FULL PAPER

A Comparison of Analogous 4f- and 5f-Element Compounds: Syntheses and X-ray Crystal Structures of the Mixed Sandwich Complexes [M(η-C$_8$H$_8$)(L){OP(NMe$_2$)$_3$}] (M = Nd or U; L = η-C$_5$Me$_5$ or η-C$_4$Me$_4$P)

Sophie M. Cendrowski-Guillaume,*[a][‡] Gildas Le Gland,[a] Martine Nierlich,[a] and Michel Ephritikhine*[a]

The series of complexes [M(COT)(L)(HMPA)] {M = Nd or U; COT = η-C$_8$H$_8$; L = η-C$_5$Me$_5$ (Cp•) or η-C$_4$Me$_4$P (tmp), HMPA = OP(NMe$_2$)$_3$} have been synthesized. [Nd(COT)(Cp•)-(HMPA)] (**1b**) was prepared by substitution of the THF ligand of [Nd(COT)(Cp•)(THF)]; [Nd(COT)(tmp)(HMPA)] (**3**) was prepared by reaction of the neodymium cation [Nd(COT)(THF)$_4$][BPh$_4$] with Ktmp followed by the addition of HMPA to the dimeric compound [Nd(COT)(tmp)]$_2$ (**2**); [U(COT)(Cp•)(HMPA)] (**4**) was isolated from the reaction of the uranium cation [U(COT)(HMPA)$_3$][BPh$_4$] with KCp•, and

[U(COT)(tmp)(HMPA)$_2$] (**5**) was obtained upon reduction of the uranium(IV) cation of [U(COT)(tmp)(HMPA)$_2$][BPh$_4$] with sodium amalgam. The X-ray crystal structures of **1b**, **3**, and **4** have been determined. In the isostructural compounds **1b** and **4**, the differences between the U–C and Nd–C bond lengths are smaller than those predicted from the ionic radii of the trivalent ions; in particular, the average M–C(Cp•) distances are equal to 2.77 Å for both M = Nd and U.
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Introduction

The differentiation of trivalent lanthanide (Ln) and actinide (An) ions should be facilitated by the precise knowledge of the metal−ligand bond and the respective role of the 4f- and 5f-electrons. Such a discrimination between Ln^{III} and An^{III} complexes represents an important problem for both its fundamental aspects and its applications, especially in the management of nuclear wastes.[1] In this context, much attention is currently focused on highlighting the possible significant variations in the structural parameters of analogous Ln^{III} and U^{III} coordination complexes.[2−5]

Recently, we reported the synthesis and structural characterization of the unique cyclooctatetraenyllanthanide cation [Nd(COT)(L)$_x$][BPh$_4$] {COT = η-C$_8$H$_8$; L = THF and x = 4; L = OP(NMe$_2$)$_3$ (HMPA) and x = 3},[6,7] of the first cationic monocyclooctatetraenyluranium(III) complex, the analog [U(COT)(HMPA)$_3$][BPh$_4$],[7] and of the first organometallic dication of an f-element, [U(COT)-(HMPA)$_3$][BPh$_4$]$_2$.[8] These cationic compounds form the [M(COT)(HMPA)$_3$]$^{n+}$ series (M = Nd and n = 1; M = U and n = 1 or 2), which allowed a direct structural com-

parison of the Nd^{III}/U^{III} and U^{III}/U^{IV} analogous derivatives.[7] These investigations revealed that the variations in the metal−ligand bond lengths were proportional to the differences in the ionic radii of the metals.

In contrast to the numerous mixed cyclooctatetraenyl-/cyclopentadienyllanthanide complexes characterized by X-ray crystallography,[9] the only such compound of actinide(III) is [U(COT)(Cp*)(Me$_2$bpy)] (Cp* = η-C$_5$Me$_5$; Me$_2$bpy = 4,4′-dimethyl-2,2′-bipyridine).[10] While phospholyl derivatives of the f-elements are well known,[11−13] a few mixed cyclooctatetraenyl/phospholyl complexes of Nd^{III}, Sm^{III},[14] and U^{III} [15] have been recently isolated; the crystal structures of [Nd(COT)(Dsp)(THF)] {Dsp = 3,4-dimethyl-2,5-bis(trimethylsilyl)phospholyl}[14] and [U(COT)-(tmp)(BH$_4$)(THF)] (tmp = η-C$_4$Me$_4$P)[15] have been determined.

