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Advances in f-element cyanide chemistry

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This Dalton perspective gives an overview of the development of cyanide chemistry of 4f- and 5f-elements, a field which was poorly explored in contrast to the attention paid to the cyanide complexes of the d transition metals. The use of the cyanide ligand led to the discovery of mono- and polycyanide complexes which exhibit unprecedented and unexpected coordination geometries. A new type of linear metallocenes including $[U(Cp^*)_2(CN)_5]^{3-}$ ($Cp^* = C_5Me_5$) and the first bent actinocenes $[An(Cot)_2(CN)]^-$ (An = Th, U; Cot = C_8H_8) were isolated. Thorocene was found to be much more reactive than uranocene since a series of sterically crowded cyanide complexes have been obtained only from $[Th(Cot)_2]$. A series of cyanido-bridged dinuclear compounds and mononuclear mono-, bis- and tris(cyanide) complexes were prepared by addition of cyanide salts to $[MN^*_3]$ (M = Ce, U) and $[UN^*_3]^+$ ($N^* = N(SiMe_3)_2$]. The Ce^{III}, U^{III} and U^{IV} ions were clearly differentiated in these reactions by cyanide linkage isomerism, as shown for example by the structures of the cyanide complex $[U^{III}N^*_3(CN)_2]^{2-}$ and of the isocyanide derivatives $[Ce^{III}N^*_3(NC)_2]^{2-}$ and $[U^{IV}N^*_3(NC)]^-$. While the U−CN/NC coordination preference towards the U^{III}/U^{IV} pair is related to the subtle balance between steric, covalent and ionic factors, DFT computations and in particular the calculated total bonding energies between the metal and the cyanide ligand allowed the observed coordination mode to be predicted. The ability of the cyanide ligand to stabilize the high oxidation states was assessed with the synthesis of U^V and U^{VI} complexes in the inorganic and organometallic series.

1. Introduction

For a long time, the cyanide ligand has occupied a prominent position in the chemistry of the d transition metals, as demonstrated by the number of reviews, some of them quite old, devoted to the fundamental aspects and applications of these complexes. [1-12] This ubiquity of the CN^- anion in various domains, from biology to material science, results from its strong coordinating ability, its capacity to stabilize a wide range of oxidation states and stereochemistries and to adopt different ligation modes, thus giving a rich variety of homo- and heteropolynuclear compounds with interesting structures and physicochemical properties. The research in this field is currently attracting much attention with the discovery of molecular-based assemblies ensured by cyanide bridges, giving magnetic materials like Prussian Blue type complexes, and providing significant insights into magnetostructural correlations.[9-13] In striking contrast, the cyanide complexes of the f-elements have been largely neglected, even though the chemistry of the lanthanides and actinides has witnessed a spectacular overall development during the recent period.[14-23]

The first report of a uranium cyanide complex dates from 1901 with the formation of an insoluble uranyl species obtained by reaction of uranyl acetate with excess KCN. This material was formulated as $[K_2][UO_2(CN)_4]$ but it was not characterized.[24] After initial attempts in 1964 at the preparation of a uranium(IV) cyanide complex by treatment of the chloride or thiocyanate precursors with mercuric cyanide or iodine monocyanide in acetonitrile solution,[25] such a compound, $[UCl_3(CN)]\cdot 4NH_3$, was isolated for the first time in 1970 from the reaction of UCl_4 and NaCN in anhydrous liquid ammonia.[26] Under such conditions, this insoluble complex did not react further with additional NEt_4CN, but the possible formation of the bis(cyanide) $[NEt_4]_2[UCl_4(CN)_2]$ from UCl_4 and NEt_4CN in liquid hydrogen cyanide was suggested. Following these results, the homoleptic lanthanide cyanides $[Ln(CN)_x]_\infty$ (x = 3 and Ln = Ce, Pr, Sm, Eu, Ho, Yb, or x = 2 and Ln = Sm, Eu, Yb) were

obtained by either of two ways: treatment of metal turnings with $Hg(CN)_2$ in liquid NH_3 gave impure products whereas electrolysis of metal pieces in the presence of HCN in liquid ammonia afforded the pure compounds in low yields.[27] The tris(cyclopentadienyl) and bis(indenyl) cerium(IV) complexes $[Ce(Cp)_3(CN)]$ (Cp = η-C_5H_5) and $[Ce(C_9H_7)_2(CN)_2]$ were reported in 1972,[28] but these results were strongly questioned.[29] The first organouranium cyanide complexes $[U(Cp)_2(CN)]$ and $[U(Cp)_3(CN)]$ were synthesized in 1974 by protonolysis of $[U(Cp)_3]$ and $[U(Cp)_4]$ with HCN in benzene, as well as $[Ln(Cp)_2(CN)]$ from $[Ln(Cp)_3]$ (Ln = Nd, Yb).[30] Other syntheses of the tris(cyclopentadienyl) derivatives $[U(C_5H_4R)_3(CN)]$ were proposed afterwards (Scheme 1): from salt metathesis reactions of $[U(C_5H_4R)_3Cl]$ (R = H, Me) with alkali metal cyanides in aqueous solution or acetonitrile,[31] oxidation of $[U(C_5H_4R)_3]$ (R = H, ^{t}Bu) with nitrile [32] or isonitrile molecules,[30,31] and addition of N^nBu_4CN to the cationic precursors $[U(C_5H_4R)_3][BPh_4]$ (R = ^{t}Bu, $SiMe_3$).[33,34] However, attempts at the preparation of the anionic derivatives $[U(C_5H_4R)_3(CN)_2]^-$ (R = H, Me) by reaction of $[U(C_5H_4R)_3(CN)]$ with an excess of alkali metal cyanide in aqueous or organic solutions were unsuccessful.[31] The poor solubility of these complexes in organic solvents and their high ν(CN) infrared stretching frequencies (between 2090 and 2110 cm^{-1}) suggested that they adopt a polymeric structure ensured by strong CN bridges. This hypothesis was confirmed with the characterization of the cyclic trimeric and hexameric samarium compounds $[Sm(Cp^*)_2(\mu\text{-}CN)(CNCy)]_3$[35] and $[Sm(Cp^*)_2(\mu\text{-}CN)]_6$[36] ($Cp^*$ = η-C_5Me_5) (Fig. 1), isolated in 1988 and 1997 respectively. These were the first cyanide complexes of the f-elements to have been structurally characterized and they were followed by a series of lanthanide analogues $[Ln(Cp^*)_2(\mu\text{-}CN)(L)]_3$ (Ln = La or Pr and L = Me_3SiCN;[37,38] Ln = Ce or Sm and L = ^{t}BuNC;[38,39] Ln = Sm and L = ^{t}BuCN)[40] synthesized either by oxidation of $[Sm(Cp^*)_2(THF)_2]$ with ^{t}BuCN,[40] or salt metathesis reaction of $[Ce(Cp^*)_2I]$ with N^nBu_4CN in the presence of ^{t}BuNC,[39] or sterically induced reductions of $[M(Cp^*)_3]$ (M = La, Pr, Sm)[37,38]

in the presence of Me_3SiCN, Me_3SiCH_2NC, $C_6H_{11}NC$, ^{t}BuNC or ^{t}BuCN (Scheme 2). It is only in 2010 that the uranium counterpart $[U(Cp^*)_2(\mu\text{-}CN)(CN^tBu)]_3$ was isolated from the reaction of $[U(Cp^*)_3]$ with ^{t}BuNC through N−C bond cleavage.[38]

Significant advances in the design of cyanido-bridged molecular-based magnetic materials during the last decade have led to the synthesis of a large number of hetero-polynuclear d–4f complexes which open new perspectives for the study of the magnetic interactions between transition and lanthanide metal ions through the cyanido bridge, with the emergence of novel properties of the magnetic materials resulting from the large and anisotropic magnetic moment of the paramagnetic metal centres.[12,41-44] These complexes, which are also attractive for their potential as multifunctional systems combining several properties such as magnetism, luminescence and catalysis, have already been reviewed and will not be further described here. By comparison, such compounds of the actinides are quite uncommon, being limited to a few thorium(IV) tetracyanoplatinates[45,46] and uranyl,[45,47] actinide(IV) (An = Th, U, Np, Pu) and actinide(III) (An = Am, Cf) hexacyanoferrates.[46,48,49] These latter species received a special attention for their interest in nuclear fuel reprocessing and subsequent lanthanide or minor actinide separation.

When we started our studies on the f-element cyanide complexes in 2007, we were surprised that, in contrast to the numerous cyanometalates, no mononuclear lanthanide complex with a terminal cyanide ligand was reported and only two such compounds of uranium were crystallographically characterized, i.e. the monocyanides $[U(C_5Me_4H)_3(CN)_{0.4}(Cl)_{0.6}]$[50] and $[U(C_5{}^tBu_3H_2)_2(CN)(OSiMe_3)]$ (Fig. 2).[51] The former was serendipitously obtained from the decomposition of the alkyl isocyanide derivative $[U(C_5Me_4H)_3(CN^tBu)]$ while the latter bis(cyclopentadienyl) complex was synthesized by treating the oxo precursor $[U(C_5{}^tBu_3H_2)_2(=O)]$ with Me_3SiCN. As for the d transition metals, the wide range of physico-chemical properties offered in developing the cyanide chemistry of

uranium and the lanthanides, in particular because of the novel structures and reactions which could be expected from their high coordination numbers and possible contribution of the f orbitals, were an incitement to prospect this field. However, in order to prevent the formation of insoluble cyanide products, soluble organometallic and amide precursors with NMR signature and limited number of coordination sites were at first carefully chosen so as to favor the formation of soluble and easily detectable cyanide compounds. By using the alkali metal or ammonium salts of the CN^- ion as cyanation reagents, we isolated a number of mono- and polycyanide complexes of cerium, thorium and uranium, in the inorganic and organometallic series. These complexes displayed novel and unexpected structures, in particular the uranium compounds which proved stable both in low and high oxidation states. The three metal ions were found to exhibit major differences in their bonding and reactions with the CN group, revealing the role of the f electrons and orbitals in the metal-cyanide bond.

2. Linear metallocenes, bent actinocenes and half sandwiches

The small size, linear shape and strong coordinating ability of the cyanide ligand have been of major interest in the synthesis of unique examples of discrete mono-and polycyanide complexes which revealed unprecedented and unexpected coordination geometries.

