Coinage metal tris(dialkylamido)imidophosphorane complexes as transmetallation reagents for cerium complexes

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Coinage metal *tris*(dialkylamido)imidophosphorane complexes as transmetallation reagents for cerium complexes

Luis M. Aguirre Quintana,[a] Ningxin Jiang,[a] John Bacsa,[a] and Henry S. La Pierre*[ab]

We report the synthesis of tetrameric Cu(I) and Ag(I) homoleptic complexes supported by the tris(piperidinyl)imidophosphorane [NP(pip)$_3$]$^{1-}$ and [NP(1,2-*bis*-*t*Bu-diamidoethane)(NEt$_2$)]$^{1-}$ ligands. These complexes demonstrate the redox stability of the imidophosphorane ligands to oxidizing salts, and the silver complexes can, in turn, serve as oxidative transmetallation reagents for the isolation of tetravalent cerium complexes from cerium metal or trivalent cerium precursors.
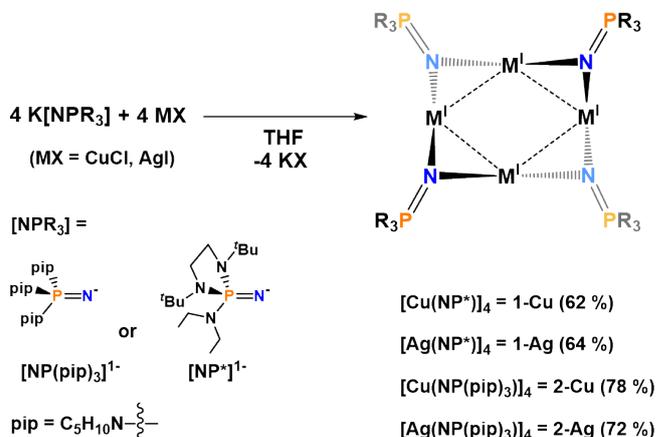
Synthetic methodology for the isolation and characterization of molecular tetravalent lanthanide complexes other than cerium is limited to a few recent examples from the Mazzanti and La Pierre groups including [Tb(OSi(O*t*Bu)$_3$)$_4$] and [Tb(NP(1,2-*bis*-*t*Bu-diamidoethane)(NEt$_2$))$_4$], [Tb(NP*)$_4$], (where Et is ethyl and *t*Bu is *tert*-butyl).[1-3] A key consideration in the design of ligands and methodology for the isolation of these reactive tetravalent complexes is the stability of the ligands to oxidation conditions.[4, 5] Historically, tetravalent praseodymium and terbium have been identified in alkaline solution spectroscopically with the use of bulk electrolysis or ozonolysis.[6] The latter approach is incompatible with organic media and the former approach is unnecessary if chemically compatible reagents can be identified.

Our group has recently tailored the design of bulky 1σ, 2π-donating *tris*(dialkylamido)imidophosphorane ligands to access stable and isolable tetravalent lanthanide complexes. In the case of cerium, the *tris*(piperidinyl)imidophosphorane ligand, [NP(pip)$_3$]$^{1-}$, produces the most reducing trivalent cerium complex, K[Ce(NP(pip)$_3$)$_4$], to-date.[7] In the case of terbium, the [NP*]$^{1-}$ ligand enabled the isolation and spectroscopic characterization of a molecular complex of Tb^{4+}.[2] These

examples highlight the effect the donor profile of the ligand can have in supporting tetravalent lanthanides. The synthesis of [Tb(NP*)$_4$] employed the relatively mild oxidant AgI in ethereal solvents. Herein, a series of Ag(I) and Cu(I) complexes supported by tris(dialkylamido)imidophosphorane ligands is reported to demonstrate the stability of these ligands under reaction conditions and to develop oxidative transmetallation routes to tetravalent lanthanide complexes.