Here we present the syntheses and X-ray crystal structures of the analogous neutral complexes in the mixed COT/Cp* or tmp series, [M(COT)(L)(HMPA)] with M = Nd or U and L = Cp* or tmp.

Results and Discussion

Synthesis and Characterization

The borohydride and cationic compounds [Nd(COT)(BH$_4$)(THF)]$_2$,[6a] and [Nd(COT)(THF)$_4$]-[BPh$_4$],[6,7] proved to be valuable precursors for the synthesis of monocyclooctatetraenyllanthanide derivatives;[6,7,16] they are also at the origin of the neodymium

complexes studied in the present work. The mixed COT/Cp* sandwich derivative [Nd(COT)(Cp*)(THF)] was prepared in high yield from either the neutral or cationic parent complex, the procedure using the cation being more efficient and more selective.[6] Exchanging the THF solvent molecule for HMPA gave the green derivative [Nd(COT)(Cp*)(HMPA)$_2$] (**1a**) in 93% yield; green crystals of [Nd(COT)(Cp*)(HMPA)] (**1b**) were obtained by crystallization from THF/pentane. These complexes are the only examples among the [Ln(COT)(Cp*)] series (Ln = Sc, Y, La, Pr, Sm, Gd, Tb, Dy, Er, Lu) that have not been prepared by a metathesis reaction from a lanthanide chloride precursor.[9] Addition of Ktmp to a THF solution of [Nd(COT)(THF)$_4$][BPh$_4$] afforded the mixed COT/tmp compound [Nd(COT)(tmp)]$_2$ (**2**), which was obtained as a green powder in 75% yield. Considering that the Nd(COT)(Cp*) species was isolated as the THF adduct [Nd(COT)(Cp*)(THF)], it is very likely that the isosteric moiety Nd(COT)(tmp), which is less electron-rich because the tmp group is less electron-donating than the Cp* ligand,[12] adopts in the solid state a dimeric structure ensured by a μ-η^5,η^1-bridging tmp ligand. The ability of the phospholyl ligand to bridge two metal centers through the available lone pair on the P atom is well documented, and can be illustrated with the structures of the U^{III} complexes [U(tmp)$_2$(BH$_4$)]$_2$ and [U(tmp)(Cp*)(BH$_4$)]$_2$.[13] Complex **2** certainly forms monomeric adducts in coordinating solvents and with Lewis bases; in the presence of HMPA, it was readily transformed into the dark green derivative [Nd(COT)(tmp)(HMPA)] (**3**), which crystallized from THF/pentane.

Treatment of [U(COT)(HMPA)$_3$][BPh$_4$] with KCp* led to the formation of [U(COT)(Cp*)(HMPA)] (**4**), which was isolated as dark brown crystals in 70% yield. The adducts U(COT)(Cp*)(L) (L = THF, Me$_2$bpy) have been synthesized in THF from the reaction of [U(Cp*)I$_2$(THF)$_2$] and K$_2$COT, in the presence of Me$_2$bpy for the latter.[10] The dark brown powder of [U(COT)(tmp)(HMPA)$_2$] (**5**) was obtained in 57% yield after reduction of the uranium(IV) cation [U(COT)(tmp)(HMPA)$_2$][BPh$_4$] with sodium amalgam. A similar reduction of a cationic tetravalent cyclooctatetraenyluranium compound was already performed to make [U(COT)(HMPA)$_3$][BPh$_4$] from [U(COT)(HMPA)$_3$]-[BPh$_4$]$_2$.[7] Complex **5** is the first mixed cyclooctatetraenyl/phospholyl complex of uranium(III). Unfortunately, no crystals suitable for X-ray diffraction analysis could be obtained. The synthesis of **4** and **5** provide further examples of the usefulness of cationic uranium compounds as precursors of derivatives in the +3 oxidation state.

As previously observed with [U(COT)(tmp)(BH$_4$)(THF)] and [U(COT)(tmp)(HMPA)$_2$][BPh$_4$],[15] protonation of the tmp ligand of **2** and **5** with NEt$_3$HBPh$_4$ afforded the parent cationic complexes. Thus, **2** was transformed in THF into [Nd(COT)(THF)$_4$][BPh$_4$], while **5** also underwent oxidation to give [U(COT)(HMPA)$_3$][BPh$_4$]$_2$ (NMR spectroscopic experiments). Protonolysis of the U–P bond was also observed with the phosphido complex [U(NEt$_2$)$_3$(PPh$_2$)],

which was transformed into [U(NEt$_2$)$_3$][BPh$_4$] by reaction with (NEt$_3$H)BPh$_4$.[17]

Complexes **1**−**5** were characterized by elemental analyses (except **4**) and ^{1}H NMR spectra. The crystal structures of **1b**, **3** and **4** have been determined.