Until recently, the linear metallocenes of the f-elements were limited to three compounds of the divalent lanthanides (Sm, Eu, and Yb) for which the linear geometry was forced by the steric crowding of the bulky substituents on the cyclopentadienyl rings.[52-54] All the other derivatives with small substituents, in particular the bisCp* compounds which are the most popular metallocenes, were found exclusively in a bent-sandwich configuration whatever the nature of the f metal ion, its oxidation state and the charge of the complex. The first linear $M_f(C_5Me_5)_2$ compounds (M_f = f-element) were synthesized by filling completely

the equatorial girdle of the bisCp* uranium fragment with five neutral or anionic donor ligands (MeCN, CN^-) and such complexes represent a new type of linear metallocenes only observed at that time with uranium.[55,56] Thus, treatment of $[U(Cp^*)_2X_2]$ [X = I, OSO_2CF_3 (OTf)] with NR_4CN gave successively the bent bis- and tris(cyanide) metallocenes $[U(Cp^*)_2(CN)_2]$ and $[NR_4][U(Cp^*)_2(CN)_3]$, and the penta(cyanide) derivative $[NR_4]_3[U(Cp^*)_2(CN)_5]$ (Fig. 3), which adopts a linear configuration (Scheme 3).[34,57,58] The bis(cyanide) $[U(Cp^*)_2(CN)_2]$ was afterwards isolated from the reaction of the fluoride $[U(Cp^*)_2F_2(py)]$ with excess Me_3SiCN.[59] The tris and penta(cyanide) U^{IV} complexes were found to be in equilibrium in solution.[34] In contrast, the bent tris(cyanide) metallocenes $[N^nBu_4]_2[M(Cp^*)_2(CN)_3]$ (M = Ce, U) (Fig. 3) were the sole products isolated from the trivalent precursors $[M(Cp^*)_2I]$ or $[M(Cp^*)_2(\mu\text{-}CN)]_n$, even in the presence of excess cyanide.[58] Theoretical calculations showed that the uranium(III) complex is not stable in the linear configuration because one electron occupies an antibonding orbital, while uranium(IV) metallocenes are stable in both the bent and linear configuration.[57] More generally, a decreasing number of 5f electrons in the $M_f(Cp^*)_2$ fragment would favor subsequent addition of ligands and a transition from bent to linear shape, and the existence of the $5f^0$ uranium(VI) complex $[U^{VI}(Cp)_2(CN)_5]^-$ was predicted by DFT calculations.[60]

The rapid and reversible electron transfer between the U^{III} and U^{IV} centres of $[U(Cp^*)_2(CN)_3]^{2-}$ and $[U(Cp^*)_2(CN)_3]^-$ was revealed by ^1H NMR spectroscopy.[58] Comparison of the crystal structures of $[N^nBu_4]_2[M^{III}(Cp^*)_2(CN)_3]$ (M = Ce, U) shows that the U–C(Cp*) and U–C(CN) distances are shorter, by 0.02–0.03 Å, than the Ce–C(Cp*) and Ce–C(CN) distances, while the ionic radius of uranium(III) is ~0.02 Å larger than that of cerium(III). Such deviations of U–X distances (X = C, N, I, P, S) from a purely ionic bonding model, which have been observed in a variety of analogous uranium(III) and lanthanide(III) complexes,[61,62] are explained by a stronger, more covalent actinide–ligand interaction. In

these anionic and monomeric complexes, the shortening of the U–C(CN) bond length with respect to the corresponding Ce–C(CN) could be an indication of a stronger σ-donation of the ligand towards uranium rather than π back-bonding, as supported by the ν(CN) frequencies.

Crystals of the mixed valence uranium(III/IV) complex $[\{U(Cp^*)_2\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$, which is a 1D coordination polymer (Fig. 4), were isolated from one attempt to prepare monomeric polycyanide compounds of trivalent uranium by mixing $[U(Cp^*)_2I]$ with an excess of NaCN.[58] This compound, which certainly resulted from oxidation of an U^{III} polycyanide species by traces of air, can be formally viewed as the association of the U^{III} and U^{IV} complexes $[U^{III}(Cp^*)_2(CN)_3\{Na(thf)\}_2]$ and $[U^{IV}(Cp^*)_2(CN)_2]$. Together with the trinuclear compound $[\{U^{IV}(Cp^*)_2Cl_2(\mu\text{-}CN)\}_2Mg(thf)_4]$ (Fig. 4) which was serendipitously formed in a mixture of $[U(Cp^*)_2Cl_2]$, NaCN and residual traces of $MgCl_2$,[34] the polymeric uranium(III/IV) complex is likely to be the first compound exhibiting f-element–C≡N–M bridges (M = main group or d transition metal) since in the aforementioned lanthanide and actinide cyanometalates, the bridging CN ligands are coordinated to the f-element via the nitrogen atom. The U–N≡C–Ag linkage was also found in the first cyanometalate of uranium(IV), $[U(Cp^*)_2(dmf)_3(\mu\text{-}NC)_2(AgI)_2{\cdot}2dmf]_\infty$ (Fig. 4), synthesized by treating $[U(Cp^*)_2I_2]$ with AgCN in dmf,[34] which is the first linear metallocene of an f-element with distinct donor ligands in its equatorial girdle,[63] and which crystallizes as a 2D assembly.

Since its discovery in 1968, uranocene $[U(Cot)_2]$ (Cot = η-C_8H_8)[64] and its derivatives in the actinide and lanthanide series all exhibited a D_{8h} symmetry and a disappointingly poor reactivity which was explained by their inability to coordinate supplementary ligands to the metal centre as the result of the steric constraints imposed by the two parallel rings. Therefore, it was generally accepted that a bis(cyclooctatetraenyl) complex could not adopt a bent configuration. Here again, the cyanide ion was useful in showing that things could be otherwise since it proved to be an efficient wedge for bending the linear uranocene and

thorocene, with formation of the monocyanide complexes [M][An(Cot)$_2$(CN)] (An = Th,[65] U;[66] M = Na(18-crown-6) or NR$_4$) (Fig. 5). Theoretical studies indicate that despite the broken symmetry, the gain in electrostatic interaction and a significant uranium–CN orbital interaction are sufficient to stabilize the bent cyanide complex with respect to uranocene. The 6d, and to a less extent 5f, uranium orbitals have a significant participation in the interaction both with the aromatic rings and the cyanide ligand.[67] However, thorocene was found to be much more reactive than uranocene since a series of sterically crowded cyanide complexes has been obtained only from [Th(Cot)$_2$], depending on the Th:CN ratio and the nature of the M^+ cation of the MCN reagent (Scheme 4). The remarkable stability of uranocene compared to cerocene and thorocene was previously noted and theoretically explained by the greater covalency due to the larger involvement of 6d and 5f orbitals in the uranium-ligand bonding.[68,69] The coordinating ability of [Th(Cot)$_2$(CN)]$^-$ was demonstrated by the structural characterizations of di-, tri- and polynuclear species with [Th]−C≡N−[Na] bridges in [Th(Cot)$_2$(μ-CN)Na(18-crown-6)][65] or [Th]−C≡N−[Th] linkages in [N^{n}Bu$_4$][{Th(Cot)$_2$}$_2$(μ-CN)], [N^{n}Bu$_4$]$_2$[{Th(Cot)$_2$(μ-CN)}$_2$Th(Cot)$_2$] and [NR$_4$][Th(Cot)$_2$(μ-CN)] (Fig. 6).[70] The polymeric arrangement of the latter monocyanide complex revealed that not only one but two coordination sites are available on a bent Th(Cot)$_2$ fragment, and this was confirmed with the synthesis of the biscyanide [N^{n}Bu$_4$]$_2$[Th(Cot)$_2$(CN)$_2$] (Fig. 6).[70]

In contrast to the relative inertness of uranocene, the distinct reactivity of thorocene was also observed in the presence of other anions and neutral mono- and bidentate Lewis bases, with formation of the bent sandwich complexes [Th(Cot)$_2$N$_3$]$^-$, [{Th(Cot)$_2$}$_2$(μ-H)]$^-$ and [Th(Cot)$_2$(L)] (L = ^{t}BuNC, py, 2,2'-bipy, 4,4'-bipy, R$_4$Phen).[71,72] From DFT calculations, this difference was accounted for by electrostatic effects, the 5f^0 thorium ion being more Lewis acidic than its 5f^2 uranium analogue.[71]

The great affinity of the CN^- ion for uranium(IV) also favoured the synthesis of some soluble heteroleptic polycyanides which might offer ways to the homoleptic $U(CN)_n$ compounds. For example, the monoCp* and monoCot complexes $[NEt_4]_3[U(Cp^*)(CN)_6]$, $[NEt_4]_3[U(Cot)(CN)_5]$ and $[NEt_4]_2[U(Cot)(CN)_4]$ (Fig. 7) were synthesized by treating the iodide and amide precursors $[U(Cp^*)I_3(THF)_2]$, $[U(Cot)I_2(THF)_2]$ and $[U(Cot)(N^*)_2]$ [N* = $N(SiMe_3)_2$] with NEt_4CN, whereas the mixed amido-cyanide complex $[NEt_4]_3[U(CN)_6(NEt_2)]$ was obtained from the cation $[U(NEt_2)_3][BPh_4]$.[73-76] Despite its strong coordinating ability, the CN^- ion proved unable to displace a Cot ligand of the actinocenes $[An(Cot)_2]$ (An = Th, U), in contrast to the amide and alkoxide groups NEt_2^- and O^iPr^- which reacted with $[U(Cot)_2]$ to give $[U(Cot)X_3]^-$ (X = NEt_2, O^iPr).[77]

When they are of sufficient quality to permit the differentiation between carbon and nitrogen atoms, the X-ray diffraction data show that the CN group is attached to the metal via the carbon atom in all the aforementioned complexes, with the exception of the cyanometalates.