The coinage metal complexes were prepared by the reaction of the potassium salt of either [NP(pip)$_3$]$^{1-}$ or [NP*]$^{1-}$ (these salts are heterocubanes in the solid-state with the full formulas of [K(NP(pip)$_3$)]$_4$ and [K(NP*)]$_4$) with AgI or CuCl by stirring a mixture of the potassium salt of the ligand and the metal halide in THF for 24 hours at room temperature in the absence of light (Scheme 1). The products, [Cu(NP*)]$_4$, **1-Cu**, [Ag(NP*)]$_4$, **1-Ag**, [Cu(NP(pip)$_3$)]$_4$, **2-Cu**, and [Ag(NP(pip)$_3$)]$_4$, **2-Ag**, were isolated in reasonable yields (62-78%) via crystallization from concentrated THF solutions stored at -35°C. X-ray quality crystals were obtained for all compounds except **2-Cu**.
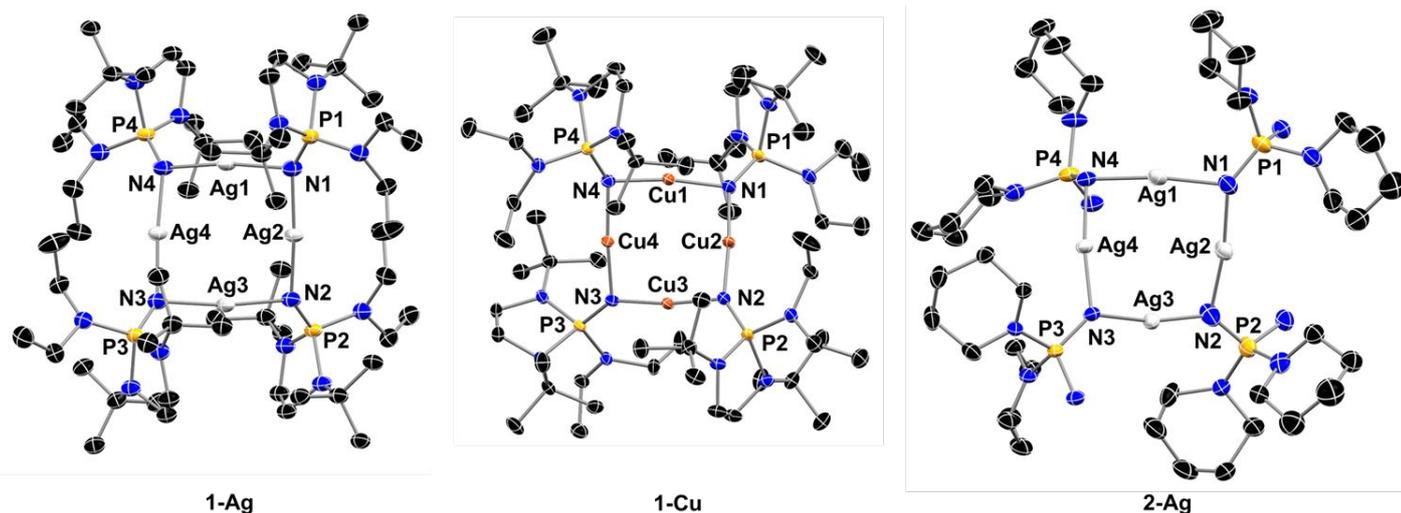
The molecular structures of **1-Ag**, **1-Cu**, and **2-Ag** are shown in Figure 1. Complexes **1-Ag**, **1-Cu**, and **2-Ag** crystallize in the *Pbcn*, *P*2$_1$/*n*, and *C*2/*c* space groups, respectively. In all cases the structure is comprised of a M(I) (where M = Ag or Cu) tetrameric

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4 K[NPR$_3$] + 4 MX $\xrightarrow[\text{-4 KX}]{\text{THF}}$

(MX = CuCl, AgI)

[NPR$_3$] =

[NP(pip)$_3$]$^{1-}$ [NP*]$^{1-}$

pip = C$_5$H$_{10}$N—

[Cu(NP*)]$_4$ = 1-Cu (62 %)

[Ag(NP*)]$_4$ = 1-Ag (64 %)

[Cu(NP(pip)$_3$)]$_4$ = 2-Cu (78 %)

[Ag(NP(pip)$_3$)]$_4$ = 2-Ag (72 %)

Scheme 1: Synthesis of **1-Cu**, **1-Ag**, **2-Cu**, and **2-Ag**.

