Organolanthanoid-halide synthons—a new general route to monofunctionalized lanthanoid(II) compounds?†

Michal Wiecko,* Glen B. Deacon and Peter C. Junk*

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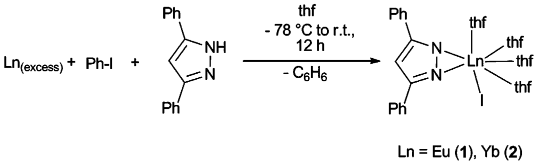
New Eu^{II} and Yb^{II} complexes $[Ln(Ph_2pz)I(thf)_4]$ were synthesized from the corresponding metals and 3,5-diphenylpyrazole (HPh_2pz) using iodobenzene as oxidizing agent. In the absence of the pyrazole, the charge separated Yb^{II}/Yb^{III} complex $[\{Yb(dme)_4\}\{YbPh_4(dme)\}_2]$ has been isolated.

The $+2/+3$ mixed valence species formed by the oxidation of the lanthanoid (Ln) metals Eu, Sm and Yb by organic halides such as PhI, MeI or $2,6\text{-}Me_2C_6H_3I$[1] have been investigated in a number of organic and inorganic transformations.[2] In many cases they show a similar reactivity towards electrophiles and acids as the well known Mg based reagents[3] and are therefore formulated as *Grignard* analogues "RLnI".[4] However the thermal lability of the Ln–C σ-bond[5] has limited pure, structurally defined products maintaining the Ln–C σ bond to compounds derived from bulky iodides. To our knowledge, the only crystallographically characterized examples are the dimeric $[Yb\{C(SiMe_3)_2(SiMe_2X\}I(OEt_2)]_2$ (X = CH=CH$_2$, OMe)[6] and both $[Yb(2,6\text{-}Ph_2C_6H_3)(thf)_3I]$ and $[Eu(2,6\text{-}Ph_2C_6H_3)_2(thf)_2]$ reported by Niemeyer, who also described a Schlenk equilibrium in these systems.[7] For calcium, which has much similar chemistry and a comparable ion size to Yb^{II},[8] more success has been achieved with the isolation and characterization of ArCaX (X = Br, I) and Ar_2Ca type complexes[9] through the use of activated Ca metal and benefiting from the absence of Ca^{2+} redox chemistry. Nevertheless, putative "PhLnI" (Ln = Eu, Yb) derivatives are a potential source of functionalized Ln(L)I (L = monoanionic ligand) compounds by protolysis reactions. Following initial results,[10] we now report syntheses and structures of $[Ln(Ph_2pz)I(thf)_4]$ (Ln = Eu, Yb; Ph_2pz = 3,5-diphenylpyrazolate), as well as isolation of a charge separated phenylytterbium(II/III) complex from reaction of Yb metal with iodobenzene in 1,2-dimethoxyethane (dme). The former demonstrates the synthetic potential of these systems in metal–organic chemistry whilst the latter demonstrates the mixed oxidation state nature of "PhYbI".

Sonication of a mixture of Yb or Eu metal and PhI at −78 °C in thf results in a quick formation of dark red or red brown solutions. When 3,5-diphenylpyrazole was added immediately to this mixture, straightforward formation of the desired Ln^{II} complexes $[Ln(Ph_2pz)I(thf)_4]$ (Ln = Eu (**1**), Yb (**2**))‡ occurred which were isolated after 12 h (Scheme 1).



Scheme 1

Both compounds were isolated in very good yields from the reaction mixture by filtration from some residual metal and crystallization from concentrated thf solution. By contrast, on attempting to obtain Yb^{II} and Eu^{II} complexes of a general composition $[Ln(L)I(solvent)_x]$, redistribution reactions giving solvated LnL_2 and LnI_2 are often observed.[11] X-Ray crystallographic studies§ show that **1** and **2** are isostructural in the solid state (Fig. 1).