3. Cyanide linkage isomerism in Ce^{III}, U^{III} and U^{IV} complexes

After the bent metallocenes $[N^nBu_4]_2[M^{III}(Cp^*)_2(CN)_3]$ (M = Ce, U) which were the first trivalent molecular polycyanide compounds of an f-element to have been structurally identified, and the first fully characterized actinide(III) cyanide,[58] new Ce^{III} and U^{III} cyanide compounds were synthesized by addition of M'CN [M' = NR_4 with R = Me, Et, ^{n}Bu or K(18-crown-6)] to the tris(silylamide) precursors $[MN^*_3]$ (M = Ce, U).[78] Thus were formed successively the cyanido-bridged dinuclear compounds $[M'][(M^{III}N^*_3)_2(\mu\text{-}CN)]$ and the mononuclear mono-, bis- and tris(cyanide) complexes $[M'][MN^*_3(CN)]$, $[M']_2[MN^*_3(CN)_2]$ and $[N^nBu_4]_2[MN^*_2(CN)_3]$ (Scheme 5). The synthesis of the polycyanide derivatives required

the use of the more soluble $^{n}Bu_4CN$ salt. The bis(cyanide) complexes were found to be in equilibrium with the mono(cyanide) complexes in solution and were slowly transformed into an equimolar mixture of the mono- and tris(cyanide) derivatives with elimination of a N* ligand. The crystal structures of $[K(18\text{-crown-6})]_2[U^{III}N^*_3(\mu\text{-}CN)_2]$ and its benzene solvate showed unambiguously the cyanide ligation mode of the CN ligand to the U atom in the U–C≡N–K bridges (Fig. 8). The 1D polymeric structure of the unsolvated complex arises from the presence of interactions between adjacent K(18-crown-6) fragments which are disrupted by benzene molecules in the solvate $[K(18\text{-crown-6})]_2[U^{III}N^*_3(\mu\text{-}CN)_2]\cdot 2C_6H_6$. The analogous cerium complexes are isomorphous with those of the uranium counterparts but not isostructural because of the distinct cyanide linkage in the Ce–N≡C–K bridges (Scheme 6). The Ce–NC bonding mode was also clearly determined in the mononuclear complex $[N^{n}Bu_4]_2[CeN^*_3(CN)_2]$ (Fig. 8). The striking difference between the cyanide and isocyanide ligation modes of the CN ligand in the uranium and cerium species can be explained by the U^{III} ion being softer than the Ce^{III} ion in the HSAB classification and having a greater affinity for the softer carbon end of the CN ligand. The preferential coordination of the cyanide and isocyanide ligands towards uranium or cerium in the trivalent bis(cyanide) complexes was corroborated by the consideration of the binding energies of these ligands to the metal ions and by the confrontation of the DFT optimized geometries and the structural crystal data. The electronic structure analysis showed that the σ-donating ability of the cyanide ligand is stronger with uranium than with cerium cations, due to the better energy matching between 6d/5f metal and ligand orbitals. This difference plays a significant role in the metal–ligand coordination preference, leading to a non negligible covalent character of the bonding in the former case.

The uranium(IV) analogues of these trivalent cyanide complexes in the UN^*_3 series, $[(UN^*_3)_2(\mu\text{-}CN)][BPh_4]$, $[UN^*_3(CN)]$ and $[M][UN^*_3(CN)_2]$ (M = NEt_4 or $K(THF)_4$) were

synthesized by successive addition of NEt_4CN or KCN to the cationic precursor $[U^{IV}N^*_3][BPh_4]$ (Scheme 7), while crystals of $[K(18\text{-crown-6})][U^{IV}N^*_3(CN)_2]$ were obtained by oxidation of $[K(18\text{-crown-6})][U^{III}N^*_3(CN)]$ with pyridine *N*-oxide.[79] The striking structural feature of these complexes (Fig. 9) is the coordination of the CN group to the U^{4+} ion through the nitrogen atom, which is opposite to the cyanide ligation mode observed in the uranium(III) counterparts. These are the first cristallographically characterized complexes with a U–NC linkage. Here again, the distinct U^{IV}–N and U^{III}–C ligation modes of the CN ligand in these couples of isocyanide and cyanide complexes can be explained from the HSAB classification by the fact that the U^{4+} ion, a harder Lewis acid than U^{III}, displays a greater affinity for the harder nitrogen end of the CN ligand. The same arguments can account for the difference in the crystal structures of the thorium(IV) $5f^0$ complex $[Th(C_5{}^tBu_3H_2)_2(NC)(OSiMe_3)]$[80] which revealed a Th–NC bonding of the CN ligand while the uranium(IV) analogue $[U(C_5{}^tBu_3H_2)_2(CN)(OSiMe_3)]$ shows a U–CN linkage,[51] a difference which has not been commented. DFT calculations on the actual complexes and their hypothetical counterparts $[UN^*_3X]^q$ (q = –1, 0) and $[UN^*_3X_2]^q$ (q = –2, –1) (X = CN or NC) shows that the stronger σ-donating ability of cyanide and isocyanide towards the U^{III}/U^{IV} pair is governed by the best energy matching between 6d/5f metal and ligand orbitals and covalency contribution (orbital mixing). This latter effect seems to play a more significant role for the observed U^{III}–CN than for the U^{IV}–NC coordination.[79]

Very recently, the U–NC bonding was unveiled by the infrared spectra and electronic structure calculations of the MeU(NC) and CH_2=U(H)(NC) complexes and the series of U(NC), $U(NC)_2$ and $U(NC)_4$ compounds obtained by reactions of laser-ablated uranium atoms with acetonitrile[81] and cyanogen,[82] respectively, in argon matrices at 4 K. These results indicate that the isocyanides bond more strongly to the uranium in the +1 to +4 oxidation states than the cyanides when no other ligands are present. It is interesting to note that the

metal-isocyanide coordination mode was also predicted for the Ti^{IV} compounds $[Ti(CN)_n]^{4-n}$ (n = 1 – 6), except for n = 6 where the cyanide isomer is preferred.[83]

However, the cyanide ligands were found to be attached via the carbon atom in $[NEt_4][UN^*(N,N)(CN)_2]$[84] [*N*,*N* = $(Me_3Si)NSiMe_2CH_2CH_2SiMe_2N(SiMe_3)$] (Fig. 10) where the N–U–N angles between the amide groups differ from those measured in [K(18-crown-6)][$UN^*_3(CN)_2$]. Similar distortions are observed in the structure of the dinuclear U^{III} complex [Na(15-crown-5)][$\{UN^*(N,N)\}_2(\mu$-CN)] (Fig. 10),[85] by comparison with that of [K(18-crown-6)][$(UN^*_3)_2(\mu$-CN)].[77] These compounds belong to a series of cyanide complexes of (*N*,*C*), (*N*,*N*) and (*O*,*N*) metallacycles of tri-, tetra- and pentavalent uranium which are derivatives of the (*N*,*C*) metallacycles [$UN^*_2(N,C)$] and [$NaUN^*(N,C)_2$] [*N*,*C* = $CH_2SiMe_2N(SiMe_3)$], as detailed in Scheme 8. The distinct U–CN coordination mode in $[UN^*(N,N)(CN)_2]^-$ by comparison with U–NC in $[UN^*_3(NC)_2]^-$ is difficult to explain because the energy difference between the actual cyanide and hypothetical isocyanide complexes is small. More generally, the U−CN/NC coordination preference towards the U^{III}/U^{IV} pair is related to the subtle balance between steric, covalent and ionic factors that govern U–CN/NC bonding. However, in all cases, DFT computations and in particular the calculated total bonding energies between the metal and the cyanide ligand allowed to predict the observed coordination mode.[79]

4. High-valent uranium cyanide complexes

The absence of any identified uranyl cyanide complex was surprising in view of the large number of studies devoted to the halides and pseudo-halides (N_3, NCS, NCO) of the ubiquitous *trans*-dioxo uranyl(VI) ion, $\{UO_2\}^{2+}$.[86] Prior to any experimental results, the cyanide ligand was claimed to be anathema to uranium(VI) because the carbon end of CN was

considered as a strong σ donor and a good π acceptor.[87] However, the coordination and bonding of the CN^- group to $\{UO_2\}^{2+}$, via U–C or U–N bonding, was further questioned[88,89] and, on the basis of DFT calculations, the penta(cyanide) derivative $[UO_2(CN)_5]^{3-}$ was predicted to be the most stable species in aqueous solution.[89] To conclude the debate, a few uranyl cyanide complexes have been recently characterized. The U–CN ligation mode of the cyanide ion was unambiguously determined in the crystal structure of $[N^nBu_4]_3[UO_2(CN)_5]$ (Fig. 11) which was obtained by reaction of $[UO_2(OTf)_2]$ with N^nBu_4CN.[90] The mean U–C(CN) distance is larger than expected by *ca* 0.3–0.4 Å when compared to the mean U–C(CN) bond length of 2.62(3) Å in the eleven-coordinate and geometrically similar trianionic U^{IV} complex $[NEt_4]_3[U(Cp^*)_2U(CN)_5]$,[57] suggesting a stronger U^{IV}–CN interaction, in agreement with the IR data.

The affinity of the cyanide ion for the uranyl fragment was also demonstrated by the formation of the *cis*-amido cyanide derivative $[NEt_4]_2[UO_2(N^*)_2(CN)_2]$ resulting from addition of NEt_4CN to $[UO_2(N^*)_2]$ in pyridine.[91]

Stabilization of high-valent organouranium complexes, especially those of the *trans* dioxo uranyl ion $\{UO_2\}^{2+}$ which is the most stable species in the +6 oxidation state, is a long-standing challenge. The first cyclopentadienyl uranyl complex, $[NEt_4]_3[UO_2(Cp^*)(CN)_3]$, was synthesized by oxidation of the linear U^{IV} metallocene $[NEt_4]_3[U(Cp^*)_2(CN)_5]$ with pyridine *N*-oxide. (Scheme 9) Its structure (Fig. 11) represents a novel coordination geometry for the uranyl ion which almost invariably adopts a polygonal bipyramidal configuration.[92] It is noteworthy that cyclopentadienyl uranyl compounds could not be synthesized by reaction of uranyl $\{UO_2\}^{2+}$ salts with cyclopentadienyl anions, which is in fact a convenient route to pentavalent derivatives of the $\{UO_2\}^+$ ion.[93]

Uranium(V) complexes are reputed to undergo facile disproportionation into U^{IV} and U^{VI} derivatives and the factors which determine their stability are not well understood. The cyanide ligand proved to be efficient in the stabilization of the +5 oxidation state, as shown by the linear metallocene $[N^nBu_4]_2[U(Cp^*)_2(CN)_5]$ obtained by oxidation of the parent U^{IV} precursor by traces of oxygen.[57] In the $5f^1$ U^V complex, only one out-of-plane f orbital is occupied, which minimizes the electronic repulsion with the CN^- lone pair and thus favours the linear form.

