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Dinitrogen Reduction and C–H Activation by the Divalent Organoneodymium Complex [$(C_5H_2t\mathrm{Bu}_3)_2\mathrm{Nd}(\mu\text{-I})\mathrm{K}([18]\mathrm{crown}\text{-}6)$]**

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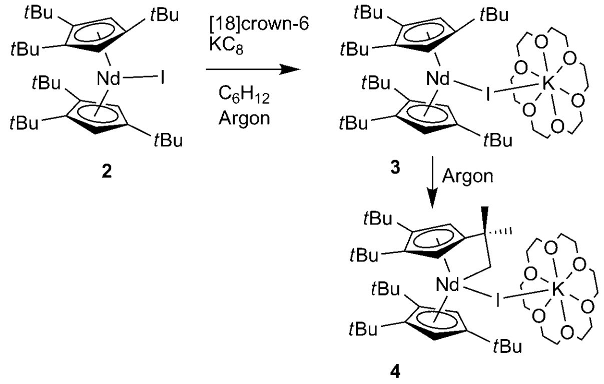
The isolation and characterization of the first molecular complex of divalent thulium, [$\mathrm{TmI_2(dme)_3}$] (dme = 1,2-dimethoxyethane),[1] ten years ago, followed by the dysprosium[2] and neodymium[3] diiodides, [$\mathrm{DyI_2(dme)_3}$] and [$\mathrm{NdI_2(thf)_5}$], opened up a new era in lanthanide chemistry.[4] Hitherto, divalent lanthanide chemistry had been restricted for decades to the "classical" $\mathrm{Eu^{II}}$, $\mathrm{Yb^{II}}$, and $\mathrm{Sm^{II}}$.[4] These "new" divalent complexes have since been investigated in numerous reactions, often revealing unexpected behavior.[5,6] However, the expectation that these precursors would lead to the isolation of divalent organometallic complexes by salt metathesis reactions was fulfilled only in the case of several very crowded $\mathrm{Tm^{II}}$ cyclopentadienyl, phospholyl, and scorpionate complexes.[7] In contrast, all reported attempts with $\mathrm{DyI_2}$ and $\mathrm{NdI_2}$, or the hypothetical [$\mathrm{NdCl_2(thf)}_x$], afforded only trivalent products.[7a,8] An early report on the identification of an organoneodymium(II) complex by elemental analysis, IR spectroscopy, and reactivity[8b] has been questioned.[8c] Lappert and co-workers attempted the synthesis of $\mathrm{La^{II}}$, $\mathrm{Ce^{II}}$, $\mathrm{Nd^{II}}$, and $\mathrm{Tm^{II}}$ complexes by reduction of trivalent precursors of the type [$\mathrm{Cp^R_3Ln}$] ($\mathrm{Cp^R} = \mathrm{C_5H_3}t\mathrm{Bu_2}$, $\mathrm{C_5H_3(SiMe_3)_2}$) using alkali metals[9] and achieved the isolation of the first crystallographically characterized $\mathrm{La^{II}}$ derivatives[9b,e] and recently a mixed $\mathrm{Ce^{II}/Ce^{III}}$ complex.[9e] A similar approach used by Cloke and co-workers afforded a mixed $\mathrm{Sc^{I}/Sc^{III}}$ compound.[10] The potential of the "new" divalent lanthanide chemistry has recently been highlighted.[11] We extended the reductive approach to obtain stable, solvent-free divalent organothulium complexes carrying cyclopentadienyl or phospholyl ligands by reduction of trivalent precursors of the $\mathrm{L_2LnX}$ type with potassium graphite in nonpolar solvents.[12] This method also gave access to the first divalent organodysprosium ate complexes [$\mathrm{Cp^{ttt}_2Dy(\mu\text{-}X)K([18]crown\text{-}6)}$] ($\mathrm{Cp^{ttt}} = \mathrm{C_5H_2}t\mathrm{Bu_3}$ and X = I (**1**), Br, $\mathrm{BH_4}$), which are powerful reducing agents.[13] Despite several attempts at reducing trivalent Nd precursors, no organoneodymium(II) complexes could be isolated, owing to decomposition of any $\mathrm{Nd^{II}}$ species in situ by interaction with solvent molecules, such as DME, THF, or benzene.[9a,c–e] We herein report on the synthesis and characterization of the first divalent organoneodymium complex, its behavior towards molecular dinitrogen, and its decomposition by C–H activation to form a structurally characterized "tuck-in" complex, the first such example for a 4f element.[14]

