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Cerium–carbon dative interactions supported by carbodiphosphorane†

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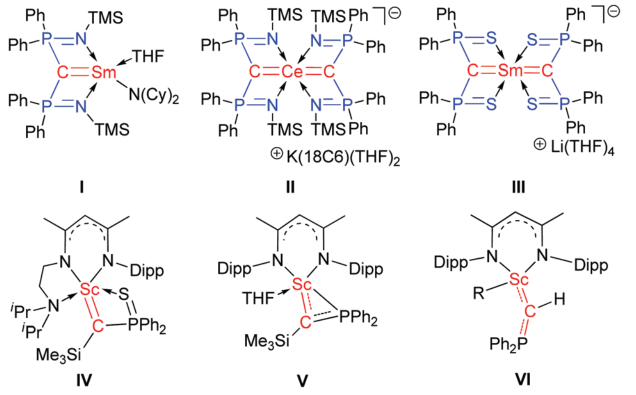
A set of complexes containing dative interactions between a rare-earth metal and carbon are reported. Complex **2**, $Br_3Ce(CDP)(THF)$, with a Ce←C bond was synthesized by the reaction of $CeBr_3$ with a carbon(0) ligand, carbodiphosphorane (CDP). More significantly, a trivalent cerium complex **3**, $[BrCe(CDP)_2](BPh_4)_2$, with two σ dative interactions C→Ce←C was also isolated, which represents an unusual example of two dative interactions formed with the same atom in a molecule. Furthermore, π donation by the second lone-pair electrons of the CDP ligand is rather weak. Single-crystal X-ray diffraction shows that the Ce–C bond lengths in these complexes are comparable with those in cerium(III)–carbene species. Density functional theory calculations support the dative interaction formation in these complexes and the strength of σ-donation in **3** is stronger than that in **2**.

Introduction

Complexes with transition metal–ligand multiple bonds have been extensively investigated due to their fascinating structures and their applications in synthetic and industrial chemistry.[1] However, for rare-earth metals, due to their energy mismatch and highly polarized nature, the metal–ligand multiple bonds are accepted to be labile and difficult to stabilize. Despite these challenges, a series of remarkable progresses of rare-earth (RE) metal–ligand multiple bonds have been reported in the past decade.[2–6] Cavell and co-workers reported the first complex with a Sm═C double bond employing bis(iminophosphinoyl)methanediide dianion, $[C(PPh_2NR)_2]^{2-}$ (R = $SiMe_3$, $BIPM^{TMS}$), as a ligand in 2000 (**I** in Scheme 1).[2] With this pioneering pincer-type chelating framework, a set of species with a rare-earth metal–carbon double bond were isolated thereafter by the groups of Liddle and Le Floch.[7] Particularly, Liddle and co-workers synthesized a set of rare-earth metal bis(carbene) species (C═RE═C) with this ligand (**II**).[7j] In addition, an analogue pincer-type precursor, $[C(PPh_2S)_2]^{2-}$, and a series of mono- and bis-carbene rare-earth complexes (**III**) were also reported by the groups of Le Floch, Mézailles and Nief.[8] Therefore, these pincer-type frameworks are effective precursors for the construction of rare-earth metal carbene complexes.[7,8] It is worth mentioning that the Chen group synthesized a series of highly reactive rare-earth alkylidene complexes from non-pincer-type methandiide dianion precursors, $[C(SiMe_3)PPh_2S]^{2-}$ (**IV**) and $[C(SiMe_3)PPh_2]^{2-}$ (**V**), as well as nonchelating phosphoniomethylidene species of scandium and lutetium (**VI**).[9] Therefore, the development of new precursors for the synthesis of complexes with rare-earth



Scheme 1 Selected complexes with a rare-earth metal–carbon double bond.