Owing to its anionic character which would favour its ready one electron oxidation and the presence of amide and alkoxide ligands which generally stabilize the high metal oxidation states, the bis metallacyclic complex $[NaU^{IV}N^*(O,N)_2]$ [*O*,*N* = *O*C(=CH_2)SiMe_2*N*(SiMe_3)] was considered as a potential precursor of U^V and U^{VI} compounds. Actually, its reaction with I_2 afforded the diuranium(V) "ate" complex $[Na][\{U^VN^*(N,O)_2\}_2(\mu\text{-}I)]$ which was transformed into the cyanide $[M][U^VN^*(N,O)_2(CN)]$ [M = NEt_4, Na(15-crown-5)] in the presence of MCN (Scheme 8, Fig. 12).[84] However, the tris(amido) bis(cyanide) complex $[U^VN^*_3(CN)_2]$ could not be isolated either from one electron oxidation of $[NEt_4][U^{IV}N^*_3(CN)_2]$[79] or substitution of the halide ligands of $[U^VN^*_3X_2]$ (X = F, Cl, Br) with Me_3SiCN or N^nBu_4CN, a failure which was explained by unfavorable thermodynamic factors.[94]

At last, the third U^V cyanide compound to have been reported is $[NEt_4][UN^*_3(=O)(CN)]$ (Fig. 12), readily obtained by addition of NEt_4CN to the oxo precursor $[U^VN^*_3(=O)]$.[94] The U–CN distance of 2.491(7) Å, shorter than those measured in $[N^nBu_4]_2[U^V(Cp^*)_2(CN)_5]$ (2.548(7) Å)[57] and $[U^VN^*(N,O)_2(\mu\text{-}CN)Na(15\text{-crown-}5)]$ (2.567(7) Å),[84] was attributed to the inverse trans influence stabilization imparted by the oxo ligand.[94-96]

Conclusion

The chemistry of cyanide complexes of the f-elements witnessed significant advances during the last decade, confirming the remarkable coordinating capacity of the small-sized and linearly shaped CN group. The cyanide ligand was useful in the synthesis of a new type of linear metallocenes and of the first actinocenes with a bent geometry, $[U(Cp^*)_2(CN)_5]^{3-}$ and $[An(Cot)_2(CN)]^-$ (An = Th, U), thus disproving the generally accepted ideas on the stability and reactivity of these complexes. Most notable is the capacity of the cyanide group to highlight the greater reactivity of thorocene by comparison to uranocene, through occupancy of a second coordination site in the bis(cyanide) $[Th(Cot)_2(CN)_2]^{2-}$ and its derivatives. The ability of the cyanide ligand to stabilize uranium compounds from the +3 to +6 oxidation states was assessed, and novel high-valent U^V and U^{VI} complexes in the inorganic and organometallic series were synthesized. The cyanide ligand was very efficient in the differentiation of the Ce^{III}, U^{III} and U^{IV} metal centres in the addition reactions with $[MN^*_3]$ (M = Ce, U) and $[UN^*_3]^+$, leading to a large series of mononuclear mono-, bis- and tris(cyanide) complexes in which the U^{III}–CN, Ce^{III}–NC and U^{IV}–NC linkages were observed. These distinct coordination modes could be accounted for by DFT computations, in particular the calculated total bonding energies between the metal and the cyanide ligand, showing that the U−CN/NC coordination preference towards the U^{III}/U^{IV} pair is related to the subtle balance between steric, covalent and ionic factors. More generally, while the CN^- ion acts as a strong σ donor and a weak π acceptor ligand with the d transition metals,[97] IR spectra and DFT analysis of the f-element cyanide complexes indicate mainly cyanide to metal σ donation with no π back-donation effects, in contrast to the CO ligand in the uranium metallocene derivatives where metal-ligand back-bonding was observed.[98,99]

Further studies including theoretical analysis are necessary to specify the influence of the nature of the metal and ancillary ligands on the coordination mode of the cyanide ligand in complexes of the f-elements. Of special interest are the mononuclear compounds with terminal cyanide ligands which could be used as valuable building blocks for the design of novel clusters and coordination polymers with interesting physicochemical properties.

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Captions to Figures

Fig. 1 Crystal structures of the first crystallographically characterized f-element cyanide complexes $[Sm(Cp^*)_2(\mu\text{-}CN)(CNCy)]_3$ (left) and $[Sm(Cp^*)_2(\mu\text{-}CN)]_6$ (right). As in all subsequent figures, nitrogen atoms are purple and carbon atoms are dark blue.

Fig. 2 Crystal structure of the complex $[U(C_5{}^tBu_3H_2)_2(CN)(OSiMe_3)]$.

Fig. 3 Crystal structure of the linear anion $[U(Cp^*)_2(CN)_5]^{3-}$ (left) and of the bent anion $[U(Cp^*)_2(CN)_3]^-$ (right)

Fig. 4 Crystal structures of the cyanido bridged complexes $[\{U(Cp^*)_2\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ (top, with the Cp* methyl groups and thf carbon atoms omitted for clarity), $[\{U(Cp^*)_2Cl_2(\mu\text{-}CN)\}_2Mg(thf)_4]$ (middle) and $[U(Cp^*)_2(dmf)_3(\mu\text{-}NC)_2(AgI)_2{\cdot}2dmf]_\infty$ (bottom, with the Cp* methyl groups and dmf nitrogen and carbon atoms omitted for clarity). Sodium is dark blue, magnesium green, silver light blue and iodine brick red.

Fig. 5 Crystal structure of the anion $[U(Cot)_2(CN)]^-$.

Fig. 6 From top to bottom and from left to right: crystal structures of the bent thorocene complexes $[Na(18\text{-crown-}6)][Th(Cot)_2(\mu\text{-}CN)]$, $[\{Th(Cot)_2\}_2(\mu\text{-}CN)]^-$, $[\{Th(Cot)_2(\mu\text{-}CN)\}_2Th(Cot)_2]^{2-}$, $[Th(Cot)_2(\mu\text{-}CN)]^-$ and $[Th(Cot)_2(CN)_2]^{2-}$. Thorium atoms are green and sodium atoms blue.

Fig. 7 Crystal structures of the mono-Cp* and mono-Cot uranium(IV) cyanide complexes $[U(Cp^*)(CN)_6]^{3-}$ (left), $[U(Cot)(CN)_5]^{3-}$ (middle) and $[U(Cot)(CN)_4]^{2-}$ (right).

Fig. 8 Crystal structures of the Ce^{III} and U^{III} cyanide complexes in the MN^*_3 series $[K(18\text{-crown-6})]_2[UN^*_3(\mu\text{-}CN)_2]$ (top), $[K(18\text{-crown-6})]_2[UN^*_3(\mu\text{-}CN)_2]\cdot 2C_6H_6$ (middle) and $[CeN^*_3(CN)_2]^{2-}$ (bottom). Uranium is yellow, cerium light blue, potassium green and silicium dark blue.

Fig. 9 Crystal structures of the U^{IV} cyanide complexes in the MN^*_3 series $[(UN^*_3)_2(\mu\text{-}CN)]^+$ (top left), $[UN^*_3(CN)]$ (top right) and $[K(THF)_4][UN^*_3(CN)_2]$ (bottom). Uranium atoms are yellow and potassium atoms green.

Fig. 10 Crystal structures of the anions $[\{UN^*(N,N)\}_2(\mu\text{-}CN)]^-$ (left) and $[UN^*(N,N)(CN)_2]^-$ (right).

Fig. 11 Crystal structures of the anions $[UO_2(CN)_5]^{3-}$ (left) and $[UO_2(Cp^*)(CN)_3]^{2-}$ (right).

Fig. 12 Crystal structures of the U^V monocyanide complex $[UN^*(N,O)_2(CN)Na(15\text{-crown-}5)]$ (left) and the anion $[UON^*_3(CN)]^-$ (right).

Captions to Schemes

Scheme 1 Syntheses of triscyclopentadienyl uranium cyanide complexes.

Scheme 2 Syntheses of trinuclear cyanide complexes $[Ln(Cp^*)_2(\mu\text{-}CN)(L)]_3$.

Scheme 3 Syntheses of bent and linear cyanide metallocenes.

Scheme 4 Syntheses of bent thorocene cyanide complexes.

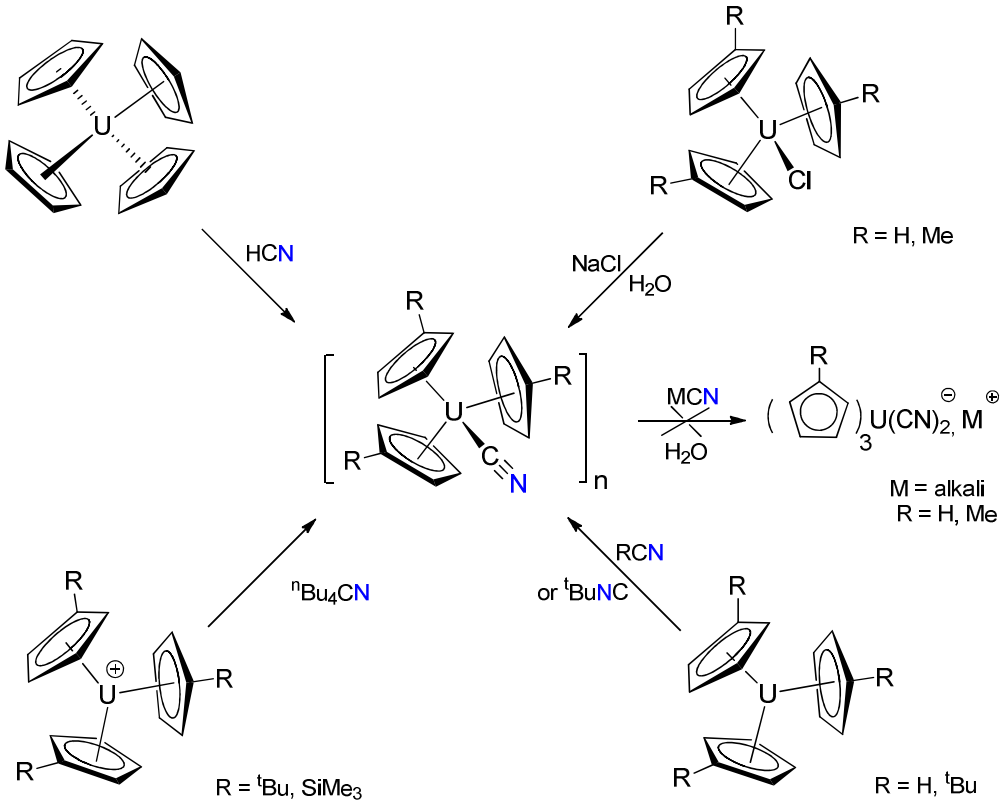
Scheme 5 Syntheses of uranium(III) cyanide complexes in the $[MN^*_3]$ series.