Crystal Structures of [Nd(COT)(Cp*)(HMPA)], [Nd(COT)(tmp)(HMPA)], and [U(COT)(Cp*)(HMPA)]

The two analogous neodymium and uranium COT/Cp* complexes **1b** and **4** are isostructural; the crystal structure of **4** is shown in Figure 1. The crystal structure of **3**, the tmp analog of **1b**, is shown in Figure 2. Selected bond lengths and angles of the three complexes are listed in Table 1.
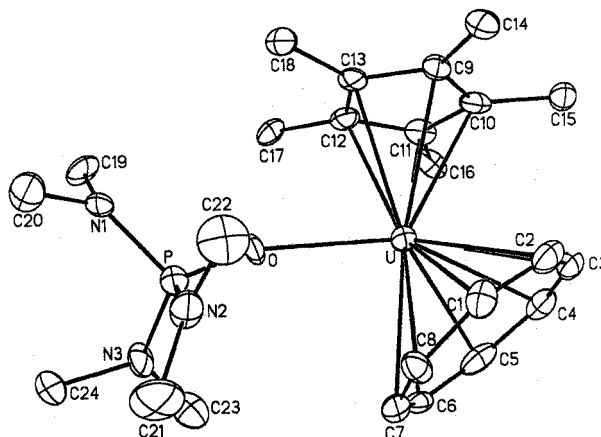

Figure 1. View of the crystal structure of [U(COT)(Cp*)(HMPA)] with thermal ellipsoids drawn at the 30% probability level
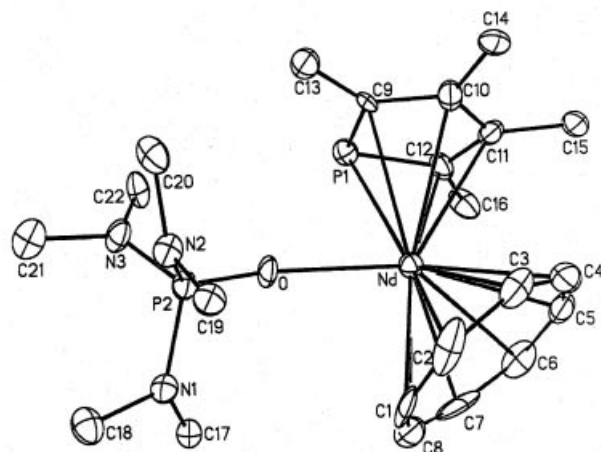
Figure 2. View of the crystal structure of [Nd(COT)(tmp)(HMPA)] with thermal ellipsoids drawn at the 30% probability level

These complexes adopt the same trigonal configuration as that encountered in [Nd(COT)(Dsp)(THF)][14] and [Gd(COT)(η-C$_5$H$_9$C$_5$H$_4$)(THF)],[18] considering the COT, Cp*, and tmp ligands as monodentate. Coordination of the COT ligand in **1b** and **3** is similar to that found in other monocyclooctatetraenylneodymium complexes; the Nd–COT(centroid) distances of 1.99(2) Å in **1b** and 1.97(1)