Reduction of the trivalent precursor [$\mathrm{Cp^{ttt}_2NdI}$] (**2**), prepared from $\mathrm{NdI_3}$ and [$\mathrm{KCp^{ttt}}$], with potassium graphite under argon in the presence of [18]crown-6 led to an immediate color change of the solution from green-blue to dark red. After 24 h, dark red crystals of the divalent ate complex [$\mathrm{Cp^{ttt}_2Nd(\mu\text{-}I)K([18]crown\text{-}6)}$]$\cdot\mathrm{C_6H_{12}}$ (**3**), suitable for X-ray crystallography, had formed. (Scheme 1 and Figure 1)



Scheme 1. Synthesis of divalent Nd ate complex **3** and trivalent Nd "tuck-in" complex **4**.

The crystal structure of **3** shows a seven-coordinate neodymium center in an open sandwich array (Cp-Nd-Cp 149.4°) with an iodine bridge to the potassium–crown ether complex. The balance of charges indicates that **3** is indeed a $\mathrm{Nd^{II}}$ complex that is best described as a [K([18]crown-6)I] adduct of the neutral [$\mathrm{Cp^{ttt}_2Nd}$] fragment. The geometrical arrangement is similar to the previously reported divalent organodysprosium ate complex **1**.[13] The longer detected Ln–I (3.16 Å for Ln = Nd, 3.06 Å for Ln = Dy) and Ln–Cp(centroid) (2.53 Å for Ln = Nd, 2.44 Å for

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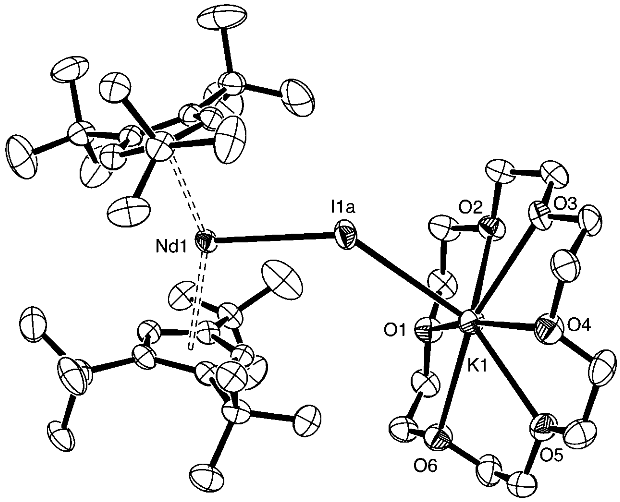

Figure 1. Molecular structure of $[\mathrm{Cp}^{\mathrm{ttt}}_2\mathrm{Nd}(\mu\text{-I})\mathrm{K}([18]\mathrm{crown\text{-}6})]$ (**3**). Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity. Cyclohexane molecules present in the lattice are not represented.

Ln = Dy) distances in **3** compared with **1** are in good agreement with the corresponding lanthanide radii.[15] Compared to the trivalent ate complex $[\mathrm{Cp}^{\mathrm{ttt}}_2\mathrm{Nd}(\mu\text{-Cl})\mathrm{AlMe}_3]$ (Nd–Cp 2.48 Å),[16] the Nd–Cp(centroid) distance is significantly longer in **3**.

The reduction of **2** was monitored by ^{1}H NMR spectroscopy in deuterated cyclohexane. Initially, the *t*Bu resonances of the trivalent precursor **2** were detected at $\delta = -0.9$, -11.6, and -18.1 ppm, with an integration of 1:1:1, in agreement with reported $[\mathrm{Cp}^{\mathrm{ttt}}_2\mathrm{LnX}]$ complexes.[12,13,16,17] Upon reduction to the divalent compound **3**, the *t*Bu resonances shift to a signal consisting of two broad overlapping peaks at $\delta = -4.8$ and -6.7 ppm and another signal at $\delta = -19.4$ ppm, in a 2:1 ratio. In addition, there is a sharp peak at $\delta = -0.05$ ppm, arising from the crown ether. These data are consistent with the solid-state structure of **3**.