Scheme 6 Cyanide linkage isomerism in the anions $[MN^*_3(CN)_2]^{2-}$ (M = Ce, U)

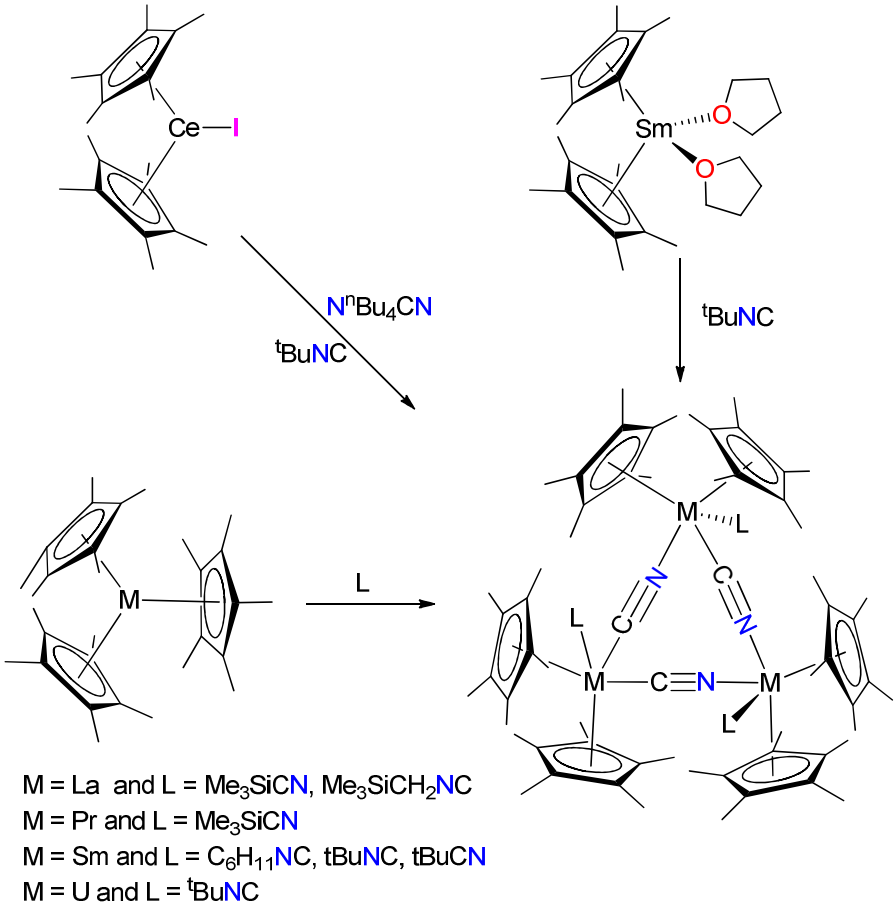
Scheme 7 Syntheses of uranium(IV) cyanide complexes in the $[MN^*_3]$ series.

Scheme 8 Cyanide complexes of (*N*,*C*), (*N*,*N*) and (*N*,*O*) metallacycles of tri-, tetra- and pentavalent uranium.

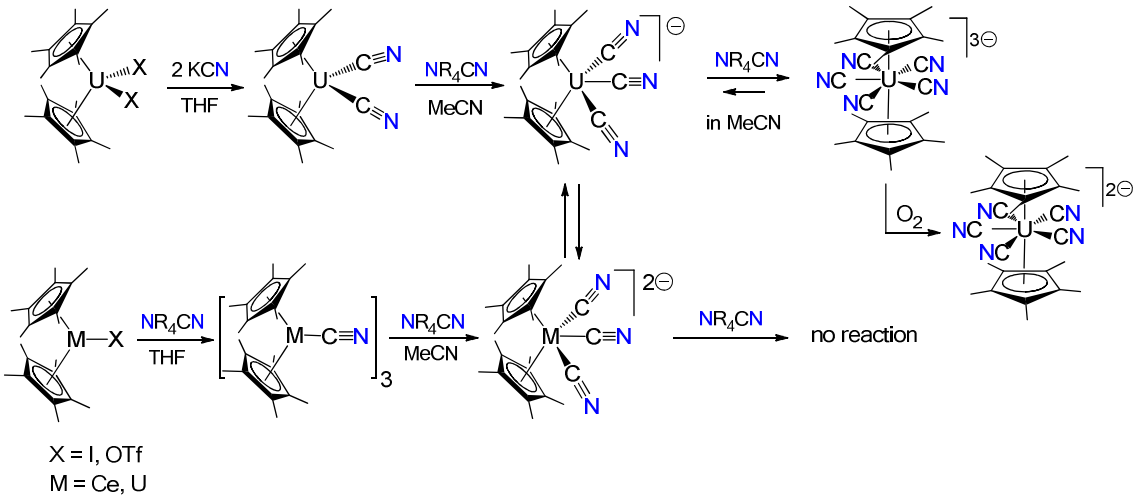
Scheme 9 Synthesis of the uranyl cyanide $[UO_2(Cp^*)(CN)_3]^{3-}$.