Figure 1. Molecular structures of **1-Ag** (left), **2-Cu** (middle), and **2-Ag** (right) shown with thermal ellipsoids at 50% probability and hydrogen atoms are omitted for clarity. Select piperidinyl carbon atoms in **2-Ag** are also omitted for clarity: see ESI for full structure.

core with μ_2-[NP*]$^{1-}$ or μ_2-[NP(pip)$_3$]$^{1-}$ ligands bridging the metal centers. The ligand backbone is directed above or below the Ag$_4$ or Cu$_4$ core in an alternating manner, giving rise to a saddle conformation of the tetramer with saddle angles for **1-Ag**, **1-Cu**, and **2-Ag** of 140.4(4)°, 128.16(9)°, and 123.56(14)°, respectively. This saddle conformation is driven primarily by sterics and has been computationally modelled previously.[8] It is also observed in tetrameric compounds bearing similar ligand frameworks including ketimide copper complexes, [Cu(μ_2-N=CPh$_2$)]$_4$ and [Cu(μ_2-N=C^{t}Bu$_2$)]$_4$.[9]

In tetrametallic cores, each metal ion is crystallographically distinct with the exception of **1-Ag**, which has two crystallographically distinct silver ions in the plane of a Ag$_4$ diamond core. However, the individual bond metrics span a small range in the complexes. The average Ag–N$_{imido}$ distances in **1-Ag** and **2-Ag** are 2.081(8) Å and 2.075(3) Å, respectively, which are shorter than the average Ag–N$_{amido}$ distance (2.148(5) Å) in [Ag(μ_2-N(SiMe$_3$)$_2$)]$_4$.[10] In **1-Cu**, the average Cu–N$_{imido}$ distance is 1.865(2) Å, which is also shorter than the average Cu–N$_{amido}$ distance (2.148(5) Å) observed in the copper amide, [Cu(μ_2-N(SiMe$_3$)$_2$)]$_4$.[11] The average P–N$_{imido}$ bond distances in **1-Ag**, **1-Cu**, and **2-Ag** are 1.537(9) Å, 1.538(2) Å, and 1.544(3) Å, which are longer than the average P–N$_{imido}$ distances of the parent potassium salts of [NP*]$^{1-}$, 1.522(1) Å, and [NP(pip)$_3$]$^{1-}$, 1.519(4) Å.[2, 7] This change in the P–N$_{imido}$ bond length on transmetallation from potassium to copper or silver could be due to either differential steric effects between the potassium heterocubane structures and the saddle structures of copper or silver or electronic differences derived from the degree of ylidic character (*i.e.* (R$_2$N)$_3$P$^+$–N^{2-} zwitterionic character) based on the Lewis acidity of the metal. To complete the description of the core, the average Ag–Ag distances in **1-Ag** and **2-Ag** are 2.979(7) Å and 2.954(5) Å, respectively. To our knowledge, the only other example in the literature that involves a homoleptic imidophosphorane compound with Ag$_4$ core is the cubane complex, [Ag$_{12}$(NP(Et)$_3$)$_8$](O$_3$SCF$_3$)$_4$ with an average Ag–Ag distance of 3.068(1) Å.[12] In the case of **1-Cu**, the average Cu–Cu
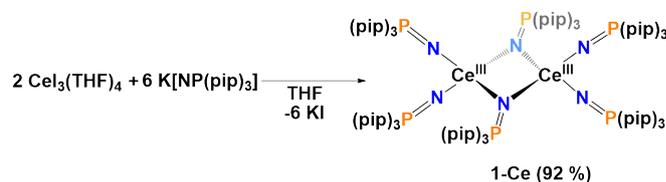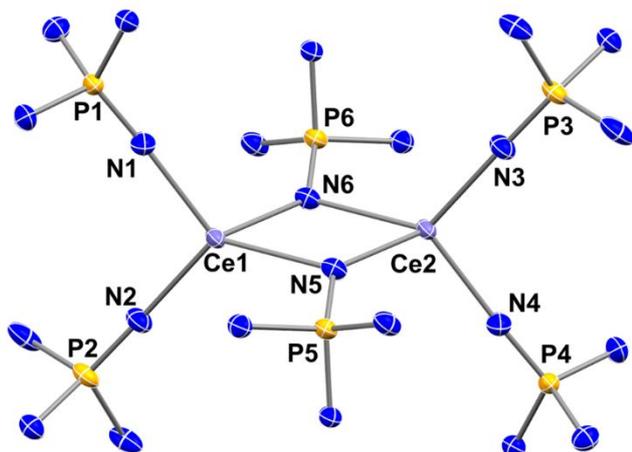