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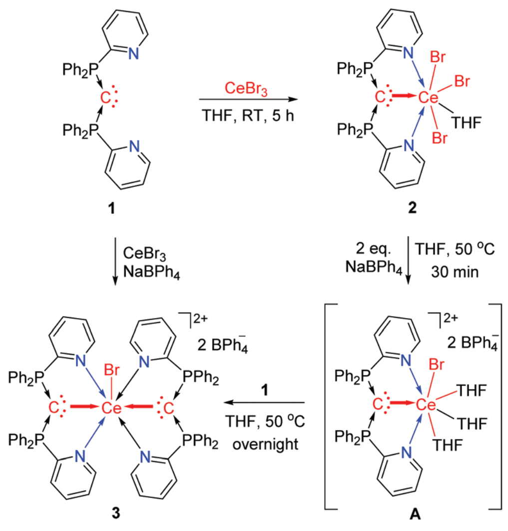
metal–carbon multiple bonds or novel bonding modes between rare-earth metals and carbon is an important issue.

Carbodiphosphorane (CDP), $C(PPh_3)_2$, which was first synthesized in 1961,[10] can be viewed as a carbon(0) compound that has a carbon atom with two lone electron pairs and forms dative bonds to phosphane ligands formulating as $Ph_3P{\rightarrow}C{\leftarrow}PPh_3$.[11] The chemistry of CDP was extensively studied as a ligand for main group and transition metal elements.[12] CDP belongs to the compound class of carbones CL_2,[13] in which complexes with other ligands such as L = CO and NHC (N-Heterocyclic Carbene) have been identified and synthesized.[12b,d,14] Complexes have been synthesized where the two electron pairs of CDP are bonded to two monodentate Lewis acids.[15] A complex with double donation to a bidentate Lewis acid $[(Ph_3P)_2C{\rightrightarrows}BH]^+$ has also been isolated.[16] We recently found that the two lone electron pairs of CDP could also coordinate to a single uranium center, leading to the formation of a double dative bond between carbon and uranium in CDP-UCl_4.[17] Due to the similar frontier orbital compositions of BIPM and CDP, a double dative bond between carbon(0) and rare-earth metals was hinted in $[Ln(BIPM)(I)(THF)_2]$ (Ln = Y and Er).[18]

Here, we describe the synthesis and characterization of an unprecedented complex containing a cerium–carbon dative interaction, CDP→$CeBr_3$, which employs CDP as a ligand for rare-earth metals for the first time. In addition, a trivalent cerium complex with two dative interactions, namely CDP→Ce(Br)←CDP, was also isolated. An analysis of the bonding situation revealed that the second donation by the π lone-pair orbital of the CDP ligands is weak.

Synthesis and characterization

The CDP–$CeBr_3$ adduct (**2**) was readily synthesized by the reaction of CDP (**1**) with $CeBr_3$ at room temperature for 5 h (Scheme 2, for other resonating structures of **2** and **3** see Fig. S1†). Complex **2** was isolated as a yellow solid in 95% yield. This complex (**2**) is the first example of a rare-earth metal species with carbon(0) as a ligand. Treatment of **2** with two equivalents of $NaBPh_4$ at 50 °C for 30 min resulted in the formation of a proposed intermediate (**A**). In spite of several attempts, however, we have been unable to isolate this intermediate. One equivalent of ligand **1** (Fig. S2–S4†) was then added to this mixture and stirred at 50 °C overnight, and yellow crystals of **3** were isolated in 78% yield, after recrystallization. Complex **3** can be synthesized more conveniently from the mixture of **1**, $CeBr_3$, and $NaBPh_4$ in a ratio of 2 : 1 : 2 at room temperature for 8 h in 66% isolated yield.



Scheme 2 Synthesis of complexes **2** and **3**.

