Reductive coupling of carbodiimides with metallic lithium: a new route to metal oxalamidino complexes

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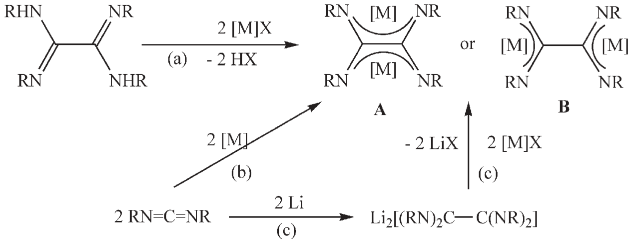
Carbodiimides $(RN)_2C$ were reductively coupled with Li powder into $[\{Li(py)_2\}_2(\mu\text{-}C_2N_4R_4)]$ (R = *p*-tolyl) (1) and $[\{Li(THF)\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy) (2), and 2 reacted with UCl_4 to give $[Li(py)_4]_2[\{UCl_4(py)\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy) (3); the crystal structures of 1 and 3·2py, the first oxalamidino compounds of an alkali metal and of a 5f-element, have been determined.

Oxalic amidinate complexes of d transition metals have recently received increasing attention for their efficient catalytic activity in olefin polymerization reactions.[1] Such "non-metallocene" catalysts are attractive because of the easy modification of both their steric and electronic properties through changes to the substituents on the nitrogen atoms. Almost all the oxalamidinate ligands have been synthesized by deprotonation of the corresponding oxalic amidines [pathway (a) in Scheme 1].[1,2] Only two examples were prepared by reductive coupling of carbodiimides [pathway (b)] and are found in the dinuclear complexes $[\{Ti(C_5H_5)_2\}_2(\mu\text{-}C_2N_4R_4)]$ (R = *p*-tolyl)[3] and $[\{Sm(C_5H_4Me)_2(HMPA)\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy, Pr^i),[4] where the bridging ligand acts as a diamide (**A**) or a diamidinate (**B**) ligand, respectively. The route (b) is elegant but requires the often not easy preparation of metals in a low oxidation state. We have found that carbodiimides $(RN)_2C$ can be reductively coupled with metallic lithium into the oxalylamidine dianions $[(RN)_2C\text{–}C(NR)_2]^{2-}$ which are clearly useful for the preparation of dinuclear oxalamidino complexes. As an illustration of this new synthetic route (c), we present here the synthesis of $[\{Li(py)_2\}_2(\mu\text{-}C_2N_4R_4)]$ (R = *p*-tolyl) (**1**), $[\{Li(THF)\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy) (**2**) and $[Li(py)_4]_2[\{UCl_4(py)\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy) (**3**), the first oxalamidinate complexes of an alkali metal and of a 5f-element; we also describe the X-ray crystal structures of **1** and a pyridine solvate of **3**.



Scheme 1 Different routes to metal oxalamidino compounds.

Treatment of *N*,*N′*-di(*p*-tolyl)carbodiimide with 1 mol. equivalent of lithium powder in THF gave a mixture of not yet identified products. The same reaction with 0.75 mol. equivalent of Li afforded, after evaporation of the solvent and crystallization of the residue from pyridine–pentane, light yellow crystals of **1**, suitable for X-ray diffraction analysis.† A view of **1** is shown in Fig. 1 with selected bond distances and angles.‡ The complex is found in the diamide structure of type **A**, which is that adopted by almost all the metal oxalamidino compounds. The C_2N_4 unit is planar with a maximum deviation of 0.05 Å and the lithium atoms Li1 and Li2 are slightly displaced on each side of this plane by 0.081(5) and −0.145(5) Å, respectively. The complete electronic delocalization over the two CN_2 subunits is indicated by the average C–N distance of 1.329(9) Å, intermediate between those of a double and a single bond; the C–C distance is typical of a single bond. Two pyridine molecules are coordinated to the Li atoms which are in the usual tetrahedral configuration. The Li–N(py) distances are *ca.* 0.1 Å larger than the Li–N(oxalamidinate) distances; the average value of the latter, 1.992(11) Å, can be compared with that of 2.05(9) Å in the lithiated diamide $[Li_2(Et_2O)_3\{R^1N(R^2R^3N)C{=}C(NR^2R^3)NR^1\}]$ (R^1 = *p*-tolyl, R^2 = Ph, R^3 = Me).[5]

