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Mono and bis carbene neodymium(III) spirocyclic complexes with a cumulene carbon metal structure

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ABSTRACT

The formation of metal carbon cumulene structures is rare in synthesis chemistry because properties of the carbene carbon and metal must match properly, such as an electron rich PCP carbene and late transition metals containing *d, f* rich orbitals, or lanthanide metals. In this study, we performed the first step reaction of $[Li_2C(Ph_2P=NSiMe_3)_2]$ (**1**) with $NdCl_3$ in 1:1 M ratio in situ, with subsequent addition of second molar ratio of **1** to the reaction solution to generate bis carbene neodymium organometallic compound of $[Nd\{C(Ph_2P=NSiMe_3)_2\}_2][Li(THF)_n]$ (**2**). The anion of this isolated compound **2** formed a rare linear carbene metal cumulene structure (C═Nd = C) demonstrated by crystal structure determination. In order to synthesize a mono carbene neodymium compound with bis(diphenyliminophosphorane)methandiide (**1**) to compare its bonding feature to the reactions of $[Li_2C(Ph_2P=NSiMe_3)_2]$ (**1**) with $NdCl_3$ and CpTl in THF, eventually crystal structure analysis showed that generated another neodymium organometallic complexes of $[Cp_2Nd\{CH(Ph_2P=NSiMe_3)_2\}_2]$ (**3**), unexpected the methandiide carbon of PCP ligand was protonated. Furthermore, DFT calculations demonstrated the presence of multiple bonding interaction in the carbon metal cumulene structure (C═Nd = C). NBO analysis revealed that the average overall C═Nd double bond contains 21.19% carbon and 14.43% Nd component respectively, indicating it is a covalent conjugated multiple bonding system. To the best of our knowledge, it is the first structural example of PCP carbene neodymium compound with the cumulene structure (C═Nd = C) unit.

1. Introduction

Lanthanide metal carbene complex chemistry is a rapidly developing area in the last few decades because of its potential application to catalysis and organic synthesis, most notably the use of lanthanide alkyls and hydrides as single-component catalysts for olefin polymerization [1]. Two-electron carbene donors to metal ions formation of typical single bond (M – C) carbene-metal complexes also play a central role in catalytic organometallic chemistry, such as lanthanide N-heterocyclic carbene (NHC) complexes including neodymium are effective regioselective C–H activation catalysts [2]. Lanthanide and actinide *f*-element complexes with real metal-carbon multiple bond character have been widely described in the past few years [3–5].

The reactions of various metal species with bis(diphenyliminophosphorane)-methandiide, $[Li_2L]$ (**1**), formed by double deprotonation of the backbone methylene of dppm has generated interesting chemistry [6]. We want to focus on its reaction with different metals to design and synthesize complexes in devising geometry, and to study their unique bonding behaviour and reactivity. In a past decade, it has been demonstrated that these types of spirocyclic pincer ligands (PCP) have abundant chemical bonding properties and reactivities with transition metals, lanthanide and actinide metals, as well as main group elements. Examples include the formation of complexes containing either single (C–M) or double (C = M) carbene–metal bonds, or formation of monomeric and bimetallic complexes, some of which showed great catalytic activities [6]. Recently, the synthesis of bis(carbene) metal complexes has been conducted, and some of these complexes form the cumulene carbon metal structure (C = M = C), such as the first crystal structure characterization of Tm(III) complex with SCS

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ligand ($Ph_2SPCPSPh_2$/C═Tm═C) [3d]. As far as we know, only two anion crystal structures of Dy(III) and Ce(III) with bis(carbene) ligand of [$C^{2-}(Ph_2P=NSiMe_3)_2$] and cation potassium (K^+) coordinated by 18-crown-6 ether and two THF were reported in the literature [4a,4b] to also contain cumelene carbon metal structures (C═Dy═C or C═Ce = C). For lanthanide neodymium(III) carbene complex, only one crystal structure of bis(iminophosphranyl) PCP ligand ([$H_2C(Ph_2P=NSi(i\text{-}Pr)_2$] was reported in literature where the structure unit of C═Nd-CH was presented [3e].

In this research, we have extended our study of this PCP [$Li_2C(Ph_2P=NSiMe_3)_2$] (Li_2L) electron rich carbene ligand to the lanthanide neodymium, and in the course of the study we have discovered a rare example of the neodymium metal center bonding directly to two PCP carbenes to form a rare linear cumulene carbon metal structure (C═Nd = C).