Table 1. Selected bond lengths [Å] and angles [°] for the complexes

	[Nd(COT)(Cp*)(HMPA)] (**1b**)	[Nd(COT)(tmp)(HMPA)] (**3**)	[U(COT)(Cp*)(HMPA)] (**4**)
M−C(1)	2.749(4)	2.698(17)	2.711(15)
M−C(2)	2.773(4)	2.67(2)	2.676(14)
M−C(3)	2.732(5)	2.635(19)	2.721(14)
M−C(4)	2.685(5)	2.665(19)	2.712(14)
M−C(5)	2.699(4)	2.636(15)	2.706(16)
M−C(6)	2.697(5)	2.657(14)	2.726(13)
M−C(7)	2.662(4)	2.625(17)	2.778(13)
M−C(8)	2.675(5)	2.72(2)	2.781(14)
M−C(9)	2.780(4)	2.840(9)	2.794(10)
M−C(10)	2.809(4)	2.884(14)	2.805(11)
M−C(11)	2.766(4)	2.943(11)	2.776(14)
M−C(12)	2.750(4)	2.887(13)	2.739(15)
M−C(13) or Nd−P	2.745(4)	2.968(8)	2.748(13)
M−O	2.441(3)	2.434(8)	2.461(8)
<M−C(COT)>	2.71(4)	2.66(3)	2.73(4)
<M−C(Cp*)>	2.77(2)	2.88(4)	2.77(2)
M−COT(centroid)	1.99(2)	1.97(2)	2.01(1)
M−Cp* or −tmp(centroid)	2.49(2)	2.59(1)	2.50(1)
COT−M−Cp* or −tmp(centroid)	141(1)	139(1)	141(1)
O−M−COT(centroid)	120(1)	120(1)	120(1)
O−M−Cp* or −tmp(centroid)	98(1)	101(1)	99(1)

Å in **3** can be compared with those measured in [Nd(COT)(η-C$_5$H$_9$C$_5$H$_4$)(THF)$_2$] (2.011 Å),[18] [Nd(COT)(Dsp)(THF)] (1.94 Å),[14] and [Nd(COT)(HMPA)$_3$][BPh$_4$] [1.984(5) Å].[7] The Cp* ligation in **1b** is also unexceptional; the Nd−Cp*(centroid) distance of 2.49(2) Å is similar to that of 2.48 Å in [Nd(Cp*)-I$_2$(pyridine)$_3$]·C$_7$H$_8$.[19] In the crystal structure of **3**, the Nd−tmp(centroid) distance of 2.59(1) Å compares well with the corresponding value of 2.57 Å in [Nd(COT)(Dsp)(THF)];[14] the Nd−P bond length is equal to 3.0195(4) Å in the latter and to 2.968(8) Å in **3**. As previously observed in other analogous tmp and Cp* compounds,[12] the Nd−tmp(centroid) distance in **3** is longer, by 0.1 Å, than the Nd−Cp*(centroid) distance in **1b**. The Nd−O distances in **1b** and **3**, 2.441(3) and 2.434(8) Å, are longer than the average Nd−O bond length of 2.36(3) Å in [Nd(COT)(HMPA)$_3$][BPh$_4$][7] while the Nd−C(COT) distances are practically the same. This feature likely results from the more positive charge on the cationic Nd^{III} center, which induces a stronger interaction with the Lewis base.

The structural parameters of the U(COT)(Cp*) unit in **4** are quite similar to those determined in [U(COT)(Cp*)-(Me$_2$bipy)].[10] The U−COT(centroid) distance is equal to 2.01(1) Å in both compounds while the U−Cp*(centroid) distances are 2.50(1) and 2.49 Å, respectively. The U−O bond length of 2.46(1) Å in **4** is, here again, longer than the average U−O distance of 2.40(6) Å in the cation [U(COT)-(HMPA)$_3$][BPh$_4$][7] while the U−C(COT) distances are identical, reflecting the weaker interaction between the metal center and the oxygen donor ligand.

More interesting is the comparison of the crystal structures of the Nd^{III} and U^{III} analogs **1b** and **4**. In contrast to what was observed in the cations [M(COT)(HMPA)$_3$]$^+$ (M = Nd, U),[7] where the differences <U−O> −