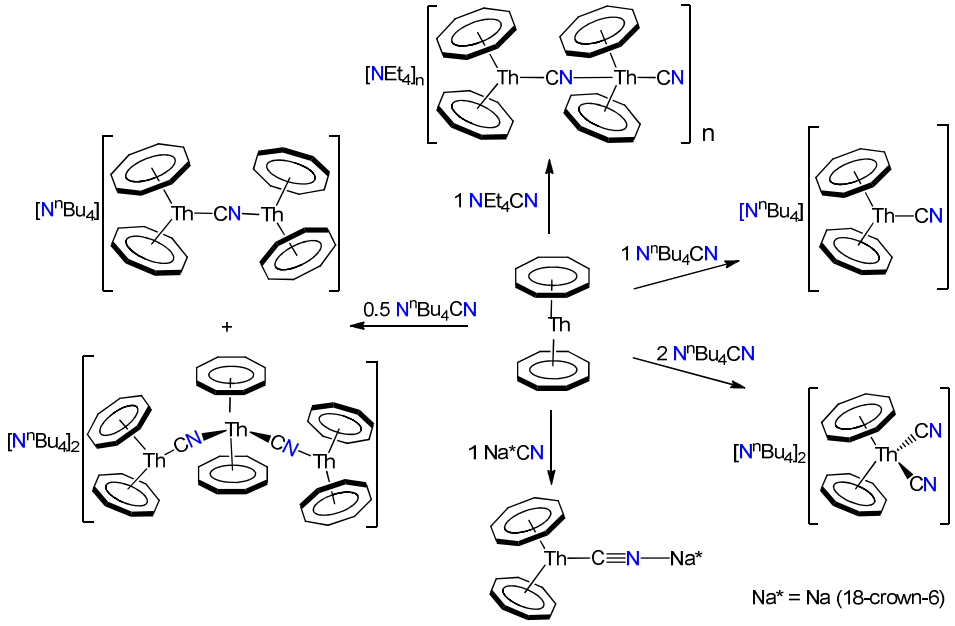
Scheme 1



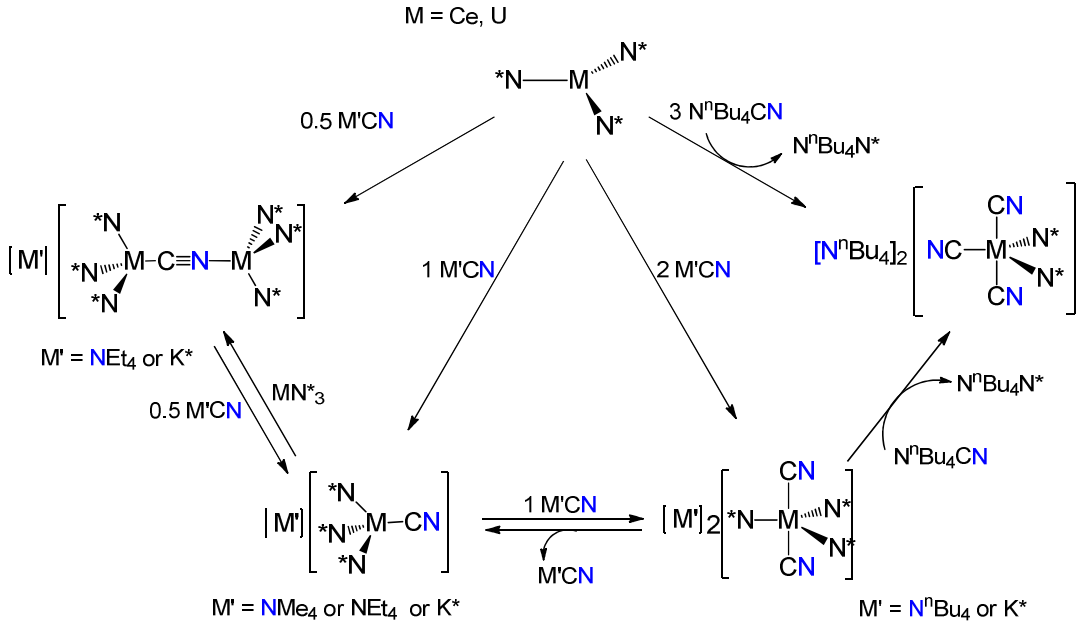
Scheme 2



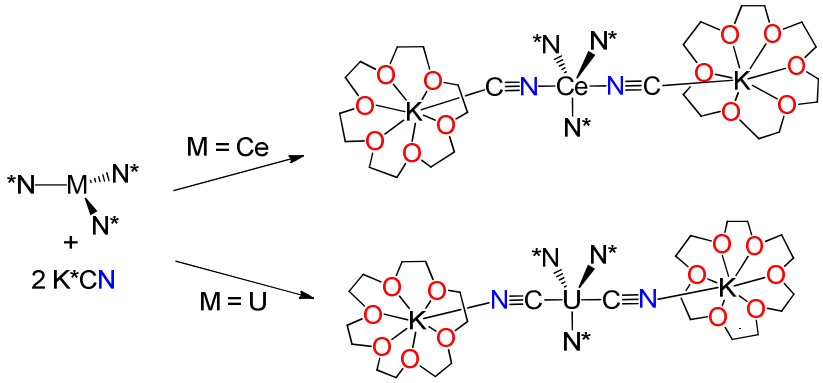
Scheme 3



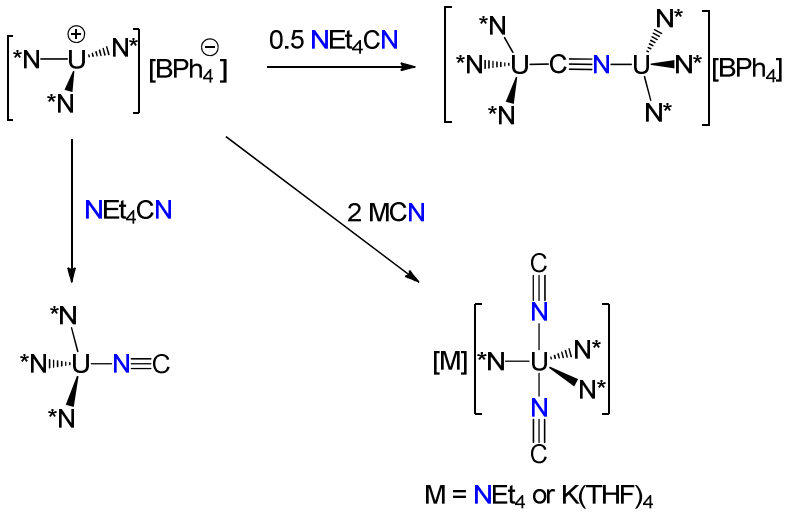
Scheme 4



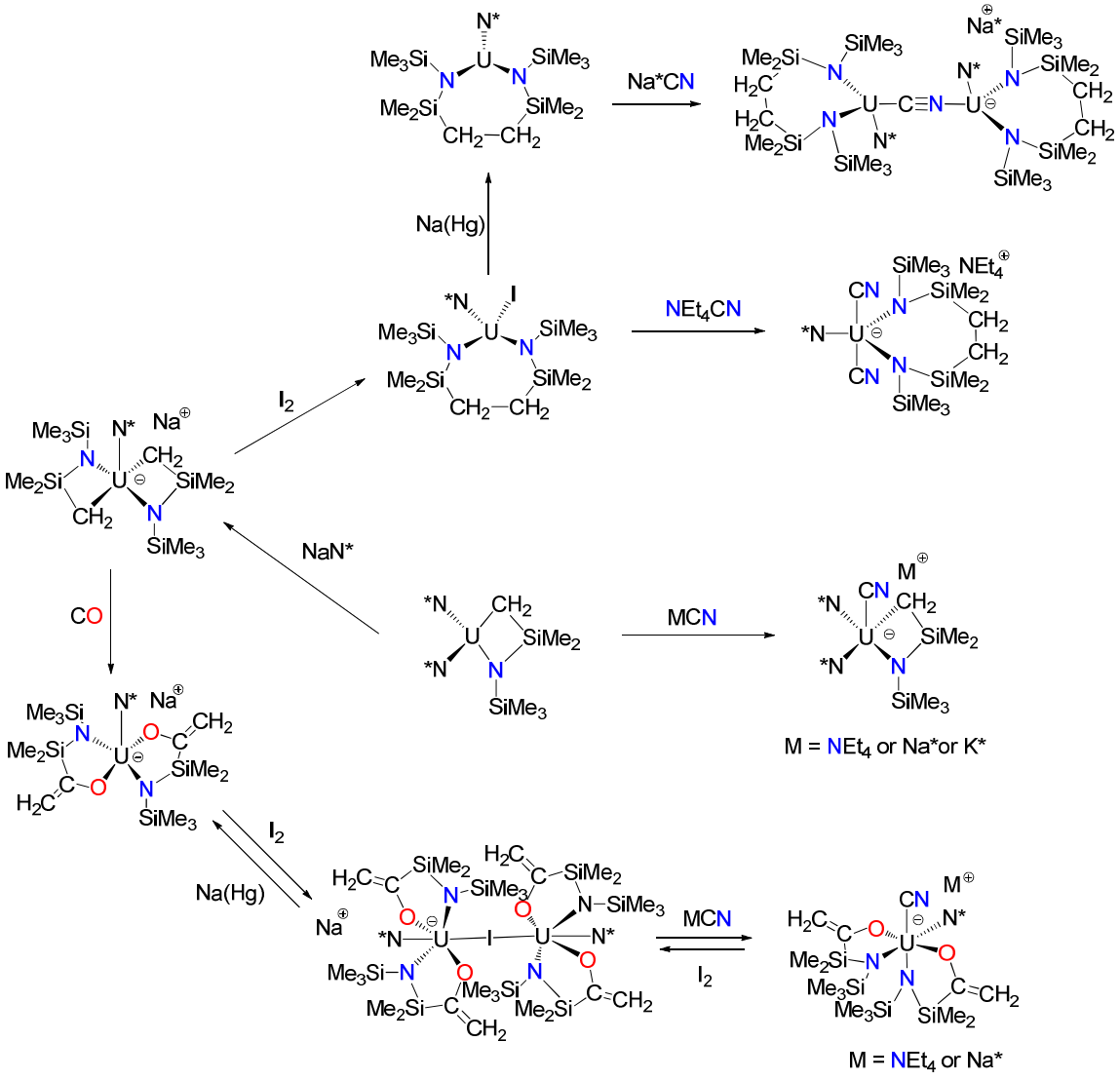
Scheme 5



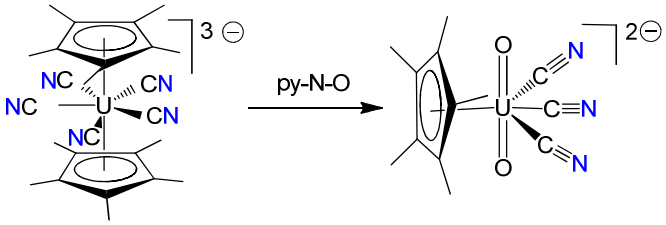
Scheme 6



Scheme 7



Scheme 8



Scheme 9

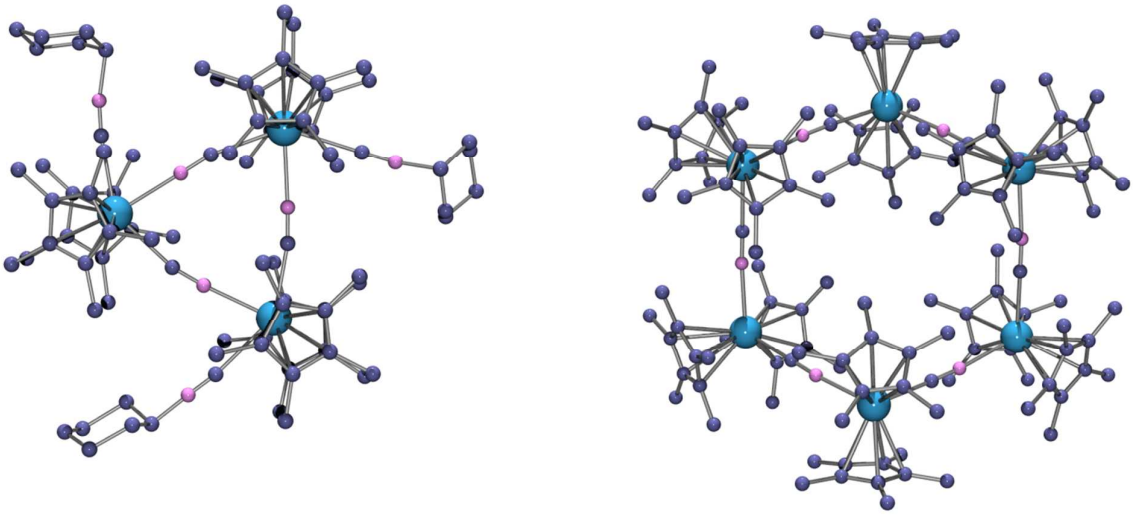