2. Experimental

2.1. General considerations

All manipulations were performed either in an Ar-filled glove box or under an Ar or N_2 atmosphere using standard Schlenk techniques. Solvents were dried over appropriate drying agents and degassed by three freeze-pump-thaw cycles prior to use. The organolithium compound [Li_2-**1**]$_2$ (**1**) was prepared according to our published procedures [7a,7b]. Warning!!! The toxicity of thallium and its compounds has been previously discussed [7c], and must be handled very carefully. NMR spectra were recorded at ambient temperature using THF-d_8 or toluene-d_8 solutions of the complexes on a Varian i400 spectrometer (161.9 MHz for ^{31}P, 100.6 MHz for ^{13}C) and referenced to residual solvent proton (^1H), solvent (^{13}C), external 85% H_3PO_4 (^{31}P). Elemental analyses were carried out at Analytical and Instrumentation Laboratory, Department of Chemistry, University of Alberta.

2.2. Synthesis of [{$C(Ph_2P=NSiMe_3)_2$}$_2$Nd][Li(C_4H_8O)$_4$] (2)

To THF solution (10 ml) of [Li_2-1]$_2$ (0.115 g, 0.10 mmol) was added anhydrous $NdCl_3$ (0.025 g, 0.10 mmol) as a solid in a single portion at room temperature. The resulting solution was stirred at room temperature for 2 h, during which the mixture turned into a clear light green solution. The filtered THF solution was evaporated on a dynamic vacuum line and the remaining powder was dissolved in 10 ml ether. The undissolved solid of LiCl was removed by centrifugation. The yellow-green solution was evaporated under vacuum to half of the volume and a few drops of dry toluene was added. The solution was kept inside the freezer (−20 °C) for a few days, during which yellow-green crystals formed. The top liquid was taken and dried under vacuum. The product of **2** was obtained (0.116 g, yield 71.0%). Anal. Calcd for $C_{82}H_{118}LiN_4NdO_5P_4Si_4$: C, 60.5; H, 7.31; N, 3.44. Found: C, 60.1; H, 7.17; N, 3.51. ^1H NMR: ^1H NMR(THF-d_8): δ 7.94 (t, phenyl), 7.69 (d, phenyl), 7.35 (t, phenyl), −0.14 (s, -Si(C**H**$_3$)$_3$). $^{13}C\{^1H, ^{31}P\}$ NMR (THF-d_8): δ 131.71(s, phenyl), 129.68(s, phenyl), 128.22(s, phenyl), 127.38(s, phenyl), 3.31 (s, Si(**C**H$_3$)$_3$) (notes: carbide signal was not resolved). $^{31}P\{^1H\}$ NMR(THF-d_8): δ 15.18 (s). IR data: 3050s, 3015 m, 2948s, 1480w, 1434s, 1272s, 1238s, 1126 m, 1113 m, 1104w, 865s, 829s, 802s, 777 m, 740 m, 697 m.

2.3. Synthesis of [(η^5-C_5H_5)$_2$Nd{k^3-CH($Ph_2P=NSiMe_3$)$_2$}] (3)

To THF solution (10 ml) of [Li_2-1]$_2$ (0.115 g, 0.10 mmol) was added anhydrous $NdCl_3$ (0.051 g, 0.20 mmol) as a solid in a single portion at room temperature. The resulting solution was stirred at room temperature for 2 h, a white solid of CpTl (0.108 g, 0.40 mmol) was added into the reaction solution. The mixture turned into a clear dark green solution. The filtered THF solution was evaporated on a dynamic vacuum line and the remaining powder was dissolved in 10 ml ether. The undissolved solid of LiCl was removed by centrifugation. The dark-green solution was evaporated under vacuum to half of the volume. The solution was kept inside the freezer (−20 °C) for a few days, during which dark-green crystals formed. The top liquid was taken and dried under vacuum. The product of **3** was obtained (0.062 g, yield 75.0%). Anal. Calcd for $C_{41}H_{49}N_2NdP_2Si_2$: C, 59.18; H, 5.94; N, 3.36. Found: C, 60.16; H, 5.69; N, 3.32. ^1H NMR(THF-d_8): δ 7.92 (t, phenyl), 7.54 (d, phenyl), 7.30 (t, phenyl), −0.13 (s, -Si(C**H**$_3$)$_3$). $^{13}C\{^1H, ^{31}P\}$ NMR (THF-d_8): δ 132.0(s, phenyl), 130.1(s, phenyl), 129.1(s, phenyl), 127.2(s, phenyl/C_5H_5), 3.62 (s, Si(**C**H$_3$)$_3$) (notes: carbide signal was not resolved). $^{31}P\{^1H\}$ NMR(THF-d_8): δ 18.68 (s). IR data: 3076s, 3058s, 2950s, 2894 m, 1590w, 1483w, 1435s, 1256s, 1246s, 1115s, 1092s, 1071 m, 1030w, 1014s, 996w, 848s, 830s, 764s, 696 m.