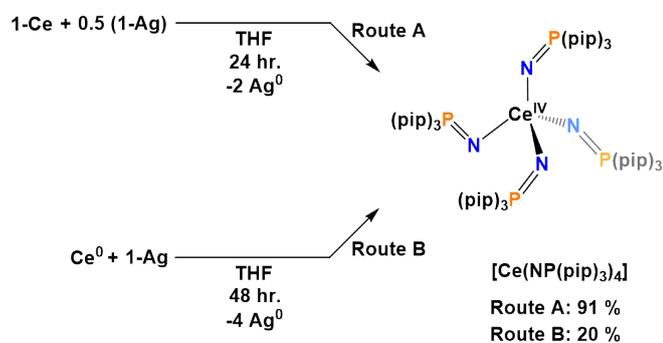**Scheme 2.** Synthesis of **1-Ce**.

distance is 2.640(6) Å, which is in range of previously reported copper imidophosphorane complexes.[8, 12, 13] In all these compounds, the Ag(I)–Ag(I) and Cu(I)–Cu(I) distances fall within the range for non-covalent argentophilic (2.5-3.4 Å) and cuprophilic (2.4-2.8 Å) interactions between the d^{10} metal centers.[14-16]

The ^{31}P{^{1}H} NMR spectra of the **1-Ag** and **2-Ag** complexes suggest that the tetrameric structures are preserved in solution. In C$_6$D$_6$, **1-Cu** and **2-Cu** show a singlet at 15.41 ppm and 26.95 ppm in their ^{31}P{^{1}H} NMR spectra. In contrast, the **1-Ag** and **2-Ag** complexes both show a 1:2:1 triplet in their ^{31}P{^{1}H} NMR spectra (18.10 ppm for **1-Ag** and 29.13 ppm for **2-Ag**). This coupling is indicative of the retention of a tetrameric structure with two equivalent silver centers bound to each imidophosphorane ligand leading to a triplet with a ^2J(^{31}P-^{109}Ag) coupling constant of 114 Hz (**1-Ag**) and 66 Hz (**2-Ag**). These ^{31}P{^{1}H} NMR signatures are diagnostic for evaluating the reactivity of these complexes.

The ability of these complexes to perform oxidative transmetallation was evaluated with both a trivalent lanthanide complex and bulk lanthanide metal. To facilitate the identification of oxidative transmetallation, a bimetallic, trivalent cerium complex was prepared. As shown in Scheme 2, **1-Ce** was prepared by the reaction of CeI$_3$(THF)$_4$ with three equivalents of K[NP(pip)$_3$] in THF in 92% yield. Single-crystal XRD revealed the molecular structure of **1-Ce** to be a dimeric, homoleptic complex (Figure 2), which crystallized in the $P\bar{1}$ space group. The average terminal Ce–N$_{imido}$ distance is 2.274(15) Å while the average Ce–μ_2–N$_{imido}$ distance is

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Figure 2. Molecular structure of **1-Ce** shown with thermal ellipsoids at 50% probability with hydrogen and carbon atoms omitted for clarity.