Figure 1

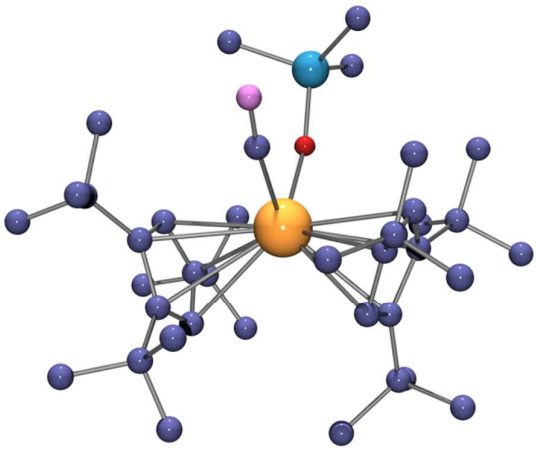


Figure 2

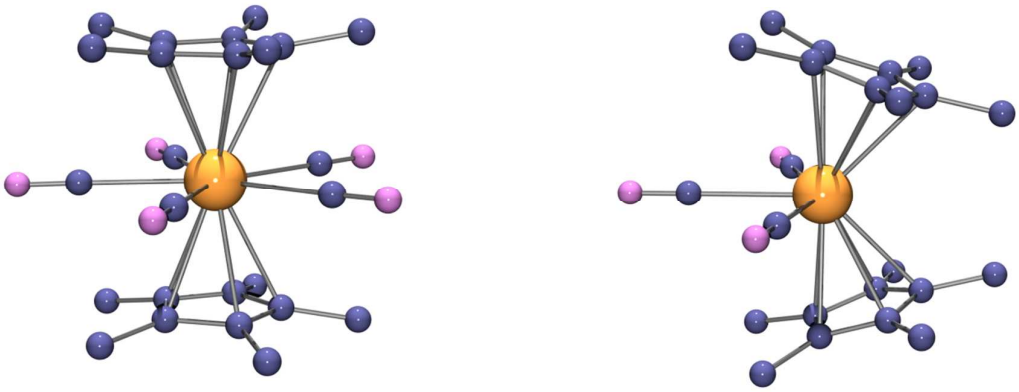


Figure 3

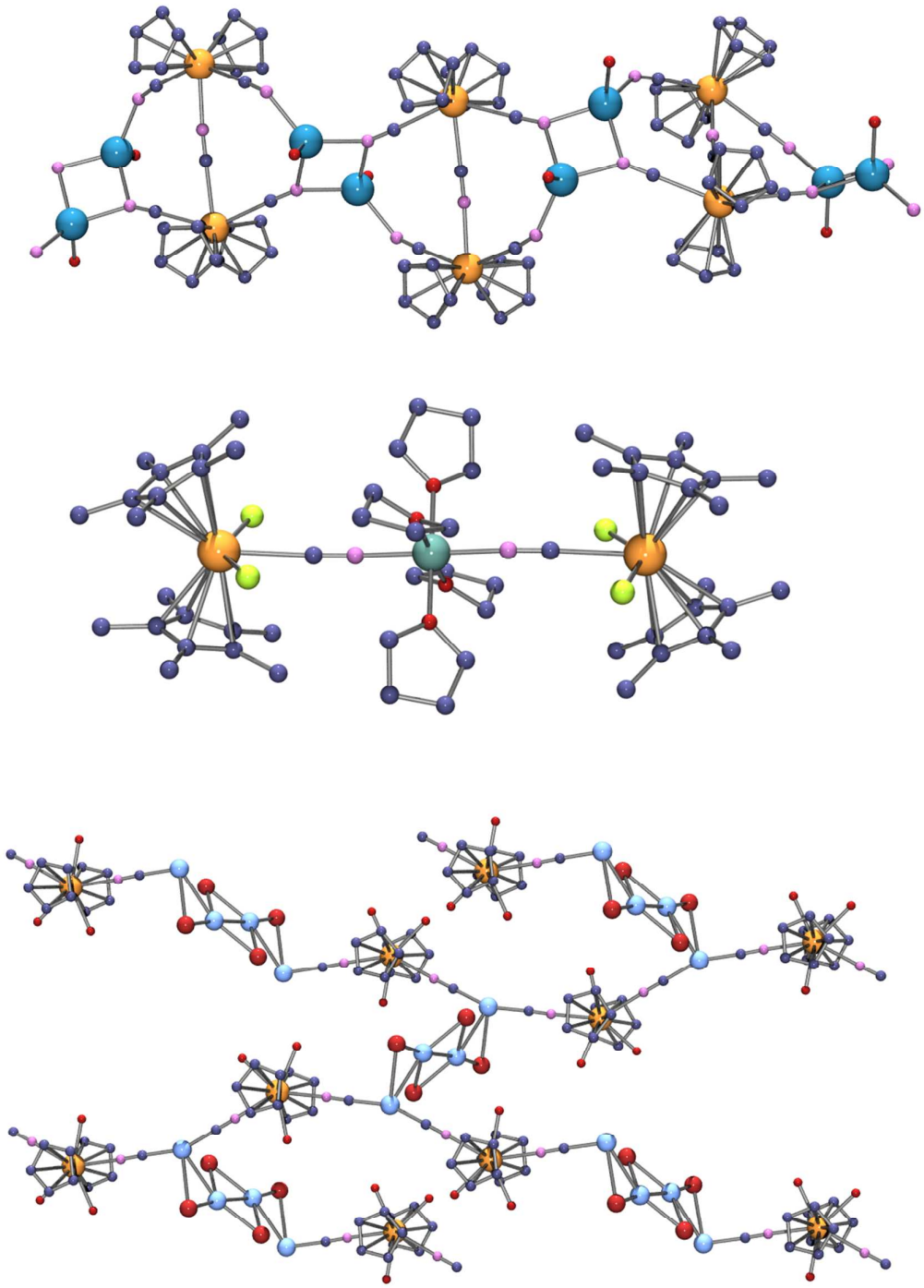


Figure 4

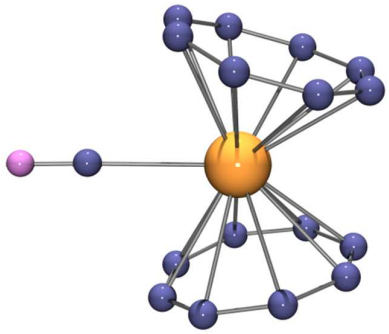
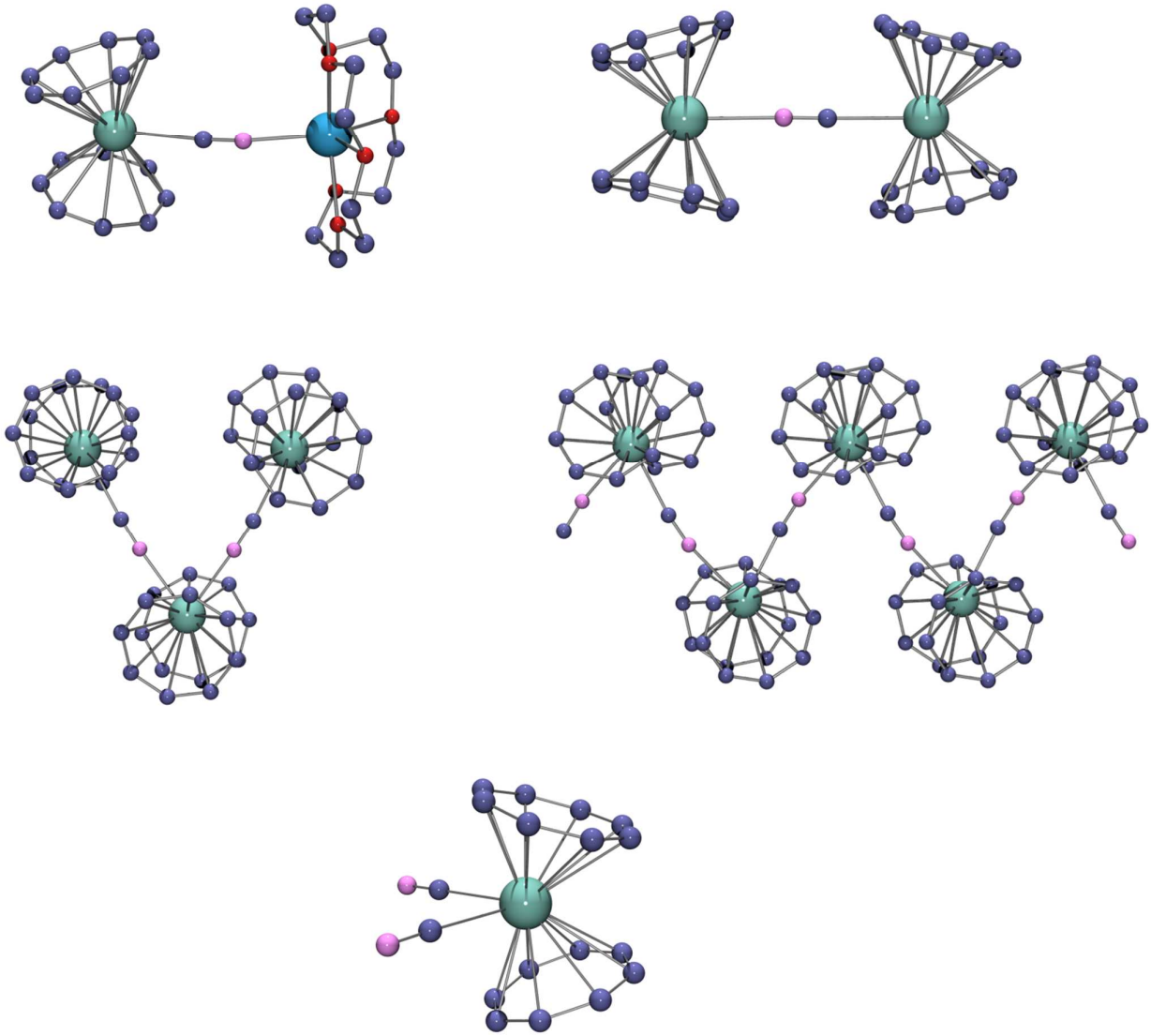


Figure 5



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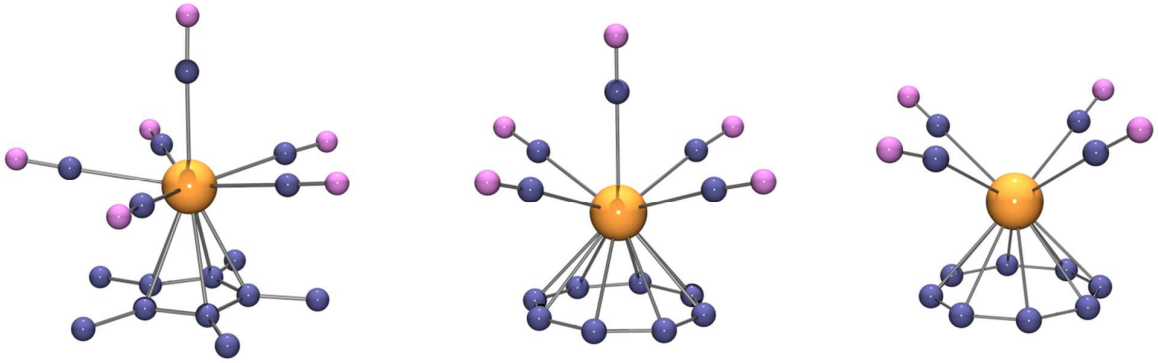