Generally, the tetravalent cerium center is expected to increase the covalency of cerium–ligand multiple bonds, rendering these species more stable than the corresponding trivalent cerium complexes.[19] Thus, the oxidation state of cerium in all isolated complexes containing a $Ce{=}O$ or a $Ce{=}N$ double bond is +IV.[5,6] However, in both complexes **2** and **3**, the oxidation state of the cerium center is +III and consequently, both of these complexes are labile, sensitive to air and moisture, and are quickly decomposed after dissolution in common solvents. Only the ^1H and $^{31}P\{^1H\}$ NMR spectra of complex **2** were obtained (Fig. S5 and S6†) and complexes **2** and **3** in the solid state were further characterized by elemental analysis and infrared spectroscopy.

The structure of **2** in the solid state was further confirmed by X-ray crystallographic analysis (Fig. 1 and Tables S1 and S2†). The cerium atom adopts a heptacoordinate pentagonal bipyramidal geometry in which the two pyridyl units on the CDP ligand are coordinated to the cerium center, each forming a five-membered ring. The bond length of Ce1–C1 is 2.597(6) Å, which is slightly longer than the Ce(III)═C double bond lengths found in $[Ce(BIPM^{TMS})(I)(DME)]$ (2.468 Å)[7g] and $[(BIPM^{TMS})Ce(BIPM^{TMS}H)]$ (2.472 Å),[7i] but it is comparable to the Ce(III)═C

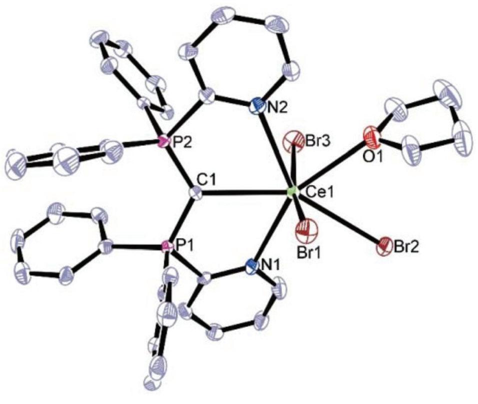


Fig. 1 Molecular structure of complex **2** (50% probability). Hydrogen atoms are omitted for clarity. Selected experimental [calculated] bond lengths (Å) and angles (°): Ce1–C1 2.597(6) [2.546], Ce1–N1 2.725(5) [2.734], Ce1–N2 2.746(5) [2.707], Ce1–Br1 2.9025(8) [2.911], Ce1–Br2 2.9929(8) [2.906], Ce1–Br3 2.8973(8) [2.882], Ce1–O1 2.584(5) [2.593], C1–P1 1.674(6) [1.672], C1–P2 1.670(6) [1.672], P1–C1–P2 122.5(4) [120.5], N1–Ce1–N2 135.6(5) [133.3] Calculated values are at the BP86-D3(BJ)/def2-TZVPP/Stuttgart RSC 1997 ECP level.

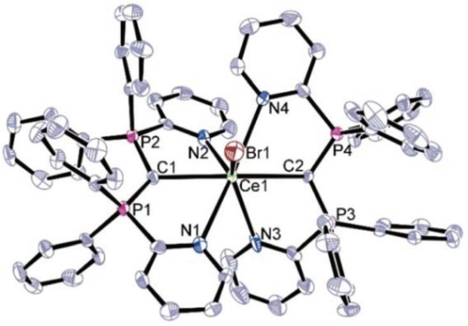


Fig. 2 Molecular structure of complex **3** (50% probability). Hydrogen atoms are omitted for clarity. Selected experimental [calculated] bond lengths (Å) and angles (°): Ce1–C1 2.573(6) [2.527], Ce1–C2 2.597(6) [2.527], Ce1–N1 2.671(6) [2.657], Ce1–N2 2.694(6) [2.677], Ce1–N3 2.734 (6) [2.657], Ce1–N4 2.744(6) [2.677], Ce1–Br1 2.854(9) [2.834], C1–P1 1.687(7) [1.711], C1–P2 1.684(7) [1.704], C2–P3 1.674(6) [1.704], C2–P4 1.691(6) [1.711], C1–Ce1–C2 162.7(2) [151.0], P1–C1–P2 120.4(4) [118.8], P3–C2–P4 120.6(4) [118.8], N1–Ce1–N2 128.3(4) [133.0], N3–Ce1–N4 126.0(1) [133.0]. The calculated values are at the BP86-D3(BJ)/def2-SVP/ Stuttgart RSC 1997 ECP level.