<Nd−O> and <U−C> − <Nd−C> perfectly reflect the +0.04 Å difference between the ionic radii of the trivalent uranium and neodymium ions,[20] it seems that the average U−O, U−C(COT), and U−C(Cp*) distances in **4** are shorter than those expected from a purely ionic model, the <U−X> − <Nd−X> differences (X = C or O) being lower than 0.04 Å. Most notably, there is no difference between the mean U−C(Cp*) and Nd−C(Cp*) bond lengths which are both equal to 2.77(3) Å. Similar small deviations (0.02−0.05 Å) between the differences in metal−ligand bond lengths and the differences in metal ionic radii, which must be considered with caution in view of the experimental errors, have previously been detected in the crystal structures of analogous uranium and lanthanide complexes with polydentate nitrogen ligands: [M(Mentb)$_2$]X$_3$ {M = La and X = ClO$_4$, M = U and X = I; Mentb = tris(N-methyl-benzimidazol-2-ylmethyl)amine},[2] [MI$_3$(tpa)(C$_5$H$_5$N)] {M = La or U; tpa = tris[(2-pyridyl)methyl]amine},[2] [MI$_3$-(bipy)(C$_5$H$_5$N)] (M = Ce or U; bipy = 2,2′-bipyridine),[3] and [M(terpy)$_3$]I$_3$·2MeCN (M = La, Ce, Nd, U; terpy = 2,2′:6′,2′′-terpyridine).[4] A difference of +0.047 Å was also measured between the average La−S and U−S distances in the complexes [M(1,4,7-trithiacyclononane)I$_3$(MeCN)$_2$] (M = La, U),[5] while the ionic radius of the U^{III} ion is only 0.01 Å shorter than that of the La^{III} ion.[20] It is solely in the phosphorous complexes [M(η-C$_5$H$_4$Me)$_3$L] {M = Ce or U; L = PMe$_3$ or P(OCH$_2$)$_3$CEt}[21] and in the tris(btp) compounds [M(btp)$_3$]I$_3$·nC$_5$H$_5$N {M = Ce or U; btp = 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine}[4] that the U−P and U−N bond lengths were found to be significantly shorter, by 0.1 Å, than the Ce−P and Ce−N distances, while the ionic radius of the U^{III} ion is 0.01 Å longer than that of the Ce^{III} ion.[20] In all these pairs of analogous Ln^{III} and U^{III} complexes, the deviations of the U−X distances

(X = N, P, S) from the ionic bonding model have been explained by a stronger π back-bonding interaction between the metal atom and the ligand that is much less likely in the lanthanide analogs. If significant, the variations observed in the crystal structures of **1b** and **4**, especially the apparent shortening of the U−C(Cp*) bonds, could also be accounted for by a metal to ligand π back-donation which, as expected,[22] is more important and detectable than in the cationic parent compounds [M(COT)(HMPA)₃][BPh₄] (M = Nd, U).

Conclusion

The synthesis of the mixed cyclooctatetraenyl/cyclopentadienyl or phospholyl compounds **1−5** further demonstrate the utility of cationic complexes as precursors in organo-f-element chemistry.[6−8,23] The crystal structures of the isostructural neodymium and uranium complexes **1b** and **4** revealed that the differences between the U−C and Nd−C bond lengths are smaller than those predicted from the ionic radii of the trivalent ions; in particular, the mean M−C(Cp*) distances are equal in both compounds. These structures would provide a unique example in which the more covalent character of the uranium−ligand bond is observed primarily with an anionic hydrocarbon ligand, and not a neutral Lewis base. Further studies on analogous Ln^III and U^III organometallic compounds are necessary to confirm these observations.

Experimental Section

General: All manipulations and reactions were carried out under argon (less than 3 ppm of oxygen and water) using standard Schlenk and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use. Deuterated solvents were dried with Na/K alloys. The ¹H NMR spectra were recorded with a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ = 0). Elemental analyses were performed by the Analytische Laboratorien at Lindlar (Germany). [Nd(COT)(THF)₄][BPh₄],[6] [Nd(COT)(Cp*)(THF)],[6] [U(COT)(HMPA)₃][BPh₄],[7] and [U(COT)-(tmp)(HMPA)₂][BPh₄][15] were synthesized as previously reported.

Synthesis of [Nd(COT)(Cp*)(HMPA)₂] (1a): HMPA (10 µL, 10.3 mg, 57.48 µmol) was added to a solution of [Nd(COT)(Cp*)-(THF)] (13.03 mg, 28.60 µmol) in THF (5 mL). After 45 min, the green solution was concentrated to dryness. After washing with toluene (5 mL), the green powder of **1a** was dried under vacuum (19.7 mg, 93%). ¹H NMR ([D₈]THF): δ = 6.12 (br. s, $w_{1/2}$ = 27 Hz, 15 H, Cp*), 3.56 (br. s, $w_{1/2}$ = 21 Hz, 36 H, HMPA), −13.52 (br. s, $w_{1/2}$ = 67 Hz, 8 H, COT) ppm. C₃₀H₅₉N₆O₂P₂Nd (741): calcd. C 48.56, H 8.01, N 11.32, P 8.35; found C 48.30, H 7.94, N 11.07. Green single crystals of **1b** were obtained at 20 °C within a week from a THF solution of [Nd(COT)(Cp*)(THF)] (24.1 mg, 52.88 µmol) and HMPA (28 µL, 28.8 mg, 160.94 µmol, 3.04 equiv.), layered with pentane.