The structures exhibit some surprising features since, especially for complexes with the larger Eu^{2+} cation, formation of halide[6,12] or ligand[13] bridged dimers is usually favoured over additional solvent coordination. Such is not the case for **1** and **2**. The compounds crystallize in monomeric units with a high degree of metal centre solvation having four coordinating thf molecules. The formally seven coordinate complex has a *cis* pseudo octahedral arrangement. A monomeric structure is favoured by steric effects. The sum of the ligand steric coordination numbers[14] is a reasonable 7.5 for **1** and **2**, whereas an iodide bridged eight coordinate dimer would have a value of 8.5 indicating crowding. The observed η^2-coordination

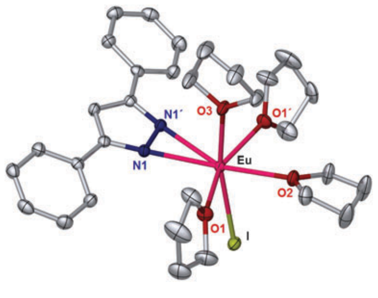


Fig. 1 Solid state structure of **1**. Drawn with ellipsoids at 50% probability and hydrogen atoms omitted. Selected bond distances [Å] and angles [°] for **1** and isostructural **2**: **1**: Eu–N1 2.5353(17), Eu–O1 2.5770(14), Eu–O2 2.616(2), Eu–O3 2.558(2), Eu–I 3.1983(2), N1–Eu–N1′ 31.58(8), O1–Eu–O1′ 155.81(7), O1–Eu–O3 86.64(4), O3–Eu–I 168.42(5), N1–Eu–I 108.60(4). **2**: Yb–N1 2.433(3), Yb–O1 2.473(3), Yb–O2 2.518(4), Yb–O3 2.441(4), Yb–I 3.0966(4), N1–N1′ 1.383(6); N1–Yb–N1′ 33.02(15), O1–Yb–O1′ 156.09(13), O1–Yb–O3 86.91(7), O3–Yb–I 168.48(9), N1–Yb–I 106.42(7).

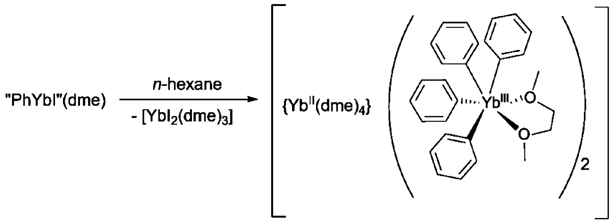
School of Chemistry, Monash University, Clayton, Victoria 3800, Australia. E-mail: peter.junk@sci.monash.edu.au, mwiecko@freenet.de; Fax: +61 (03)99054597; Tel: +61 (03)99054570

† Electronic supplementary information (ESI) available: Details of the structure determination for **1–3**. CCDC 776742–776744. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01317j

of the $\{Ph_2pz\}^-$ ligand is highly symmetric, as indicated by the crystallographic mirror plane bisecting the N–N vector.

The reaction depicted in Scheme 1 presumably proceeds *via* an initial formation of the +2/+3 mixed valent, temperature sensitive reagent "PhLnI(thf)$_n$" followed by a ligand exchange of Ph^- with HPh_2pz with concomitant formation of C_6H_6 and a subsequent reduction of remaining Ln^{III} species by residual Ln metal. To further understand the nature of "PhYbI(thf)$_n$" we decided to study the reaction mixtures in more detail. Components of "PhYbI(thf)$_n$" were crystallized by addition of a few mL of *n*-hexane. Along with amorphous material, abundant crystals of $[YbPh_3(thf)_3]$[15] and $[YbI_2(thf)_4]$[16] were found in the resulting solid. To identify decomposition or side products we also investigated hydrolysis products of "PhYbI(thf)$_n$" and a concentrated filtrate following isolation of **2**, by GC/MS. Qualitatively the data show the expected benzene and the byproduct biphenyl. While some components could not be identified the data indicate that some phenyl-tetrahydrofuran was formed, which could be a Wurtz coupling product of short-lived α-metallated thf with PhI.[17]

With the goal of stabilizing PhYbI or $YbPh_2$ type species with a bidentate donor, we alternatively performed the oxidation of Yb metal with PhI in dme. Fractional crystallization of "PhYbI(dme)$_n$" from dme/*n*-hexane at −25 °C gave $[YbI_2(dme)_3]$[18] and subsequently the charge separated $[\{Yb^{II}(dme)_4\}\{Yb^{III}Ph_4(dme)\}_2]$ (**3**) in low isolated yield (Scheme 2 and Fig. 2). Mixed oxidation state rare earth(II/III) metal–organic compounds are uncommon, especially charge separated complexes.[19]