bond lengths found in cerium(III) bis(carbene) $[Ce(BIPM^{TMS})_2][K(18C6)(THF)_2]$ (2.598 and 2.603 Å).[7j] The Ce1–C1 bond distance is significantly shorter than 2.702 Å, which has been observed in the adducts of NHC with cerium(III).[20] Consequently, the bond between carbon(0) and cerium can potentially be viewed as a formal Ce═C double bond. The bond length of Ce1–Br2 (2.9929(8) Å) was clearly longer than that in Ce1–Br1 (2.9025(8) Å) or Ce1–Br3 (2.8973(8) Å), probably due to the *trans*-influence from the strongly donating group (C1) in the *trans* position of Br2.

The molecular structure of complex **3** was also determined by single-crystal X-ray crystallography. As shown in Fig. 2, the cerium center in this case is heptacoordinated to four nitrogen atoms, two carbon atoms, and one bromine atom. The most salient feature of the structure of **3** is the C1–Ce1–C2 moiety. The C1–Ce1–C2 bond angle was observed to be 162.7(2)°, which is slightly smaller than the ideal value for metallaallenes (180°). The bond lengths of Ce1–C1 and Ce1–C2 are 2.573(6) and 2.597(6) Å, respectively, which are very close to the Ce(III)═C bond lengths found in $[Ce(BIPM^{TMS})_2][K(18C6)(THF)_2]$ (2.598 and 2.603 Å).[7j]

Electronic structure analysis

DFT calculations were performed (see the ESI† for computational details) to understand the stability and the nature of the bonding in complexes **2** and **3**. The computed structures are in good agreement with the experimental values (Fig. 1 and 2), taking into account the solid state effects in the experimental values and the accuracy of the theoretical level. Calculations suggest that both **2** and **3** have an electronic doublet ground state, while the quartet states are significantly higher in energy (42.0–46.9 kcal mol^{-1}) than the doublets (Fig. S7†).

We also evaluated the stability of **2** and **3** by computing the bond dissociation energies (BDE) at 0 and 298 K for the dissociation processes (Table S3†). The calculated BDE value (D_e = 81.2 kcal mol^{-1}) for the dissociation **2** → CDP + $CeBr_3(THF)$ implies a fairly strong interaction between the Ce and the CDP unit. The dissociation of two CDP units from **3** involves a very large energy, D_e = 420.0 kcal mol^{-1}. Inspection of the step-wise dissociation of **3** shows that the dissociation of the first CDP needs a considerably smaller BDE value (D_e = 145.1 kcal mol^{-1}) than that of the second CDP (D_e = 274.9 kcal mol^{-1}), implying that the first CDP dissociation is more feasible than the second one. Alternatively, the dissociation pathway of **3** → $2CDP^+$ + CeBr needs a considerably lower BDE value (D_e = 260.5 kcal mol^{-1}). The inclusion of zero-point energy and basis set superposition error somewhat diminishes the BDE values, and the BDE values with thermal and entropic corrections at 298 K, ΔG^{298}, are still in the range of 60.6–384.7 kcal mol^{-1}. Therefore, the computed values indicated the high thermochemical stability of the title complexes against dissociation.

The computations of IR frequency for the title complexes reveal highly IR active Ce1–C1 (**2**) and C1–Ce1–C2 (**3**) stretching modes, with wavenumbers of 802.8 and 772.3 cm^{-1}, respectively. Note that the symmetric C1–Ce1–C2 stretching wavenumber for **3** at 787.5 cm^{-1} has very low intensity. Given the fact that the corresponding experimental bond lengths are somewhat longer than the computed values, these wavenumbers match with the peaks at 744.1 (**2**) and 733.2 (**3**) cm^{-1} in the experimental data.