Compound **3** was isolated as a dark red powder, which was stable under argon at low temperature for several days, but degraded rapidly at room temperature. Once isolated, **3** was only very slightly soluble in cyclohexane, even after heating up to 60 °C, whereupon decomposition occurred. Attempts to use other solvents, such as benzene, toluene, diethyl ether, THF, or DME, led to the immediate decomposition of **3**, as indicated by a color change to the typical blue-green color of trivalent Nd compounds, in stark contrast to the divalent Dy complexes, which are stable in toluene for several days.[13]

The room-temperature magnetic moment of solid **3** ($2.8\mu_{\mathrm{B}}$), obtained by SQUID susceptibility measurements, corresponds very well to the theoretical value for Nd$^{\mathrm{II}}$ in the $4f^{[4]}$ configuration ($2.83\mu_{\mathrm{B}}$) and to that for $[\mathrm{NdI}_2(\mathrm{thf})_5]$ ($2.7\mu_{\mathrm{B}}$),[3b] and is markedly different from that for Nd$^{\mathrm{III}}$ ($3.68\mu_{\mathrm{B}}$).[18] This confirmation of the oxidation state by magnetic moment is in contrast to the failure of the technique for the divalent Dy complex **1**, owing to the similarity of the values for Dy$^{\mathrm{II}}$ and Dy$^{\mathrm{III}}$ ($10.6\mu_{\mathrm{B}}$).

A UV/Vis/NIR spectrum was recorded for a fresh, deep red solution of **3** generated in situ in cyclohexane (ruling out extinction coefficient data). Absorption bands at 400 (m), 578 (br, sh), and 1500–2200 nm (br) were attributed to Nd$^{\mathrm{II}}$, as they were not present in the spectrum of the solution after exposure to air, or in the spectrum of **2**. Furthermore, each of these bands occurs in regions corresponding to one or more f←f bands of Pm^{3+},[19] which is isoelectronic with Nd^{2+}. The relative intensity of the band at 400 nm is greater than normal for an f←f absorption, suggesting a contribution from a d←f transition, as are featured in the visible spectra of Sm^{2+}, Eu^{2+}, and Yb^{2+}.[20]

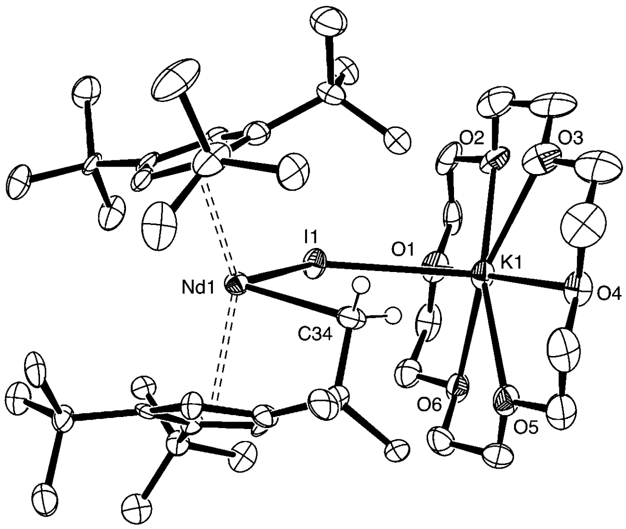

Figure 2. Molecular structure of the "tuck-in" complex $[\mathrm{Cp}^{\mathrm{ttt}}\{\mathrm{C}_5\mathrm{H}_2t\mathrm{Bu}_2\mathrm{C}(\mathrm{CH}_3)_2(\mathrm{CH}_2)\}\mathrm{Nd}(\mu\text{-I})\mathrm{K}([18]\mathrm{crown\text{-}6})]$ (**4**). Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity (except for the methylene group). Hexane molecules present in the lattice are not represented.

The red solution of **3** in [D$_{12}$]cyclohexane decomposed over several days to a green-blue solution, which afforded a complex ^{1}H NMR spectrum. No product could be identified from this solution because freezing of cyclohexane prevents crystallization at low temperatures. On reduction of **2** in hexane under the usual conditions, the initial dark red Nd$^{\mathrm{II}}$ solution turned yellow-green within 30 min. Cooling this solution to −30 °C led to the formation of a small quantity of blue crystals. X-ray crystallographic analysis of these crystals revealed the first crystallographically identified "tuck-in" complex in the lanthanide series, $[\mathrm{Cp}^{\mathrm{ttt}}\{\mu\text{-}\mathrm{C}_5\mathrm{H}_2t\mathrm{Bu}_2\mathrm{C}(\mathrm{CH}_3)_2(\mathrm{CH}_2)\}\mathrm{Nd}(\mu\text{-I})\mathrm{K}([18]\mathrm{crown\text{-}6})]\cdot\mathrm{C}_6\mathrm{H}_{14}$ (**4**, Scheme 1, Figure 2). In this sandwich complex, the trivalent eight-coordinate Nd center forms a metallacycle with a methylene group from the Cp$^{\mathrm{ttt}}$ ligand and is bound to {K([18]crown-6)I} to form an ate complex, analogous to **3**. The poor precision of the structure does not allow a detailed analysis but the bond length between Nd and the inserted methylene carbon (2.5 Å) is in the typical range of Nd–C σ bonds, for example 2.515 Å in $[(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{NdCH}(\mathrm{SiMe}_3)_2]$.[21] The formation of **4** may result from the activation of one C–H bond of a *t*Bu group in the coordination sphere of the strongly reactive Nd$^{\mathrm{II}}$ center. Andersen and co-workers prepared the related complex

