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A Soft Alternative to the Dominant $\{(C_5Me_5)_2U\}$ Motif

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In contrast to the metallocene compounds $[(C_5H_5)_2MCl_2]$ (M = Ti, Zr, Hf) and $[(C_5H_5)_2LnCl]$ (Ln = lanthanide) which are cornerstones of Group 4 and 4f organometallic chemistry, such species appeared to be unstable for the actinides, suffering from ligand redistribution reactions.[1] With the discovery by Marks et al. of the bis(pentamethylcyclopentadienyl) complex $[(C_5Me_5)_2AnCl_2]$ and its derivatives (An = Th, U),[2] the $(C_5Me_5)_2$ ligand set proved to be remarkably suitable for supporting non-aqueous actinide chemistry. Not only does this system stabilize the complexes against ligand-dissociation and exchange reactions, but also supports a variety of oxidation sates, from +3 to +6 for uranium. In addition, the steric bulk and electronic saturation provided by this ligand framework allow only a few coordination sites to be available for chemistry. These features explain the dominance in actinide chemistry of the bis(C_5Me_5) metallocene complexes which attract considerable attention for various aspects, ranging from theory to catalytic applications. However, the C_5Me_5 ligand suffers from two major drawbacks, the release of the organic $(C_5Me_5)_2$ dimer upon oxidation reactions of $\{(C_5Me_5)_2U\}$ complexes[3] and the existence of a single rigid η^5-C_5Me_5 coordination mode. Many efforts have been made to go beyond the metallocene actinide chemistry by using a variety of new heteroatom-based ligands which, in view of the electropositive nature of the f elements, were generally designed with hard oxygen and nitrogen atoms. While some of these ligands supported structures and reactions that are not currently available for the cyclopentadienyl systems, none of these proved as successful. In particular, the tris(pyrazolylborate) ligand, which is considered as the inorganic complement of C_5Me_5, undergoes easy cleavage of its B−N bonds when coordinated to highly electropositive metals.[4] The amidinate ligand which would also be an alternative to the cyclopentadienyl group, was found to stabilize uranium compounds in the +3 to +6 oxidation states,[5] but comparative reactivity studies with the $\{(C_5Me_5)_2U\}$ complexes are still lacking.

Exciting comparisons between the structures and reactions of $\{(C_5Me_5)_2U\}$ and $\{(PNP)_2U\}$ complexes, recently reported by Kiplinger et al., represent a step forward.[10] The soft and robust Ozerov's PNP pincer ligand[6] was already established in transition-metal chemistry for stabilizing highly reactive species such as Group 4 alkylidenes, alkylidines, phosphinidenes, and imides. This ligand was introduced into f element chemistry by Hou et al. with the synthesis of the lanthanide complexes $[(PNP^{Ph})Ln(CH_2SiMe_3)(thf)_2]^+$ ($PNP^{Ph} = [2\text{-}(Ph_2P)C_6H_4]_2N$), which are efficient catalysts of isoprene polymerization with high *cis*-1,4 selectivity and very narrow molecular weight distribution.[7] Kiplinger et al., after preparing the first lanthanide phosphinidene complex $[\{(PNP)Lu(\mu\text{-}PMes)\}_2]$ (PNP = bis[2-(diisopropylphosphino)-4-methylphenyl]amido),[8] attached the PNP ligand to uranium and isolated Lewis base adducts of $[(PNP)UCl_3]$ and $[(PNP)UI_2]$ and the first complexes featuring two PNP ligands coordinated to a single metal center, $[(PNP)_2UCl_2]$ and $[(PNP)_2UI]$.[9] Comparison of the structures of these mono(PNP) and bis(PNP) complexes with their respective C_5Me_5 analogues clearly demonstrated that the PNP ligand provides a more sterically congested environment and is more electron donating than the cyclopentadienyl group. The crystal structures also showed that the PNP ligand can adopt new coordination modes when bonded to uranium, exhibiting a *pseudo*-meridional or *pseudo*-facial geometry when it is κ^3-(P,N,P') coordinated. The structure of $[(PNP)_2UCl_2]$ in the solid state and in solution revealed the novel κ^2-(P,N) coordination motif of PNP binding and the ability of this ligand to act as a hemilabile ligand.