The shape of the singly occupied molecular orbital (SOMO) of **2** and **3** indicates that the unpaired electron is mainly localized in an f orbital of cerium atom, implying that the valence electron configuration of Ce is $4f^15d^06s^0$ (Fig. 3 and S8†).

This corroborates with the shape and location of the spin densities (Fig. S9†). In **2**, the highest occupied molecular orbital (HOMO) and HOMO−9 represent the π and σ dative interactions. The HOMO suggests only weak π donation, while the HOMO−9 indicates strong σ donation from CDP to Ce. This result indicates that the best description of **2** is given in terms of only two-electron σ donation $(THF)Br_3Ce{\leftarrow}CDP$. Inspection of the relevant orbitals in **3** shows that the HOMO and HOMO−1, and HOMO−2 and HOMO−22 correspond to out-of-phase (+,−) and in-phase (+,+) combinations of two sets of π and σ dative interactions where the π interaction appears to be small (Fig. S8†). This is consistent with the finding that π-bonding is weak/absent in rare-earth carbene complexes employing BIPM as a ligand.[7e,18]

A more detailed insight into the bonding situation in **2** and **3** and a quantitative estimate of the strength of σ and π donation can be obtained from the energy decomposition analysis in conjunction with natural orbital for chemical valence (EDA-NOCV) theory.[21] The numerical results of the EDA-NOCV calculations are given in Tables S4 and S5† (see Table S6† for an alternative partition scheme of **3**). The breakdown of the orbital term ΔE_{orb} into the pairwise orbital interactions in **2** shows that the CDP–Ce interaction is dominated by the σ donation CDP→Ce, while the π donation contributes only

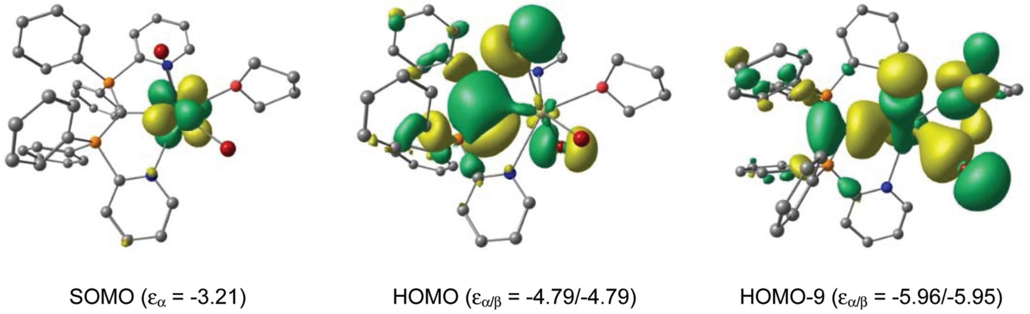
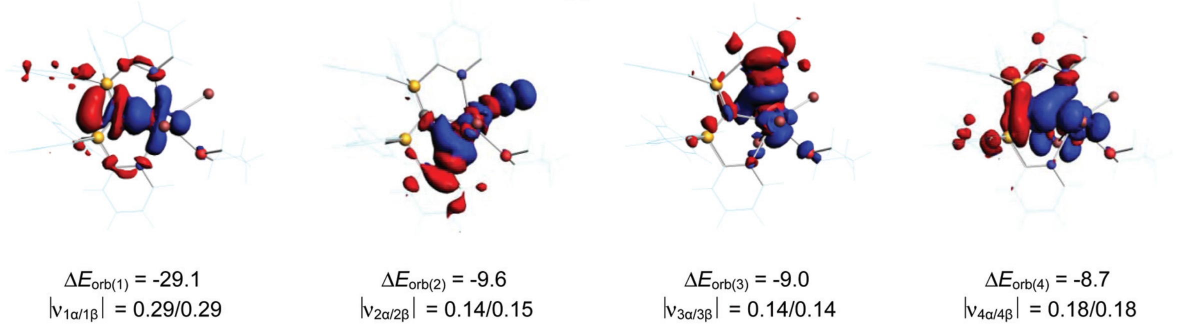