3

Scheme 2

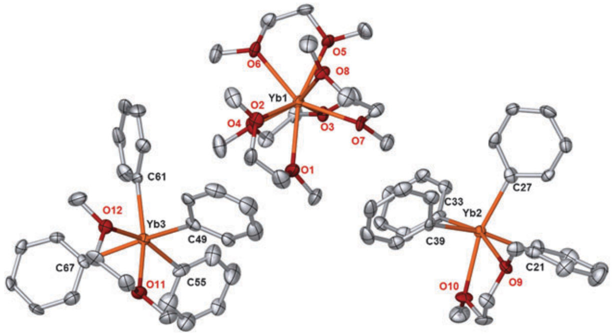


Fig. 2 Solid state structure of **3**. Drawn with ellipsoids at 50% probability and hydrogen atoms omitted. Selected bond distances [Å] and angles [°] for the anion around Yb2: Yb2–O9 2.441(5), Yb2–O10 2.481(6), Yb2–C21 2.458(9), Yb2–C27 2.427(9), Yb2–C33 2.432(8), Yb2–C39 2.475(9); O9–Yb2–O10 66.94(18), C21–Yb2–O9 85.2(2), C27–Yb2–O9 95.4(2), C33–Yb2–O9 157.2(3), C39–Yb2–O9 81.3(2), C21–Yb2–O10 82.1(3), C27–Yb2–O10 161.3(2), C33–Yb2–O10 91.5(2), C39–Yb2–O10 87.8(2), C21–Yb2–C27 90.9(3), C21–Yb2–C33 99.7(3), C21–Yb2–C39 165.5(3), C27–Yb2–C33 106.8(3), C27–Yb2–C39 95.6(3), C33–Yb2–C39 90.8(3).

In the solid state **3** consists of distinct ionic units with the phenyl ligands attached to the Yb^{III} centres which is presumably favoured by the ionic character of the Yb–C bonds and by the higher charge and smaller ionic radius of Yb^{3+}. The Yb–C bond distances ranging from 2.41 to 2.48 Å are slightly longer than in $[YbPh_3(thf)_3]$,[15] presumably due to the negative charge on the fragment. Compound **3** is chemically related to $[Yb_2Ph_5(thf)_4]$[20] which also contains Yb in both stable oxidation states forming a molecular dinuclear species whereas **3** contains solvent separated ionic units. A comparison of the ligand geometry of the $\{Yb(dme)_4\}^{2+}$ cation (average Yb–O 2.52 Å) with the only literature example $[Yb(dme)_4][Hg_2(C_6H_5Se)_6]$ ($\langle$Yb–O$\rangle$ = 2.51 Å)[21] verifies the assignment of the oxidation states of this cation in **3**.

The ^{171}Yb-NMR spectrum of **3** at −30 °C shows a sharp resonance at δ = 476 ppm for the $\{Yb(dme)_4\}^{2+}$ ion while resonances for the anions containing paramagnetic Yb^{III} could not be observed. While solid **3** can be stored at low temperature for several days, solutions in dme slowly decompose at −30 °C forming a dark viscous solid.

As shown by GC/MS experiments performed after hydrolysis of the dme reaction mixture a much more complicated mixture of byproducts is formed (ESI†).[22] Polyaromatic compounds such as 1,4-$Ph_2C_6H_4$ or 1,3,5-triphenyl-benzene indicate a complex and as yet unclear decomposition mechanism of "PhYbI(dme)$_n$" even if handled at −78 °C.

The formation of **3** supports the view that both Ln^{II} and Ln^{III} species are present in solutions of "PhLnI". However, the isolation of **1** and **2** shows that this evidently does not diminish the value of "PhLnI" reagents as precursors for functionalized Ln^{II} iodide species, which can then be used in further reactions, *e.g.* as reducing agents or metathesis reagents. To increase the reaction scope of the organolanthanoid-halide route we are currently investigating other ligand systems and alternative commercially available organic halides in analogous reactions.