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$[Cp^{ttt}\{(\mu\text{-}C_5H_2tBu_2C(CH_3)_2(CH_2)\}Ce]$ by thermolysis of $[Cp^{ttt}_2Ce(CH_2Ph)]$, but it was not characterized by X-ray crystallography.[17] Recently, Evans et al. reported the structure of a uranium "tuck-in"–"tuck-over" complex with the C_5Me_5 ligand.[14]

Dinitrogen activation by well-defined divalent organolanthanide complexes has to date only been achieved with $[SmCp^{*}_2]$ and in the reaction of a Tm^{II} alkyl complex with an amine under dinitrogen.[6,7e] Other dinitrogen-containing complexes were obtained either by salt metathesis under a dinitrogen atmosphere using the divalent lanthanide diiodides LnI_2 (Ln = Sm, Tm, Dy, Nd) or by the $LnZ_3/K/N_2$ system (Z = substituted Cp, phenoxide, or amide ligands) and other in situ reduction systems.[6,22]

Reduction of **2** with KC_8 under a dinitrogen atmosphere in hexane at room temperature gave a yellow solution. Single crystals of $[(Cp^{ttt}_2Nd)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]\cdot C_6H_{14}$ (**5**) with a distinct orange-green dichroism and which were suitable for X-ray diffraction studies were isolated after cooling the solution at −30 °C for several days. The crystal structure of **5** (Figure 3) incorporates two $\{Cp^{ttt}_2Nd\}$ sandwich moieties bridged by a reduced dinitrogen molecule. The formation and stability of this binuclear complex is surprising given the steric bulk of the ligand: the Cp^{ttt}-Nd-Cp^{ttt} angle is reduced to 131.8° compared with 149.4° in **3**, leading to an elongation of the Cp^{ttt}(centroid)–Nd distance in trivalent **5** which is nearly identical to that in divalent **3**. The N=N bond length in **5** (1.23 Å) is in the range of other reported Nd dinitrogen complexes[23] and significantly shorter than the O–O bond length in peroxo-bridged complexes, for example in $[Yb_2\{N(SiMe_3)_2\}_4(\mu\text{-}O_2)(thf)_2]$ (1.543 Å).[24] A Raman spectrum of crystalline **5** with a very low laser power showed a sharp strong peak at 1622 cm^{-1}, which was attributed to the symmetric stretching of the N=N double bond. This assignment was confirmed by the shift of this signal to 1569 cm^{-1} for the ^{15}N-labeled complex ^{15}N-**5** (expected value: 1567 cm^{-1}). This significant weakening of the N=N bond ($\tilde{\nu}[\text{free } N_2]) = 2331\ cm^{-1}$) is in agreement with other organometallic dinitrogen-containing complexes, such as LFeNNFeL (L = β-diketiminate).[25] To our knowledge, this is the first N=N double bond in lanthanide complexes detected by Raman spectroscopy.[26] The ^1H NMR spectrum of **5** in $[D_6]$benzene shows three sharp resonances at $\delta = 10.61$, −1.77, and −23.48 ppm, which indicates that, as in **2**, free rotation of the Cp^{ttt} ligand is hampered. In contrast to **2**, which shows coalescence at 50 °C, no coalescence occurs for **5** at 60 °C. When the reduction was carried out in $[D_{12}]$cyclohexane, the same resonances were detected. Despite several attempts, no clearly defined signal could be obtained in the ^{15}N NMR spectrum of ^{15}N-**5**. This contrasts the resonances for the slightly less paramagnetic Ce and Pr dinitrogen complexes.[27]