Fig. 3 The shape and energy of the SOMO and relevant occupied molecular orbitals responsible for Ce–C interactions in **2**. The isosurface value is 0.025 e Å^{-3}. Energy eigenvalues are in eV. SOMO (ε_α = −3.21), HOMO ($\varepsilon_{\alpha/\beta}$ = −4.79/−4.79), HOMO−9 ($\varepsilon_{\alpha/\beta}$ = −5.96/−5.95).

9.2% to ΔE_{orb}. Fig. 4a shows the important pair-wise orbital contributions, $\Delta E_{\text{orb}(n)}$ and the associated deformation densities, $\Delta\rho_{(n)}$ of **2** (see Fig. S10† for the shape of the associated interacting orbitals responsible for $\Delta\rho_{(n)}$). The situation is a bit more complicated in **3** than in **2**, because the σ donation is coupled with the π donation. However, inspection of the deformation densities shown in Fig. 4b reveals that the two strongest interactions $\Delta E_{\text{orb}(1)}$ and $\Delta E_{\text{orb}(2)}$ in **3** are the symmetric (+,+) and asymmetric (+,−) CDP→Ce(Br)←CDP σ-donations, which contribute 30.8% of the total ΔE_{orb} (Table S5†). The $\Delta E_{\text{orb}(3)}$ and $\Delta E_{\text{orb}(4)}$ terms originate from the two sets of CDP→Ce(Br)←CDP π-donations which are slightly coupled with σ-donation from pyridyl rings and (+,+) donation from C centers, respectively (Fig. 4). They together generate only 11.6% of the covalent interaction. The next four orbital terms, $\Delta E_{\text{orb}(5)-(8)}$, are derived mainly from σ-donation from pyridyl rings (Fig. S11†). It becomes obvious that the π donation is much weaker than the σ donation. Thus, the EDA-NOCV calculations suggest that the best representation of the CDP–Ce(Br) interactions in **3** shows only two σ donation CDP→Ce(Br)←CDP. Note that for both the cases the large $\Delta E_{\text{orb(rest)}}$ contribution (*e.g.*, 32%–41%) mainly originates from the combined effect of several small-sized intra- and inter-fragment charge polarization terms.

We further analyzed the electron density distribution in **2** and **3** with the quantum theory of atoms-in-molecules (QTAIM).[22] The numerical results are given in Table S7† and the contour plots of the Laplacian of electron density, $\nabla^2\rho(r)$, are provided