Synthesis of [Nd(COT)(tmp)]₂ (2): A flask was charged with [Nd(COT)(THF)₄][BPh₄] (160.1 mg, 187.02 µmol), Ktmp (33.2 mg, 186.40 µmol) and THF (25 mL). After stirring for 3 h at 20 °C, the green solution was filtered and the solvents evaporated to dryness.

Table 2. Crystal data and structure refinement for the complexes

	[Nd(COT)(Cp*)(HMPA)] (**1b**)	[Nd(COT)(tmp)(HMPA)] (**3**)	[U(COT)(Cp*)(HMPA)] (**4**)
Empirical formula	C₂₄H₄₁N₃NdOP	C₂₂H₃₈N₃NdOP₂	C₂₄H₄₁N₃OPU
M [g mol⁻¹]	562.81	566.73	656.60
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Pbca	Pna2₁	Pbca
a [Å]	18.324(4)	27.919(6)	18.396(4)
b [Å]	14.538(3)	7.481(1)	14.523(3)
c [Å]	19.201(4)	11.669(2)	19.288(4)
V [Å³]	5115.0(18)	2437.2(8)	5153.1(18)
Z	8	4	8
$\rho_{calcd.}$ [g cm⁻³]	1.462	1.545	1.693
μ (Mo-K_α) [mm⁻¹]	2.112	2.279	6.381
Crystal size [mm]	0.20 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.12 × 0.10 × 0.05
T_{min}/T_{max}	0.772/0.801	0.728/0.785	0.401/0.752
$F(000)$	2312	1156	2568
T [K]	123(2)	123(2)	123(2)
2θ range [°]	2.77−24.72	2.82−24.79	2.62−24.70
No. of data collected	32170	12796	31863
No. of unique data	4311	3904	4321
Observed data [$I > 2\sigma(I)$]	3168	2840	2262
R_{int}	0.0532	0.1232	0.1240
No. of parameters	271	262	271
R_1 [a]	0.0317	0.0581	0.0609
wR_2 [b]	0.0697	0.1199	0.1062
S	1.012	1.035	0.947
$\Delta\rho_{min}$ [e·Å⁻³]	−0.644	−0.723	−1.595
$\Delta\rho_{max}$ [e·Å⁻³]	0.538	0.993	1.023

[a] $R_1 = \Sigma(||F_o| − |F_c||)/\Sigma|F_o|$ (observed reflections). [b] $wR_2 = [\Sigma w(||F_o| − |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$ (observed reflections).

The resulting product was further extracted with THF (15 mL) and after evaporation of the solvent, the green powder of **2** was washed with toluene (5 mL) and dried under vacuum (54.0 mg, 75%). ^{1}H NMR ([D$_8$]toluene): δ = 11.01 (br. s, $w_{1/2}$ = 42 Hz, 6 H, Me), 1.20 (br. s, $w_{1/2}$ = 40 Hz, 6 H, Me), −15.62 (br. s, $w_{1/2}$ = 95 Hz, 8 H, COT) ppm. ^{1}H NMR ([D$_8$]THF): δ = 10.64 (br. s, $w_{1/2}$ = 20 Hz, 6 H, Me), 2.70 (br. s, $w_{1/2}$ = 22 Hz, 6 H, Me), −15.0 (br. s, $w_{1/2}$ = 50 Hz, 8 H, COT) ppm. C$_{16}$H$_{20}$PNd (387): calcd. C 49.59, H 5.20, P 7.99; found C 49.32, H 5.33, P 8.13.

Synthesis of [Nd(COT)(tmp)(HMPA)] (3): HMPA (64.0 μL, 65.9 mg, 0.37 mmol), was added to a solution of **2** (118.4 mg, 0.153 mmol) in THF (30 mL); the initial green solution became darker. After stirring at 20 °C for 2 h, the solution was concentrated to dryness, leaving a dark green powder of **3** (159.4 mg, 92%). ^{1}H NMR ([D$_8$]THF): δ = 12.30 (br. s, $w_{1/2}$ = 20 Hz, 6 H, Me), 5.68 (br. s, $w_{1/2}$ = 62 Hz, 18 H, HMPA), −2.32 (br. s, $w_{1/2}$ = 27 Hz, 6 H, Me), −12.20 (br. s, $w_{1/2}$ = 53 Hz, 8 H, COT) ppm. C$_{22}$H$_{38}$N$_3$OP$_2$Nd (660): calcd. C 46.62, H 6.76 N 7.41, P, 10.93; found C 46.41, H 6.86, N 7.55, P 10.67. Green crystals of **3** were grown from a saturated THF solution layered with pentane.