Figure 7

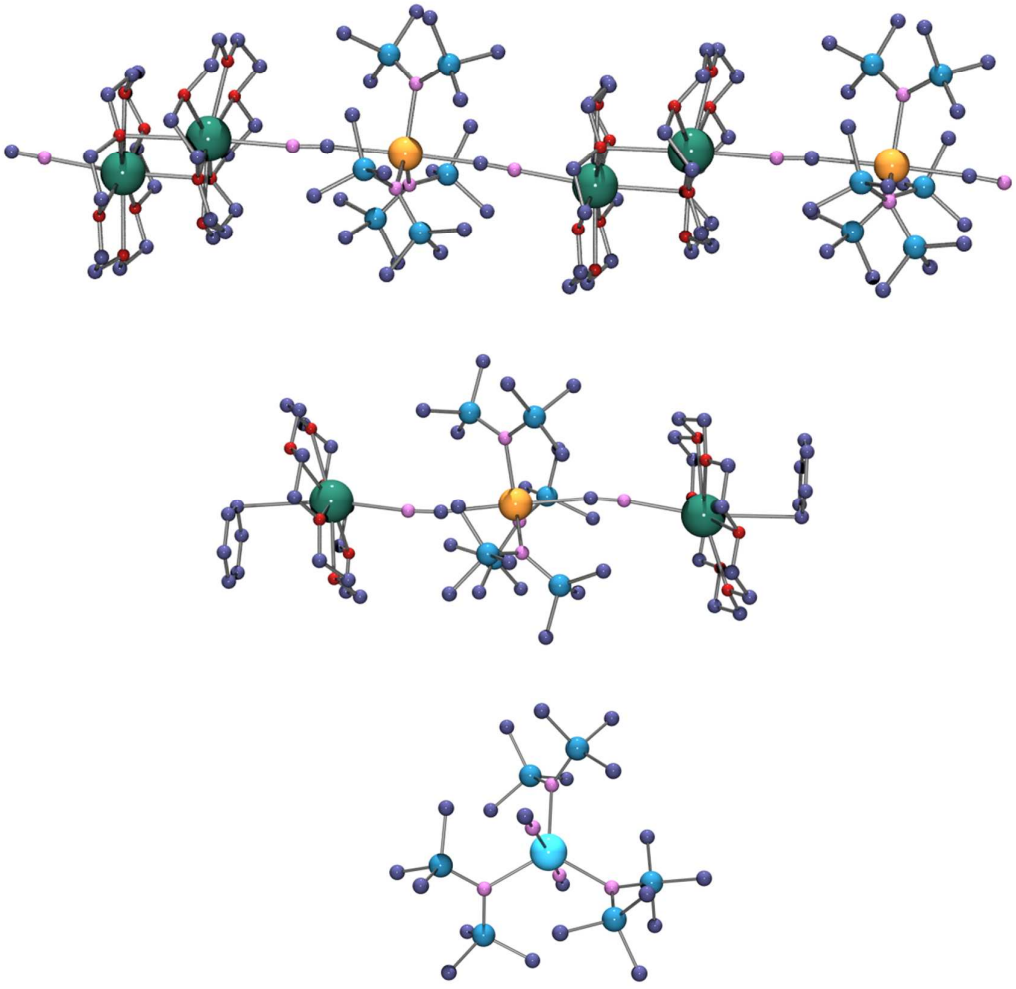


Figure 8

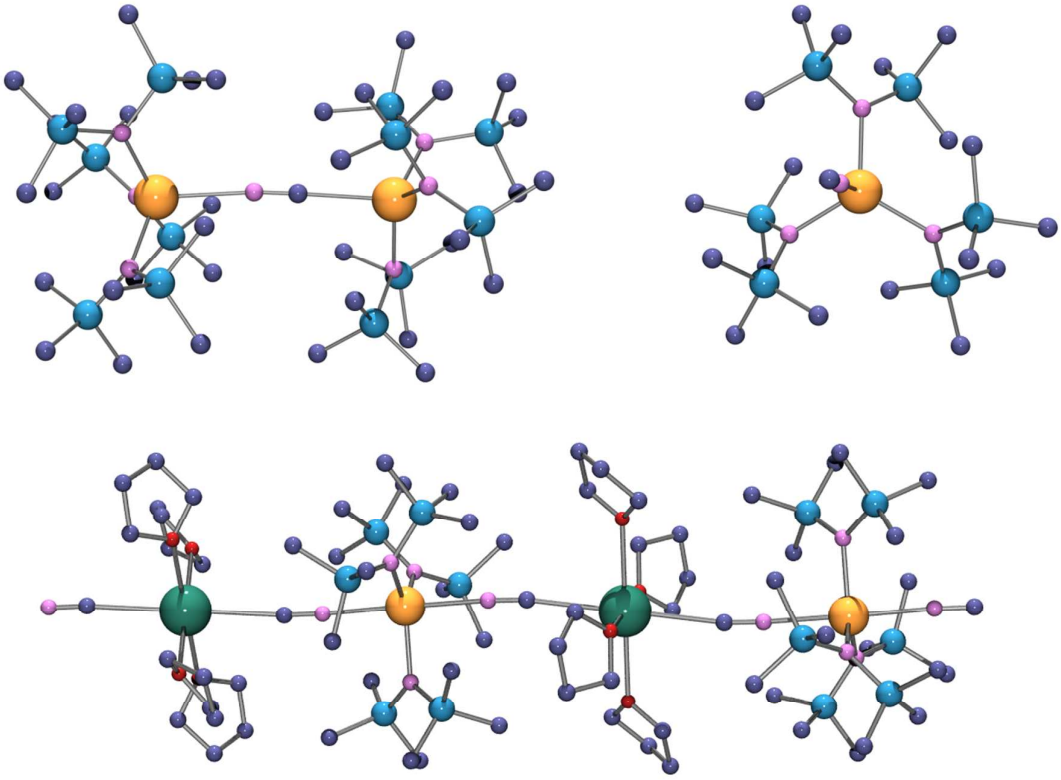


Figure 9

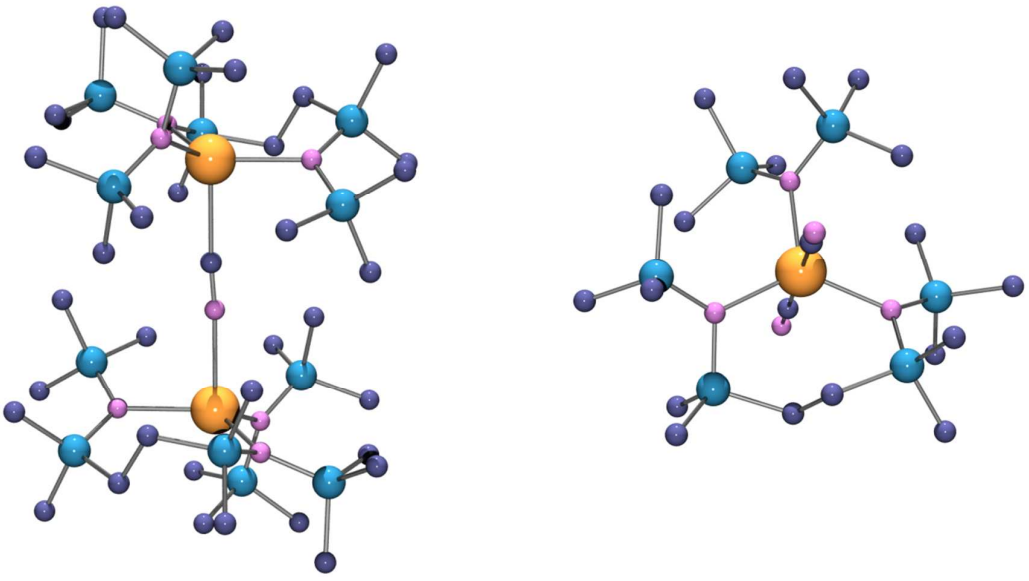


Figure 10

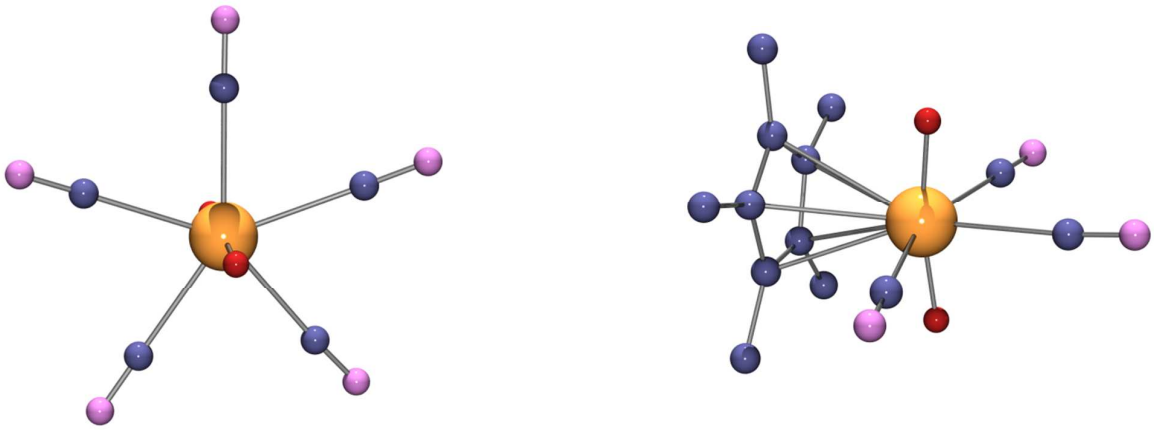


Figure 11

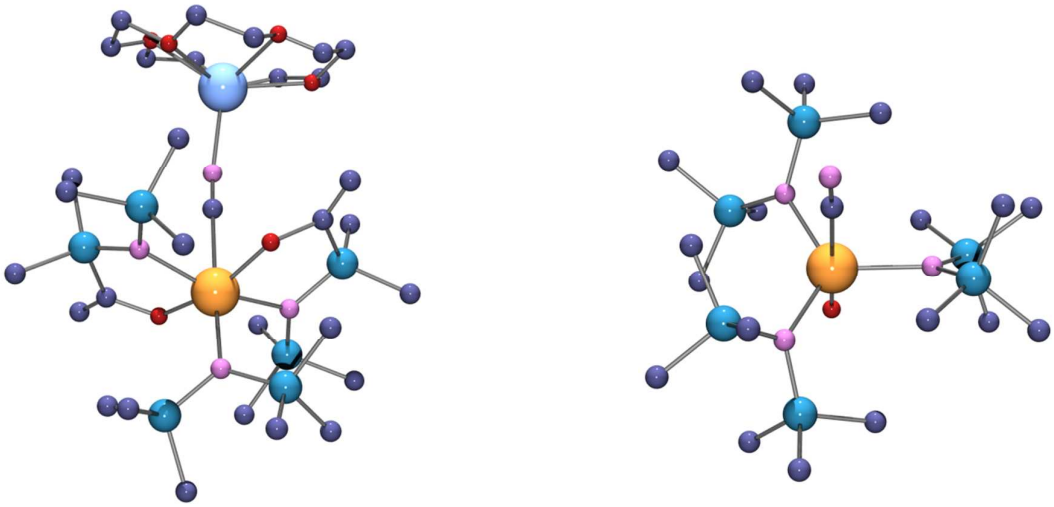
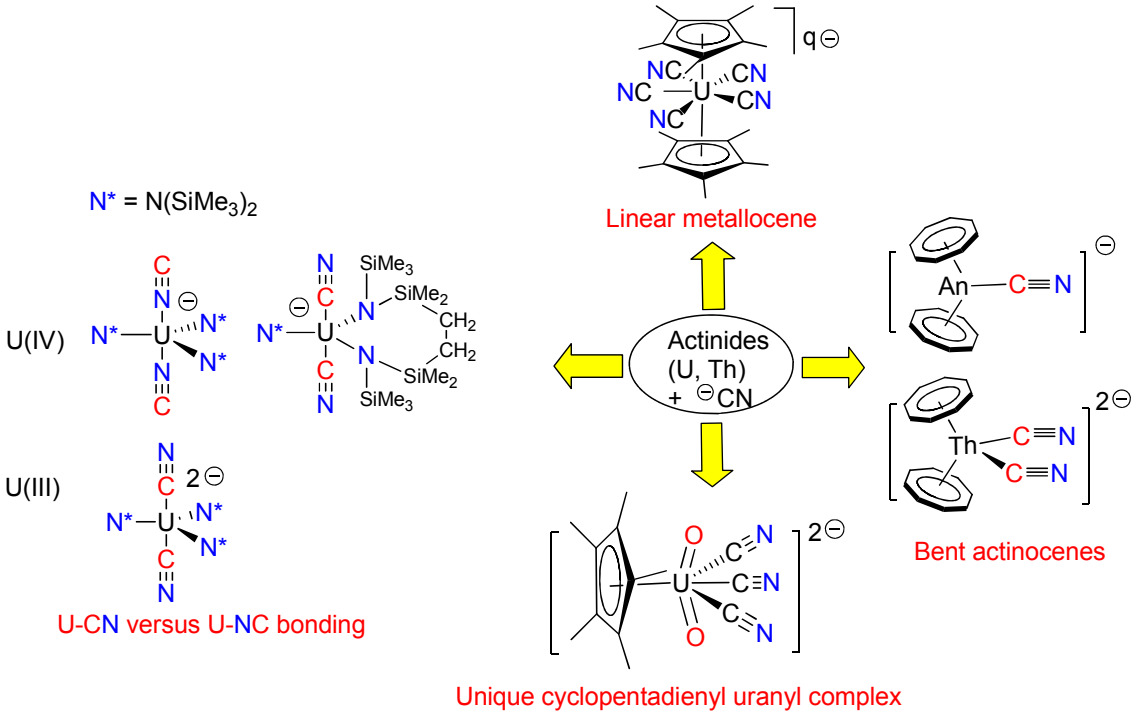


Figure 12

Graphical Abstract



By using the cyanide ligand, acinide compounds with unprecedentd structures, U^{III}–CN^{III} vs Ce^{III}–NC and U^{III}–CN vs U^{IV}–NC coordination modes, and novel high-valent uranium complexes were revealed.