic confirmation of the existence this ion before its use in organic synthesis was examined.

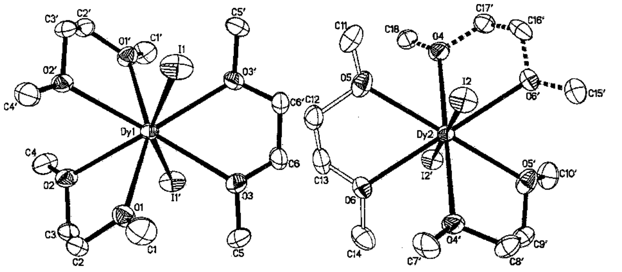

Figure 1. Structure of DyI$_2$(DME)$_3$ with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Dy1−O1, 2.587(2); Dy1−O2, 2.603(2); Dy1−O3, 2.622(2) Dy1−I1, 3.2628(3); Dy2−O4, 2.585(2); Dy2−O5, 2.630(2); Dy2−O6, 2.678(21); Dy2−I2, 3.2371(3); I1−Dy1−I1′, 157.322(12); I2−Dy2−I2,′ 180.000(9).

We report here the first crystallographic data on a molecular complex of Dy(II) as well as a more convenient synthesis of solid DyI$_2$ that allows it to be stored as a solid and conveniently solubilized for use in organic syntheses. We also describe some preliminary reactions that demonstrate the utility of this reagent in organic synthesis including the reduction of naphthalene.

Crystals of DyI$_2$(DME)$_3$,[12] prepared by the method of Bochkarev, were grown from DME at −20 °C in a nitrogen-containing glovebox over a period of 36 h. These crystals were found to be isomorphous with SmI$_2$(DME)$_3$.[13] Since we were suspicious that we could actually isolate such a reactive species, the same crystal examined by X-ray diffraction was also examined by energy dispersive absorption X-ray spectroscopy (EDAX) which confirmed that it was truly a dysprosium complex. DyI$_2$(DME)$_3$, like its samarium analogue, has an unusual structure in which there are two independent molecules in the unit cell, one of which has a linear I−Dy−I component and the other which has a bent I−Dy−I moiety, Figure 1. Each molecule has three chelating DME ligands that generate a hexagonal bipyramidal geometry in the linear I−Dy−I case and a distorted dodecahedral geometry in the bent I−Dy−I system. This differs from the structure of TmI$_2$(DME)$_3$ which contains one η^1-DME and is 7-coordinate.[8] This difference is consistent with the smaller radial size of Tm.[14]

Once the existence of DyI$_2$(DME)$_3$ was crystallographically established, we sought a more convenient preparation that would allow it to be used as a routine reagent. Solid DyI$_2$ can be conveniently prepared in multigram quantities by reacting dysprosium filings and iodine in an alumina or quartz crucible contained within a quartz tube connected to a Schlenk line.[15] The solid mass of DyI$_2$ that forms can be easily separated from residual metal. The DyI$_2$ can be crushed with a mortar and pestle under an inert atmosphere and stored for long periods under nitrogen until needed.

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(12) Experimental data for DyI$_2$(DME)$_3$: IR (Nujol): 1471m, 1444s, 1374s, 1301w, 1282w, 1239w, 1193w, 1116m, 1058s, 1027m, 860s, 722s cm^{-1}; UV/Vis (DME): λ = 412, 476, 577, 716 nm; Calcd for DyIC$_{12}$H$_{30}$O$_6$: C, 20.99; H, 4.40; I, 36.96; Dy, 23.66. Found: C, 20.81; H, 4.29; I, 37.11; Dy, 24.4. DyI$_2$(DME)$_3$ crystallizes in the space group $C2/c$ with a = 24.9195(13) Å, b = 13.0439(7) Å, c = 14.4466(8) Å, α = 90°, β = 115.8070(10)° γ = 90°, V = 4227.5(4) Å^3 and ρ_{calcd} = 2.158 g/cm^3 for Z = 8 at 163 K. At convergence, wR2 = 0.0592 and GOF = 1.033 for 246 variables refined against 5091 data (As a comparison for refinement on F, R1 = 0.0232 for those 4501 data with $I > 2.0\sigma(I)$).

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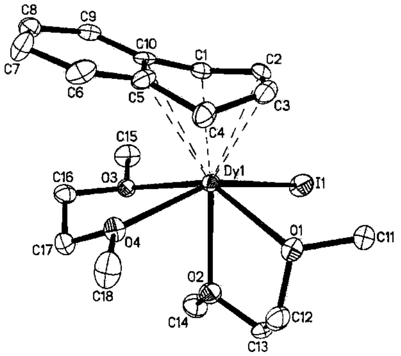
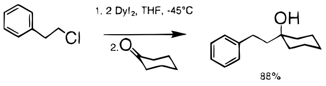


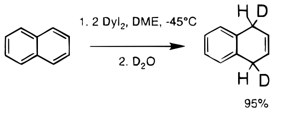
Figure 2. Structure of $(C_{10}H_8)DyI(DME)_2$ with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Dy−O1, 2.467(3); Dy−O2, 2.562(4); Dy−O3, 2.411(3); Dy−O4, 2.430(3); Dy−C1, 2.510(5); Dy−C2, 2.599(5); Dy−C3, 2.605(5); Dy−C4, 2.486(5); Dy−C5, 2.992(5); Dy−C10, 3.002(4); Dy−I, 3.1382(4).