Synthesis of [U(COT)(Cp*)(HMPA)] (4): Addition of KCp* (22.5 mg, 129.1 μmol) to [U(COT)(HMPA)$_3$][BPh$_4$] (153.6 mg, 128.1 μmol) in THF (40 mL) induced a color change of the solution from dark green to dark brown within 30 min. After stirring at 20 °C for 2 h, the solution was filtered and the solvents were evaporated to dryness to give a brownish solid that was then extracted with toluene (10 mL). After concentration to dryness, the dark brown solid was crystallized from THF/pentane, affording brown crystals of **4** (60.1 mg, 70%). ^{1}H NMR ([D$_8$]toluene): δ = 1.67 (d, 7 Hz, 18 H, HMPA), −10.07 (s, 15 H, Cp*), −50.18 (s, 8 H, COT) ppm. ^{1}H NMR ([D$_8$]THF): δ = 1.97 (d, 9 Hz, 18 H, HMPA), −8.45 (s, 15 H, Cp*), −48.94 (s, 8 H, COT) ppm.

Synthesis of [U(COT)(tmp)(HMPA)$_2$] (5): Reduction of [U(COT)-(tmp)(HMPA)$_2$][BPh$_4$] (303.3 mg, 261.7 μmol) with 2% Na(Hg) (596.5 mg, 518.7 μmol of Na) in THF (40 mL) over 24 h afforded a dark brown suspension. After filtration and concentration to dryness, the crude product was extracted with toluene (3 × 15 mL) and then precipitated upon addition of pentane, affording a dark brown powder of **5** (125.5 mg, 57%). ^{1}H NMR ([D$_8$]toluene): δ = 1.87 (s, 36 H, HMPA), −3.91 (s, 6 H, Me), −25.57 (s, 6 H, Me), −43.16 (s, 8 H, COT) ppm. ^{1}H NMR ([D$_8$]THF): δ = 3.07 (s, 36 H, HMPA), −1.15 (br. s, $w_{1/2}$ = 60 Hz, 6 H, Me), −22.39 (br. s, $w_{1/2}$ = 90 Hz, 6 H, Me), −41.44 (br. s, $w_{1/2}$ = 55 Hz, 8 H, COT) ppm. C$_{28}$H$_{56}$N$_6$O$_2$P$_3$U (839): C 40.05, H 6.72, N 10.01, P 11.07; found C 39.94, H 6.63, N 9.79, P 10.80.

Reactions of 2 and 5 with (NEt$_3$H)BPh$_4$. a) An NMR tube was charged with **2** (8.1 mg, 10.45 μmol) and (NEt$_3$H)BPh$_4$ (9.0 mg, 21.35 μmol) in [D$_8$]THF (0.3 mL). After 45 min at 20 °C, the spectrum of the green solution showed the formation of [Nd(COT)(THF)$_4$][BPh$_4$] as the sole organometallic product. **b)** An NMR tube was charged with **5** (7.3 mg, 8.64 μmol) and (NEt$_3$H)BPh$_4$ (5.0 mg, 11.8 μmol) in [D$_8$]THF (0.3 mL). Precipitation of an orange solid was immediate. The precipitate was identified as [U(COT)(HMPA)$_3$][BPh$_4$]$_2$ by its ^{1}H NMR spectrum in pyridine.

X-ray Crystallography of 1b, 3, and 4: Diffraction collections were carried out with a Nonius Kappa-CCD diffractometer. The lattice parameters were determined from 10 images recorded with 2° Φ-scans and later refined on all data. A 180° Φ range was scanned with 2° steps and 10 s of exposure time per frame with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz

polarization and absorption effects.[24] The structures were solved by the heavy-atom method and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH$_2$) or 1.5 (CH$_2$, CH$_3$) times that of the parent atom. All calculations were performed with an O2 Silicon Graphics Station using the SHELXTL package.[25] Crystal data and details of data collection and refinement are given in Table 2. CCDC-195294 (**1b**), -195292 (**3**), and -195293 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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