Scheme 3. Reaction scheme for the synthesis of [Ce(NP(pip)$_3$)$_4$].

2.457(15) Å. These Ce–N$_{imido}$ distances are comparable to the previously reported monometallic, homoleptic Ce^{3+} imidophosphorane complexes K(Et$_2$O)[Ce(NP(pip)$_3$)$_4$] and K(2.2.2-cryptand)[Ce(NP(pip)$_3$)$_4$].[7] The terminal ligands are nearly linear with a Ce–N$_{imido}$–P angle of 176.04(10)°, whereas the Ce–N$_{imido}$–P angle for the μ_2-bridging ligands average 124.98(4)°.

The reaction of **1-Ce** with **2-Cu** or **2-Ag** was attempted in THF. No reaction was observed with **2-Cu**, as determined by ^{31}P{^{1}H} NMR. However, the reaction with **2-Ag** proceeded to produce the previously reported homoleptic Ce^{4+} complex, [Ce(NP(pip)$_3$)$_4$],[7] in 91% isolated yield (Route A, Scheme 3). The comparable oxidative transmetallation reaction with **2-Cu** or **2-Ag** with cerium metal (Route B, Scheme 3) was also evaluated. As with **1-Ce**, no reaction was observed between **2-Cu** and the Ce^0 shavings. By contrast, **2-Ag** reacted sluggishly with Ce^0 shavings in THF. Upon analysis of the crude reaction mixture by ^{31}P{^{1}H} NMR, only two species were found in solution: unreacted **2-Ag** (evidenced by its triplet centered at 29.13 ppm) and the tetravalent product [Ce(NP(pip)$_3$)$_4$] (singlet centered at -12.30 ppm). No evidence of intermediates or trivalent cerium complexes was observed despite the presence of excess Ce^0 metal in the reaction mixture. This reaction is an unusual example of an oxidative transmetallation transformation

producing a tetravalent product from the bulk lanthanide metal without an identifiable trivalent intermediate.[17-30]

In summary, we have reported the synthesis of the coinage metal *tris*(dialkylamido)imidophosphorane complexes **1-Ag**, **1-Cu**, **2-Ag**, and **2-Cu** supported by the [NP(pip)$_3$]$^{1-}$ or [NP*]$^{1-}$, ligands. The oxidative transmetallation reactions of **2-Ag** and **2-Cu** were evaluated with the trivalent cerium complex, **1-Ce**, and Ce^0 shavings to afford a tetravalent cerium complex without the production of an alkali-metal halide salt. The complex **2-Cu** showed no reactivity in either case, while **2-Ag** showed reactivity in both reaction conditions and provided [Ce(NP(pip)$_3$)$_4$] in excellent yield in the reaction with **1-Ce**.

Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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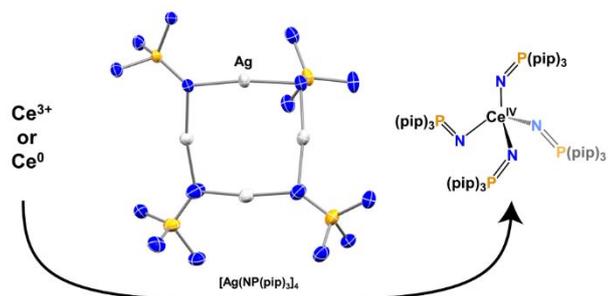
The synthesis of coinage metal *tris*(dialkylamido)imidophosphorane complexes are reported, and the use of the silver(I) salt as an oxidative transmetallation reagent for the formation of a cerium(IV) complex is described.