2.4. Crystal structure determination

Suitable crystals of **2** to **3** were mounted on glass fibers by means of mineral oil, and data were collected using graphite-monochromated MoKα radiation (0.71073 Å) on a Bruker PLATFORM/SMART 1000 CCD diffractometer. Programs for diffractometer operation, data collection, data reduction and absorption correction were all supplied by Bruker. The structure was solved by direct methods using Patterson Search/Structure Expansion [8a], and these structures were all refined using full-matrix least-squares on F^2 (*SHELXL-97*) [8b-8c]. All non-hydrogen atoms in the structure compound were refined with anisotropic displacement parameters. Selected crystal data and structure refinement details for **2**–**3** are listed in Table 1.

2.5. Computational details

The geometric optimization and energy calculations were performed with the Gaussian03 program [9] based on the density functional theory (DFT) method. DFT calculations were performed using the B3PW91 [9] functional, the SDD basis set on Nd, 6-311G** basis set on P, N and 6-31G* basis set on Si, C and H. The partial outside phenyl rings were replaced with methyl and methyl was replaced with H. The SDD basis is constructed with a quasir-elativistic effective core potential that allows the incorporation of scalar relativistic effects in nonrelativistic calculation.

3. Results and discussion

The preparation was conducted as one-pot, two-step reaction under anaerobic conditions. Neodymium trichloride ($NdCl_3$) was treated with an equivalent molar ratio of Li salt [Li_2L] (**1**) in THF. The pink suspension of **1** quickly turned yellow as the $NdCl_3$ solid dissolved in this solution, therefore generating the intermediate compound as shown (Scheme 1) which is similar to our previously reported Sm(III) compound [6a]. After 20 min reaction, another 1 M equivalent of [Li_2L] (**1**) was added to the solution which was continuously stirred for a few hours. The final product of complex [Nd{$C(Ph_2P=NSiMe_3)_2$}$_2$Li(THF)$_n$] (**2**) was isolated by evaporation of the THF, redissolution in ether, elimination of solid LiCl by centrifugation followed by low temperature precipitation from the ether solution inside the dry glove box freezer. In addition, 2 M equivalent of TlCp was added to the intermediate solution (Scheme 1) and isolated via the same procedure. However, instead of forming the expected ion pair compound [Cp_2Nd{$C(Ph_2P=NSiMe_3)_2$}$_2$][Li(THF)$_n$], a neutral compound of [Cp_2Nd{$CH(Ph_2P=NSiMe_3)_2$}$_2$] (**3**) was isolated from the solution. This

Table 1
Crystal data and structure refinement details for complexes **2**–**3**.