(a) **2**



(b) **3**

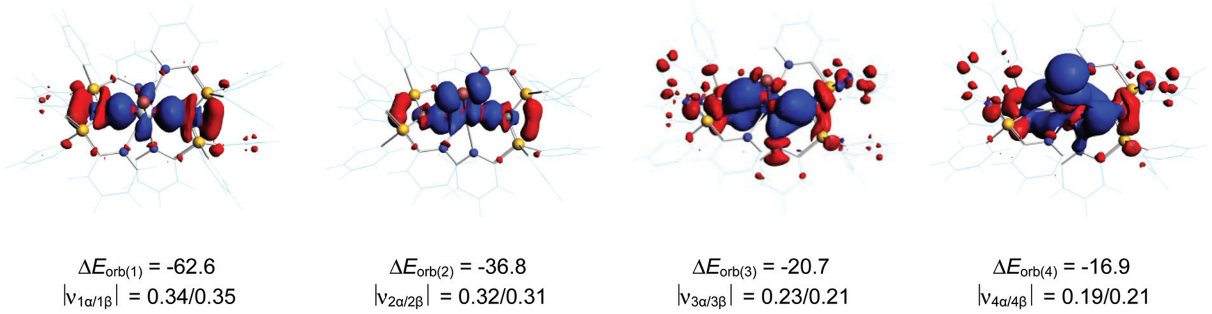


Fig. 4 Shape of the deformation densities $\Delta\rho_{(1)-(4)}$, which are associated with the orbital interactions $\Delta E_{\text{orb}(1)-(4)}$ in (a) **2** and (b) **3** and eigenvalues $|\nu_n|$ of the charge flow. The isosurface values are 0.001 for $\Delta\rho_{(1)}$ and 0.0003 for $\Delta\rho_{(2)-(4)}$. For $\Delta\rho_{(2)}$ in **3**, the isosurface value is 0.001.

in Fig. S12.† For **2** and **3**, the total energy density $H(r_c)$ values are negative for both Ce–C and Ce–N bonds, which agrees with the normal covalent bond character.[23] Generally, the ellipticity of electron density, $\varepsilon(r_c)$,[24] is approximately zero for single and triple bonds, but larger than zero for double bonds. Notably, the $\varepsilon(r_c)$ values in different chelated complexes containing U═C and Ce═C bonds are within the range 0.22–0.52.[7g,25] In **2**, $\varepsilon(r_c)$ the value for the Ce–C bond is only 0.11, whereas the $\varepsilon(r_c)$ values for the Ce–C bonds in **3** are 0.18 and 0.19. These values indicate mainly the single bond nature of Ce–C bonds in the title complexes with only slight perturbation from the cylindrical distribution of $\rho(r)$, whereas this perturbation in **3** is slightly larger than that in **2**. Furthermore, the Nalewajski–Mrozek bond order,[26] computed from valence indices based on the partitioning of Tr($\mathbf{P}^*\Delta\mathbf{P}$) (**P** = first-order density matrix), is found as 0.73 for the Ce1–C1 bond of **2** and 0.81 for both the Ce1–C1 and Ce1–C2 bonds of **3**. The calculated bond orders also indicate the Ce–C single bond in the title complexes.

The much weaker π donation of the CDP ligands to Ce in complexes **2** and **3** is in contrast to our previous finding about the donation of CDP to uranium, where we found a significant contribution of π bonding besides the σ donation.[17] It is possible that the 4f orbitals of the lanthanides are less prone to genuine chemical bonding than the 5f orbitals of the actinides. A recent theoretical study of the lanthanide octacarbonyl anions $[\mathrm{Ln(CO)_8}]^-$ (Ln = Tm, Yb, Lu) showed only negligible contributions of the metal 4f AOs to the dative interactions with the CO ligands,[27] while the metal–CO interactions in the actinide octacarbonyls $[\mathrm{An(CO)_8}]^{+/-}$ (An = Th, U) revealed a significantly higher input.[28] We are studying the difference between 4f and 5f bonding in lanthanide and actinide compounds in future work.

Conclusions

In summary, a carbon(0) ligand has been employed as a scaffold for rare-earth metals, leading to the formation of a complex with a cerium–carbon dative interaction. In the presence of $\mathrm{NaBPh_4}$, the species with two dative interactions to the same element has been successfully prepared and characterized. Single-crystal X-ray diffraction analysis confirms a short cerium–carbon bond in these complexes. DFT calculations reveal that dominantly σ dative interactions are formed between carbon and cerium in $\mathrm{Br_3Ce{\leftarrow}CDP}$ and $\mathrm{CDP{\rightarrow}Ce(Br){\leftarrow}CDP}$ with only weak additional π-donation. Both σ- and π-donations are stronger in the latter complex than in the former. Our findings suggest that both rare-earth metals and actinide metals can form dative bonds with carbone ligands where the lanthanides appear to be less prone to use their 4f orbitals for additional π interaction with the second lone-pair orbital of the carbone.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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