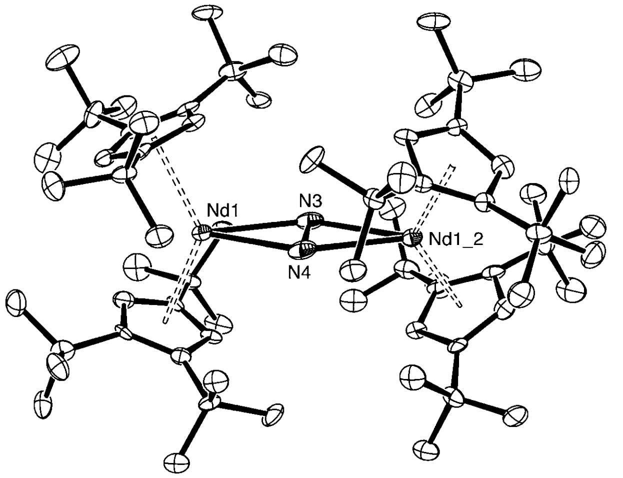
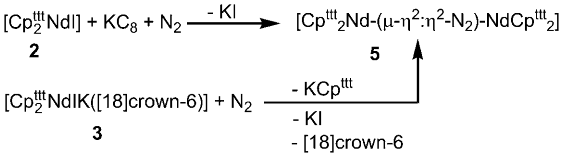


Figure 3. Molecular structure of $[(Cp^{ttt}_2Nd)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**5**). Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity. Hexane molecules present in the lattice are not represented.

When a solution of **3** in $[D_{12}]$cyclohexane was exposed to dinitrogen, an immediate color change from dark red to yellow occurred, and a white precipitate formed. The ^1H NMR spectrum of the yellow solution showed as main product the three sharp peaks identical to the solution of isolated **5**, in addition to several broad peaks that could not be assigned. The white precipitate was found to contain KI, KCp^{ttt}, and [18]crown-6 (Scheme 2).



Scheme 2. Synthesis of dinitrogen-containing dinuclear Nd complex **5**.

In summary, a careful choice of ligand and solvent system allowed the isolation of the first divalent organoneodymium complex. The highly reactive Nd^{II} center can activate C–H bonds to form a "tuck-in" complex. The reactivity of the divalent complex with dinitrogen led to the formation of the same product as in the $[Cp^{ttt}_2NdI]/K/N_2$ system. Further reactivity studies on the three isolated products are currently in progress.

Experimental Section

Divalent **3** is exceptionally reactive to air, moisture, and solvents, much more so than Tm^{II} and Dy^{II} complexes,[7a–d,12] and solid **3** is also thermally unstable. Compound **4** is thermally unstable and must also be handled under high-purity argon.

3: a) In an argon atmosphere, KC_8 (5.0 mg, 0.037 mmol) was added to a solution of **2** (10 mg, 0.014 mmol), and [18]crown-6 (3.6 mg, 0.014 mmol) in $[D_{12}]$cyclohexane (1 mL) in an NMR tube fitted with a J. Young valve, and the reaction mixture was shaken immediately to give quantitatively a dark red solution of **3.** Crystals of **3** suitable for X-ray diffraction formed over 24 h from this solution at room temperature. ^1H NMR (300 MHz, $[D_{12}]$cyclohexane): $\delta = -0.05$ (s, 24 H, [18]crown-6), −4.8 and −6.7 (br s, 36 H, $\omega_{1/2} \approx 1$ kHz, *t*Bu), −19.4 ppm (br s, 18 H, $\omega_{1/2} \approx 0.5$ kHz, *t*Bu).

b) In a similar experiment, the reaction of **2** (20 mg, 0.027 mmol), [18]crown-6 (7.2 mg, 0.027 mmol), and KC_8 (10 mg, 0.074 mmol) was carried out in cyclohexane (3 mL) in a centrifugation tube. The solids

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were removed by centrifugation and the solvent was carefully removed under vacuum. The residue was washed with fresh cyclohexane (2 mL) to afford **3** as a dark red powder (14 mg, 0.014 mmol, 51 %). $\mu_{\text{eff}} = 2.8\mu_B$. IR (Nujol): $\tilde{\nu} = 1580$ (w), 1352 (m), 1260 (w), 1239 (w), 1111 (s), 1019 (m), 963 (m), 798 cm^{-1} (m). UV/Vis/NIR (C_6H_{12}): $\nu = 400$ (m), 578 (br, sh), 1500–2200 nm (vvbr).