Capitalizing on these first results on the coordination chemistry of the PNP ligand towards U^{III} and U^{IV} halides, Kiplinger et al. demonstrated that this ligand framework opens up new reactivity patterns for the actinides.[10] Like the $[(C_5Me_5)_2UI(thf)]/KC_8$ system, $[(PNP)_2UI]$ in the presence of potassium-graphite represents a new uranium(II) synthon, as shown by its reaction with hexachloroethane which afforded the uranium(IV) compound $[(PNP)_2UCl_2]$, thus demonstrating that the PNP ligand can support low-valent uranium. The reducing ability of $[(PNP)_2UI\ ]$(**1**) was explored towards diphenyldiazomethane and pyridine-*N*-oxide and most significantly, every single reaction showed a behavior distinct from that of $[(C_5Me_5)_2UI(thf)]$ (**2**), leading to structures unknown for the actinides or the transition-metals (Scheme 1). Whereas $Ph_2C{=}N_2$ reacted with **2** to give the bis(imido) uranium(VI) complex $[(C_5Me_5)_2U({=}N{-}N{=}CPh_2)_2]$, the PNP complex **1** was transformed into the uranium(IV) derivative $[(PNP)_2U\{\eta^2\text{-}(N,N'){=}N{-}N{=}CPh_2\}]$ which is the first actinide hydrazonido complex and the first example of such a ligand stabilized by a single metal atom. Moreover, the two PNP ligands provide a novel coordination environment with κ^3-(P,N,P') and κ^2-(P,N) ligation modes,

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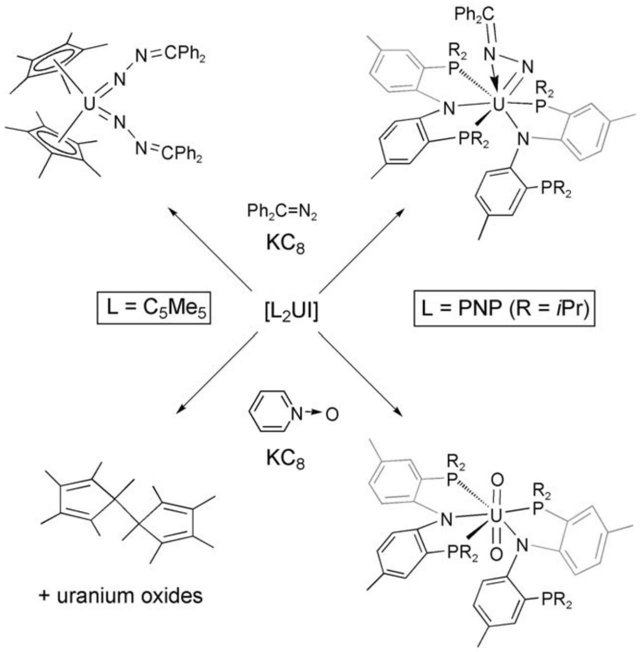

Scheme 1. The distinct reactions of $[(C_5Me_5)_2UI]$ (left) and $[(PNP)_2UI]$ (right).

thus confirming the flexibility of the pincer ligand which can adapt to the steric and electronic demands at the metal centre. This hydrazonido complex is quite attractive since it is anticipated to be a good starting point for exploring the chemistry of actinide metallanitrene compounds from N–N bond cleavage, a field of research currently under extensive investigation in the transition-metal series.[11] These reactions of **1** and **2** with $Ph_2C{=}N_2$ also afforded $[(PNP)_2UI_2]$ and $[(C_5Me_5)_2UI_2]$ which, in the presence of KC_8, were reduced back to **1** and **2**, thus allowing total conversion into the hydrazonido and bis(imido) compounds.

The reduction chemistry with $[(PNP)_2UI]$ is not limited to the formation of uranium(IV) complexes, this was demonstrated by its reaction with pyridine-*N*-oxide which gave the uranyl(VI) compound $[(PNP)_2UO_2]$, obtained as the sole product by using 2 equivalents of C_5H_5NO in the presence of KC_8. This complex, where the PNP ligands exhibit again a κ^3 and κ^2 denticity, is the first uranyl phosphine compound, disproving the general assumption, that the $[UO_2]^{2+}$ ion cannot be coordinated by a neutral and soft ligand, and confirming that the PNP group can support high valent uranium. In striking contrast, reaction of $\mathbf{2}/KC_8$ with pyridine-*N*-oxide gave unidentified uranium products and the $(C_5Me_5)_2$ dimer as the only C_5Me_5-containing compound. This comparison clearly shows that the PNP framework can provide stability where C_5Me_5 fails to and that dead-ends in the metallocene chemistry of the actinides can be circumvented by using this soft PNP ligand.

In conclusion, the PNP ligand has been shown to be flexible, hemilabile, and capable of stabilizing low- and high-valent uranium species. The bis(PNP) framework is a valuable alternative to the $(C_5Me_5)_2$ ligand set, offering distinct structures and reaction patterns. While $[(C_5Me_5)_2AnCl_2]$ and $[(C_5Me_5)_2UI(thf)]$ have proven to be important precursors for many derivatives that can be prepared by halide substitution, it remains to be demonstrated whether or not the PNP counterparts can undergo such reactions with a variety of functional groups. The products of such reactions could be highly reactive neutral and cationic species with many useful applications, especially in catalysis.

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