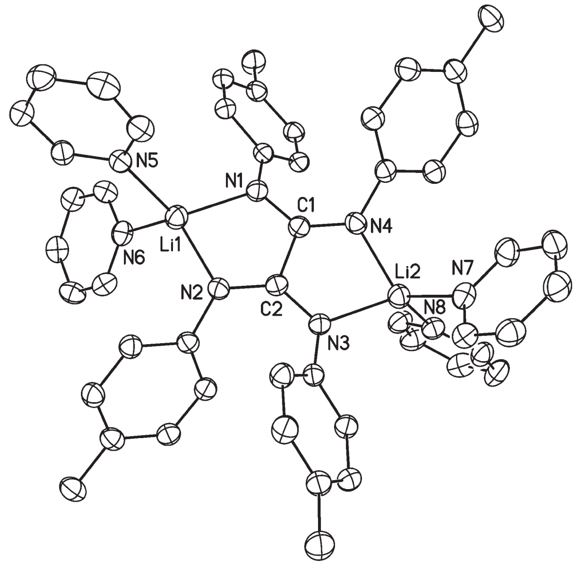


Fig. 1 View of **1**. Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Li1–N1 2.009(5), Li1–N2 1.992(4), Li2–N3 1.979(5), Li2–N4 1.987(5), C1–N1 1.340(3), C1–N4 1.318(3), C2–N2 1.323(3), C2–N3 1.333(3), C1–C2 1.545(3); N1–Li1–N2 82.80(18), N3–Li2–N4 82.66(18).

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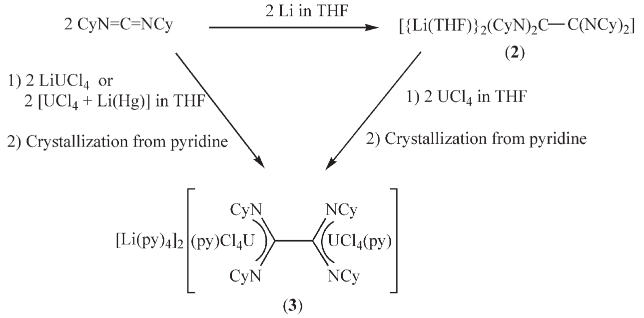
In contrast to **1**, the dilithium salt **2** was isolated in almost quantitative yield as an analytically pure microcrystalline powder from an equimolar mixture of *N*,*N*′-dicyclohexylcarbodiimide and lithium powder in THF.[†] The use of excess metal was not detrimental to the reaction, and **2** was recovered in a pure form after filtration and evaporation of the solution.

Compound **2** was reacted with 2 mol. equivalent of UCl_4 in THF; after evaporation of the green solution to dryness, the microcrystalline powder was dissolved in pyridine and dark green crystals of **3**·2py were obtained in 94% yield upon addition of pentane (Scheme 2). Because UCl_4 can be reduced into $LiUCl_4$ (or UCl_3 + LiCl),[6] it was possible to prepare **3** by reaction of these uranium(III) chlorides with $(CyN)_2C$. The reductive coupling of the carbodiimide is similar to that which gives the aforementioned $\mathrm{Ti^{III}}$ and $\mathrm{Sm^{III}}$ complexes, from $\mathrm{Ti^{II}}$ and $\mathrm{Sm^{II}}$. The reaction was carried out either in two steps, *i.e.* reduction of UCl_4 with lithium amalgam followed by addition of $(CyN)_2C$, or in a one-pot procedure by mixing all the three reactants in THF; after usual work-up, crystals of **3**·2py were isolated with yields larger than 90%. It is noteworthy that the carbodiimide molecule is not reduced by Li(Hg) under these experimental conditions. The synthesis of **3** is reminiscent of that of the diuranium(IV) pinacolate complex $[\{UCl_3(THF)_2\}_2(\mu\text{-}OCMe_2CMe_2O)]$ which was obtained either by reacting acetone with the UCl_4–Li(Hg) system or by treatment of UCl_4 with 0.5 mol. equivalent of the dilithium pinacolate.[7]