Since solutions of DyI_2 are so reactive, they should be prepared immediately before use. DyI_2 may be used conveniently by making a saturated solution in THF or DME at temperatures below −20 °C. The solubility of DyI_2 in THF is 0.025 M at −45 °C. The utility of $DyI_2(THF)_x$ in ketone coupling reactions with alkyl halides appears to be similar to that of $TmI_2(THF)_x$ [7] except that Dy(II) is much more reactive. Hence, reductions of alkyl chlorides that take 60 min at 0 °C with $TmI_2(THF)_x$ and would not occur at all with $SmI_2(THF)_x$/HMPA,[16] proceed immediately at −45 °C with $DyI_2(THF)_x$. For example, addition of 2-chloroethylbenzene to $DyI_2(THF)_x$ at −45 °C immediately dissipates the dark green color. After reaction with cyclohexanone an 88% isolated yield of the coupled product, phenethylcyclohexanol, is obtained (eq 1).[17]



(1)

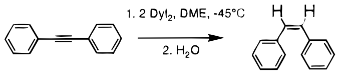
DyI_2 in DME is a strong enough reductant to immediately react with naphthalene at −45 °C to form a dark purple solution from which $(C_{10}H_8)DyI(DME)_2$,[18] Figure 2, crystallizes at −20 °C. Since addition of D_2O generated 1,4-dideuteronaphthalene, eq 2, this reaction is equivalent to a Birch reduction.



(2)

The isolation of a naphthalenide dianion complex is not unique in f element chemistry and several examples are known.[19] However, in each case, these have been formed by reduction of naphthalene with an alkali metal and reaction of the alkali metal naphthalene dianion with an f element halide or by reaction of the lanthanide metal with naphthalene in liquid ammonia. This is the first case in which a low-oxidation state lanthanide metal complex has reduced naphthalene directly in ethereal solvents.

$DyI_2(DME)_3$ alone does not appear to reduce benzene or anisoles, but it will reduce alkynes. Reduction of PhC≡CPh followed by hydrolysis forms exclusively *cis*-stilbene, eq 3.



(3)

In summary, the existence of a molecular complex of Dy(II), namely $DyI_2(DME)_3$, has been established and a convenient protocol has been developed so that DyI_2 can be used like $SmI_2(THF)_x$ in THF or DME. Preliminary reactivity studies show that this reagent provides an option for metal-based reductions in organic synthesis that is intermediate between Birch reducing agents and Sm(II)/Tm(II) reagents. It is expected that, as in the case of $SmI_2(THF)_x$,[4] the unique utility of DyI_2 in reductive organic synthesis will become more fully defined as this reagent is more thoroughly examined.

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Supporting Information Available: Coupling procedure, tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) DyI_2. In air, Dy filings (3.0 g, 18.4 mmol) were spread evenly in a layer on the bottom of a 10-mL alumina or quartz crucible. Iodine (4.75 g, 18.7 mmol) was then layered on top of the metal. The charged crucible was placed in a 20 × 4.5 cm quartz test tube fitted with a 55/50 joint which is connected to a trap and a Schlenk line in a well-shielded hood. The tube was evacuated and refilled with N_2 three times to remove oxygen. During the synthesis, the apparatus was under a nitrogen atmosphere connected to a mineral oil bubbler. The apparatus was tipped at a 60° angle to avoid directly heating the joint and the bottom of the tube containing the crucible was heated with a Meeker burner at maximum heat. The tube initially fills with I_2 vapor and a bright light flash indicates ignition of the metal. Heating is continued at the bottom of the tube for about 2 min, during which time I_2 is consumed. Vacuum is then applied to transfer unreacted I_2 to the trap. A nitrogen atmosphere is reestablished in the vessel and heating is continued for 15 min during which time part of the mixture melts. The system is allowed to cool to room temperature and the apparatus is transferred to a nitrogen-filled glovebox. The solid mass of DyI_2 is removed from the crucible with a spatula and crushed with a mortar and pestle. The unreacted metal (1.25 g), which is left as a nugget, is easily identified and removed while the DyI_2 is being ground. DyI_2 (3.8 g, 85% based on metal consumed) is recovered as a violet powder suitable for synthetic reactions. Since solutions in DME or THF are light and temperature sensitive, they should be prepared immediately before use.

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(17) The procedure follows that in ref 7 and is described in the Supporting Information.

(18) $(C_{10}H_8)DyI(DME)_2$. In a glovebox, addition of naphthalene (0.017 g, 0.13 mmol) to a dark khaki green solution of DyI_2 (0.14 g, 0.33 mmol) in DME (15 mL) at −20 °C caused an immediate color change to violet. After 0.5 h, light gray insoluble materials (90 mg, 90% if $DyI_3(DME)_x$) were removed. The solvent was removed in vacuo leaving a purple solid (75 mg, 95%). Dissolution of the solid in DME followed by cooling to −20 °C yielded crystals suitable for X-ray diffraction. IR (Nujol): 1459s, 1378s, 1339w, 1270m, 1239w, 1185w, 1112m, 1027s, 976w, 849s, 780m, 760w, 737m, 695w cm^{-1}; UV/Vis (DME): $\lambda = 508, 904, 939$ nm. Calcd for $C_{18}H_{28}O_4DyI$: Dy, 27.18. Found: Dy 28.4. $(C_{10}H_8)DyI(DME)_2$ crystallizes in the space group $Pca2_1$ with $a = 15.0111(7)$ Å, $b = 9.8564(5)$ Å, $c = 13.8731(7)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. $V = 2052.60(18)$ Å^3 and $\rho_{calcd} = 1.934$ g/cm^3 for $Z = 4$ at 163 K. The hydrogen atoms associated with carbon atoms C(1) and C(4) could not be located or placed accurately and were not included in the refinement. At convergence, wR2 = 0.0538 and GOF = 1.068 for 218 variables refined against 4717 independent data (As a comparison for refinement on F, R1 = 0.0257 for those 4368 data with $I > 2.0\sigma(I)$).

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