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Notes and references

‡ *Preparation of* **1** *and* **2**: Eu metal filings (380 mg, 2.5 mmol) were suspended in thf (20 mL) and at −78 °C PhI (408 mg, 2.0 mmol) was added. The mixture was sonicated for 10 s developing a red-brown colour. Solid HPh_2pz (440 mg, 2.0 mmol) was added and the mixture stirred at −78 °C for another 3 h and at rt overnight. Filtration through a pad of Celite and concentration resulted in the formation of large yellow crystals. Further concentration of the mother liquor yielded 1.21 g (76%) **1**. IR (Nujol): 1600 (m), 1531 (m), 1512 (w), 1260 (m), 1172 (w), 1073 (m), 1041 (s), 878 (m), 774 (m), 702 (w). Anal. calcd for $C_{27}H_{35}IN_2O_3Eu$ (**1**–THF): C, 45.39; H, 4.94; N, 3.92%. Found: C, 45.40; H, 5.17; N, 3.75%. **2** was prepared accordingly yielding 1.40 g (87%) as orange crystals. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ = 1.27 (br, 16H, THF), 3.52 (br, 16H, THF), 7.10 (t, J = 6.7 Hz, 2H, *p*-H), 7.14 (s, 1H, pz-H), 7.24 (dd, J = 6.7, 7.4 Hz, 4H, *m*-H), 8.08 (d, J = 7.4 Hz, 4H, *o*-H). ^{13}C-NMR (100.4 MHz, C_6D_6, 25 °C): 25.7 (THF), 68.5 (THF), 102.3 (pz-*C*H), 125.8, 126.6, 129.1, 136.3 (Ph). IR (Nujol): 1600 (m), 1512 (m), 1172 (m), 1039 (s), 874 (s),

774 (s), 703 (m). Anal. calcd for $C_{31}H_{43}IN_2O_4Yb$: C, 46.10; H, 5.37; N, 3.47%. Found: C, 45.39; H, 5.26; N, 3.57%. *Preparation of* **3**: Yb metal (430 mg, 2.5 mmol) was suspended in dme (15 mL) and at −78 °C PhI (408 mg, 2.0 mmol) was added. The mixture was placed in a sonic bath immediately developing a yellow-brown colour. Sonication for 3 h at around −78 °C resulted in a dark red-brown mixture which was pump-filtered through a glass frit to remove residual metal and colourless precipitate containing $[YbI_2(dme)_3]$. The solution was topped with 5 mL of *n*-hexane. Upon storage at −25 °C overnight some colourless crystals of $[YbI_2(dme)_3]$ (unit cell identification[18]; ^{171}Yb-NMR (dme), 52.6 MHz, −30 °C: δ = 380 ppm) and light brown single crystals of **3** had formed. The compounds were separated manually in a glovebox yielding 25 mg (5%) **3**. ^{171}Yb-NMR (dme), 52.6 MHz, −30 °C: δ = 476 ppm. Anal. calcd for $C_{72}H_{100}O_{12}Yb_3$: Yb 30.96. Found: Yb 31.34% (too unstable for C,H,N microanalysis).

§ *Crystal data for* **1–3**: Bruker X8 Apex II CCD, MoKα radiation, λ = 0.71073 Å. **1**: $C_{31}H_{43}EuIN_2O_4$, M = 786.53, yellow prism, 1.00 × 0.50 × 0.50 mm, orthorhombic, *Pmn*21 (No. 31), a = 17.7513(3), b = 8.7645(2), c = 10.3139(2) Å, V = 1604.65(6) Å^3, Z = 2, D_c = 1.628 g cm^{-3}, F_{000} = 782, T = 123(1) K, $2\theta_{max}$ = 55.0°, 13 764 reflections, 3616 unique (R_{int} = 0.0204). Final *GooF* = 1.060, R_1 [$I > 2\sigma(I)$] = 0.0136, wR_2 (all data) = 0.0319. **2**: $C_{31}H_{43}IN_2O_4Yb$, M = 807.61, orange prism, 0.50 × 0.50 × 0.30 mm, orthorhombic, *Pmn*21 (No. 31), a = 17.6761(8), b = 8.7327(4), c = 10.1877(5) Å, V = 1572.57(13) Å^3, Z = 2, D_c = 1.706 g cm^{-3}, F_{000} = 796, T = 123(1) K, $2\theta_{max}$ = 55.0°, 13 478 reflections, 3722 unique (R_{int} = 0.0492). Final *GooF* = 1.002, R_1 [$I > 2\sigma(I)$] = 0.0246, wR_2 (all data) = 0.0489. 2(**3**.dme): $C_{152}H_{220}O_{28}Yb_6$, M = 3533.52, brown prism, 0.20 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 20.1461(7), b = 20.3068(6), c = 22.5761(12) Å, α = 110.121(2)°, β = 103.298(2)°, γ = 106.657(2)°, V = 7734.1(5) Å^3, Z = 2, D_c = 1.517, F_{000} = 3552, T = 123(1) K, $2\theta_{max}$ = 50.0°, 54 801 reflections, 27 110 unique (R_{int} = 0.0578). Final *GooF* = 0.992, R_1 [$I > 2\sigma(I)$] = 0.0485, wR_2 (all data) = 0.0972.

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