A view of one of the two independent and quite identical dianions in the crystal structure of **3**·2py is shown in Fig. 2 with selected bond lengths and angles. Both anions possess a binary axis containing the two uranium atoms, the two central carbon atoms of the diamidinate ligand and the nitrogen atoms of the coordinated pyridine molecules. Complex **3** is, after the aforementioned samarium(III) compound, a new example of crystallographically characterized oxalamidino complex which exhibits the type **B** diamidinate structure. The two $(CyN)_2C$ fragments of the bridging tetradentate ligand are nearly perpendicular to one another, the dihedral angles between the two UN_2C mean planes being 89.9(4) and 88.2(4)° in the two anions, respectively; such a geometry minimizes the interactions between the cyclohexyl groups. The C–N and C–C distances within the C_2N_4 unit are very close to those measured in **1** and the samarium compound. The uranium atoms are hepta-coordinate in a distorted pentagonal bipyramidal configuration in which two chlorine atoms and the three nitrogen atoms define the basal plane and the other two chlorine atoms are in apical positions. The U–N(py) and U–Cl bond lengths, which average 2.68(3) and 2.66(2) Å, respectively, are unexceptional for U(IV) complexes and may be compared with those of 2.702(1) and 2.638(4) Å in $[UCl_4(py)_4]$.[8] The mean U–N(oxalamidino) bond length [2.417(7) Å] matches that in the uranium(IV) trisamidinate $[U\{MeC(NCy)_2\}_3Cl]$ [2.43(4) Å].[9]



Scheme 2 Synthesis of the lithium and uranium oxalamidinate complexes **2** and **3**.

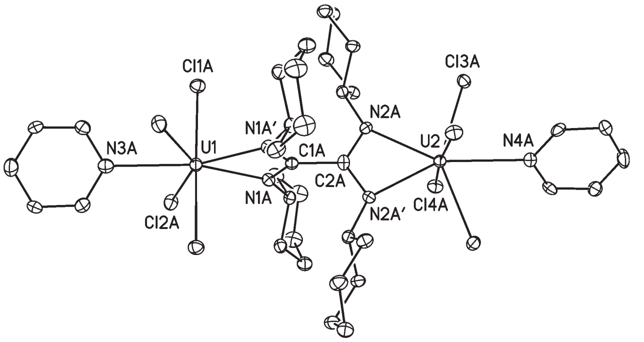


Fig. 2 View of one of the two independent dianions in **3**·2py. Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ′ = 0.5 − *x*, *y*, 1.5 − *z*. Selected bond lengths (Å) and angles (°): U1–Cl1A 2.6387(19), U1–Cl2A 2.6923(15), U2–Cl3A 2.6754(17), U2–Cl4A 2.6429(16), U1–N1A 2.411(4), U2–N2A 2.428(4), U1–N3A 2.646(7), U2–N4A 2.690(6), C1A–C2A 1.534(11), C1A–N1A 1.327(6), C2A–N2A 1.337(6); N1A–U1–N1A′ 55.9(2), N2A–U2–N2A′ 55.7(3).

In conclusion, the syntheses of the first oxalamidinate complexes of an alkali metal and of a 5f-element show that carbodiimides can be reductively coupled with lithium metal into the lithium salts of oxalic amidinates which are useful for the preparation of metal oxalamidino compounds. This new synthetic route is particularly attractive for metal ions which are in their highest oxidation state or which are too stable to be easily oxidized.