4: In a similar synthesis to **3** (b), the reaction of **2** (10 mg, 0.013 mmol), [18]crown-6 (3.6 mg, 0.014 mmol), and KC_8 (5.0 mg, 0.037 mmol) was carried out in hexanes (2 mL) in a centrifugation tube. After centrifugation for 5 min at 3900 rpm the solution was cooled to −30 °C, yielding **4** as blue crystals suitable for X-ray analysis (1.5 mg, 0.002 mmol, 15 %). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 24.1$ (s, 3 H, CMe$_2$), 14.0 and 12.4 (br s, 12 H, $\omega_{1/2} \approx 0.3$ kHz, *t*Bu and CMe$_2$), 2.8 (s, 9 H, *t*Bu), 0.73 (s, 24 H, [18]crown-6), −0.7 (s, 9 H, *t*Bu), −10.1 (s, 9 H, *t*Bu), −15.4 ppm (br s, 9 H, $\omega_{1/2} \approx 0.2$ kHz, *t*Bu). No signal for the Cp ring and methylene protons was detected.

5: a) In a dinitrogen atmosphere, a mixture of **1** (20 mg, 0.027 mmol), KC_8 (36 mg, 0.270 mmol), and [D$_{12}$]cyclohexane (1 mL), in an NMR tube fitted with a J. Young valve, was kept at 50 °C for 24 h. After removal of the solvent under reduced pressure, recrystallization from hexanes at −30 °C afforded **5** as orange-green dichroic crystals suitable for X-ray analysis (22 mg, 0.017 mmol, 62 %). A similar procedure was applied for the synthesis of the ^{15}N-labeled compound ^{15}N-**5**. ^{1}H NMR (300 MHz, [D$_{12}$]cyclohexane): $\delta = 24.6$ (s, 8 H, Cp–H), 10.6 (s, 36 H, *t*Bu), −1.7 (br s, 36 H, *t*Bu), −23.4 ppm (s, 36 H, *t*Bu). Raman: 2963 (m), 2939 (s), 2875 (s), 1742 (w), 1622 (s) [$(\tilde{\nu}_s(^{14}N_2)$], 1448 (m), 816 cm^{-1} (w). For ^{15}N-**5** [$(\tilde{\nu}_s(^{15}N_2)$] 1569 cm^{-1} (s).

b) A dark red solution of **3** (14 mg, 0.014 mmol) in [D$_{12}$]cyclohexane (1 mL) was exposed to dinitrogen, leading to an immediate color change to yellow and the slow formation of a white precipitate. After 24 h, the white solid was removed by centrifugation and identified as a mixture of KI, [18]crown-6, and KCp^{ttt}, as confirmed by ^{1}H NMR and IR spectroscopy and by qualitative analysis. The ^{1}H NMR spectrum of the remaining solution showed compound **5** as the major product. The solvent was removed under reduced pressure and the crude product recrystallized from hexane at −30 °C to afford **5** (6 mg, 0.004 mmol, 34 %).

X-ray Crystallographic Data

3: Space group $P\bar{1}$; $a = 13.593(1)$, $b = 14.136(1)$, $c = 16.101(1)$ Å; $\alpha = 81.546(1)$, $\beta = 74.412(1)$, $\gamma = 70.613(1)°$; $V = 2805.4(3)$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.332$ Mg m^{-3}; $R1 = 0.0607$ [$I > 2\sigma(I)$]; $wR2 = 0.1587$; GOF = 1.025.

4: Space group $P\bar{1}$; $a = 13.561(3)$, $b = 13.850(3)$, $c = 15.982(3)$ Å; $\alpha = 88.92(3)$, $\beta = 68.66(3)$, $\gamma = 85.59(3)°$; $V = 2787.7(1)$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.342$ Mg m^{-3}; $R1 = 0.0882$ [$I > 2\sigma(I)$]; $wR2 = 0.1514$; GOF = 1.119.

5: Space group $P2/n$; $a = 18.342(4)$, $b = 10.403(2)$, $c = 19.369(4)$ Å; $\beta = 108.77(3)°$; $V = 3499.4(1)$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.268$ Mg m^{-3}; $R1 = 0.0728$ [$I > 2\sigma(I)$]; $wR2 = 0.1341$; GOF = 1.209.

The synthesis of **2** is presented in the Supporting Information together with X-ray collection and processing details. CCDC 704850, 704850, 704852 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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