Notes and references

[†] *Complex 1*. All manipulations were carried out under an atmosphere of argon. A flask was charged with *N*,*N*′-di(*p*-tolyl)carbodiimide (66.6 mg, 0.30 mmol) and Li powder (1.5 mg, 0.225 mmol) in THF. After stirring for 12 h at 20 °C, the solution was evaporated to dryness, the yellow residue dissolved in pyridine (2 mL) and light yellow crystals of **1** (30 mg, 26%) were obtained upon addition of pentane (6 mL). *Complex 2*. A flask was charged with $(CyN)_2C$ (60 mg, 0.29 mmol) and Li powder (2.1 mg, 0.29 mmol) in THF (10 mL). After stirring for 12 h at 20 °C, the solution was filtered and evaporated to dryness, leaving an off-white powder of **2** (80 mg, 96%). ^1H NMR (THF-d_8, 200 MHz): δ 3.50 (m, 2H, THF), 2.74 (m, 1H, NCH), 1.64 (m, 2H, THF), 1.48 and 0.98 (m, 5H + 5H, Cy). Anal. calc. for $C_{34}H_{60}N_4O_2Li_2$: C, 71.55; H, 10.60; N, 9.82; Li, 2.43. Found: C, 71.31; H, 10.50; N, 10.00; Li, 2.52%. *Complex 3:* (a) A flask was charged with **2** (57 mg, 0.10 mmol) and UCl_4 (76 mg, 0.20 mmol) in THF (5 mL). After 3 h at 20 °C, the solvent was evaporated off, the green residue dissolved in pyridine (2 mL) and green crystals of **3**·2py were obtained upon addition of pentane (5 mL). The crystals were filtered off and dried under vacuum, giving a green microcrystalline powder of **3** (186 mg, 94%). ^1H NMR (pyridine, 200 MHz): broad signals between +3 and −2 ppm. Anal. calc. for $C_{76}H_{94}Cl_8N_{14}Li_2U_2$: C, 46.17; H, 4.79; N, 9.92; Li, 0.70. Found: C, 46.41; H, 4.83; N, 9.99; Li, 0.83%. (b) A flask was charged with UCl_4 (38 mg, 0.10 mmol), 1% lithium amalgam (70 mg, 0.10 mmol Li) and $(CyN)_2C$ (20.6 mg, 0.10 mmol) in THF (3 mL). By following the same work-up as in (a), crystals of **3**·2py were obtained in 90% yield.

[‡] *Crystal data*: for **1**: $C_{50}H_{48}Li_2N_8$, M = 774.84, orthorhombic, space group $Pca2_1$, a = 17.7798(8), b = 15.1565(6), c = 15.7185(7) Å, V = 4235.8(3) $Å^3$, Z = 4, D_c = 1.215 g cm^{-3}, μ(Mo Kα) = 0.072 mm^{-1}, F(000) = 1640, T = 100(2) K, 4178 independent reflections out of 130067 measured reflections (R_{int} = 0.022) were used for refinement of 545 parameters, leading to $R1$ = 0.037 [3810 reflections with $I > 2\sigma(I)$], $wR2$ = 0.095 (all

data), S = 1.066, $\Delta\rho_{max}$ = 0.18, $\Delta\rho_{min}$ = −0.15 e Å^{-3}. For **3**·2py: $C_{86}H_{104}Cl_8Li_2N_{16}U_2$, M = 2135.39, monoclinic, space group $P2/n$, a = 15.4340(5), b = 24.5917(5), c = 25.6952(7) Å, β = 107.322(2)°, V = 9310.3(4) Å^3, Z = 4, D_c = 1.523 g cm^{-3}, μ(Mo Kα) = 3.755 mm^{-1}, F(000) = 4232, T = 100(2) K, 17403 independent reflections out of 136445 measured reflections (R_{int} = 0.084) were used for refinement of 1035 parameters, leading to $R1$ = 0.039 [10272 reflections with $I > 2\sigma(I)$], $wR2$ = 0.076 (all data), S = 0.975, $\Delta\rho_{max}$ = 0.49, $\Delta\rho_{min}$ = −0.88 e Å^{-3}. Data were recorded on a Nonius Kappa-CCD area detector diffractometer and the structures were solved by direct methods and refined by full-matrix least-squares on F^2. CCDC 287348 and 287349. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515285b

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