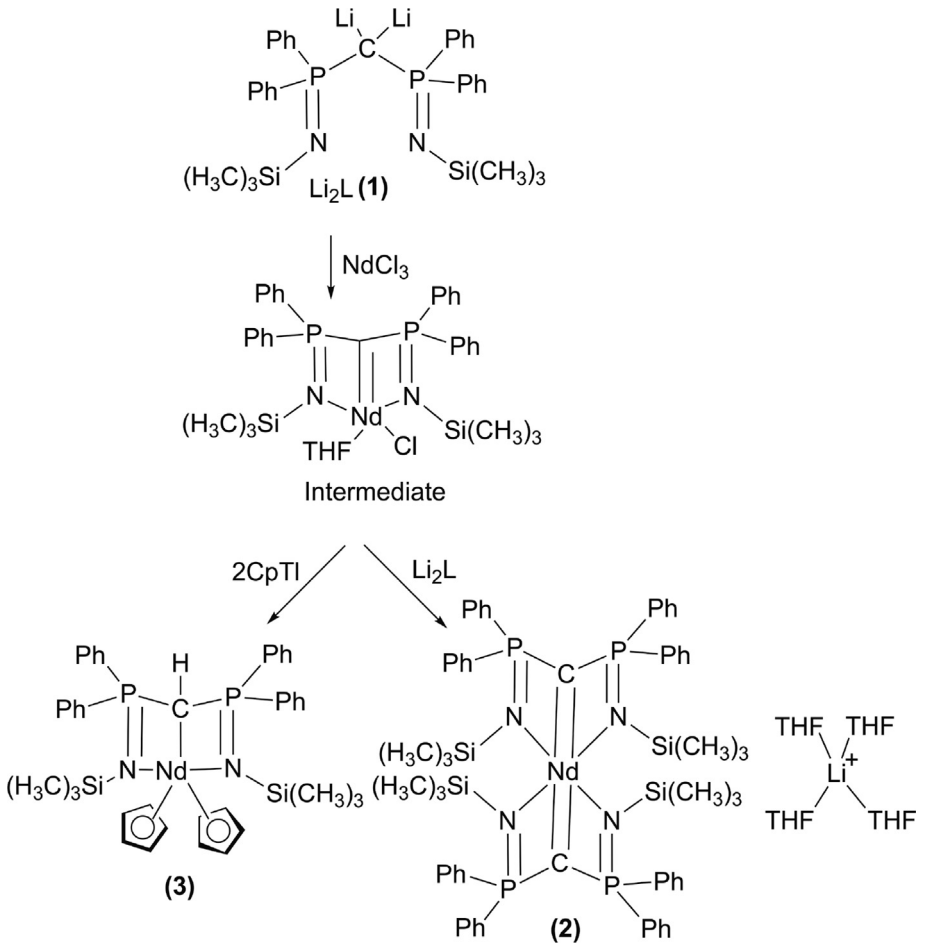
Empirical formula	$C_{82}H_{119.33}LiN_4NdO_5P_4Si_4$ (2)	$C_{41}H_{49}N_2NdP_2Si_2$ (3)
Formula weight	1628.57	832.18
Crystal system	Monoclinic	Triclinic
Crystal Dimensions	0.56 × 0.33 × 0.18 mm	0.38 × 0.25 × 0.22 mm
Space group	$P2_1/n$ (an alternate setting $P2_1/c$ [No. 14])	$P\bar{1}$ (No. 2)
Unit cell parameters		
a (Å)	14.5299 (11)	10.3729 (7)
b (Å)	26.530 (2)	11.8156 (7)
c (Å)	22.6679 (17)	17.7298 (11)
α (°)		73.8725 (8)
β (°)	90.4329 (11)	76.8455 (8)
γ (°)		77.0371 (8)
Volume (Å^3)	8737.6 (11)	2002.3 (2)
Z	4	2
Calculated density (g cm^{-3})	1.238	1.380
Temperature, K	173.2(1)	173.2(1)
μ (Mo Kα), (mm^{-1})	0.771	1.466
θ range for data collection (°)	0.3 to 26.95	0.3 to 27.49
Index ranges		
	$-18 \le h \le 18$	$-13 \le h \le 13$
	$-33 \le k \le 33$	$-15 \le k \le 15$
	$-28 \le l \le 28$	$-22 \le l \le 23$
Independent reflections	18975	9081
Observed reflections	14223	8537
Data/restraints/parameters	18975/14/900	9801/0/433
Goodness-of-fit on F^2	1.072	1.077
Final R indices		
$[F_0^2 \ge 2\sigma(F_0)]$	$R_1 = 0.0432$	$R_1 = 0.0234$
wR_2 $[F_0^2 \ge -3\sigma(F_0^2)]$	w$R_2 = 0.1122$	w$R_2 = 0.0616$
Large difference peak and hole	−0.424 and 1.343 e/Å^3	−0.263 and 0.971 e/Å^3

Table 2
Selected bond lengths (Å) and angles (°) for compounds **2**–**3**.

Compound 2			
Nd–C(1)	2.585 (3)	C(2)–P(4)	1.629 (3)
Nd–C(2)	2.583 (3)	P(1)–N(1)	1.618 (3)
Nd–N(1)	2.522 (3)	P(3)–N(3)	1.613 (3)
Nd–N(3)	2.536 (3)	P(3)-C(2)-P(4)	173.4 (2)
		P(2)-C(1)-P(1)	172.4(2)
Nd–N(4)	2.536 (3)	C(1)-Nd-C(2)	178.21 (10)
C(1)–P(1)			1.637 (3)
C(1)–P(2)			1.633 (3)
C(2)–P(3)			1.635 (3)
Compound **3**			
Nd–C(1)	2.7401 (17)	P(1)–C(1)	1.7164 (17)
Nd–N(1)	2.5700 (15)	P(2)–C(1)	1.7225 (17)
Nd–N(2)	2.5821 (15)	P(1)–N(1)	1.6026 (15)
Nd–C(50)	2.7815 (19)	P(2)–N(2)	1.6015 (15)
Nd–C(51)	2.781 (2)	N(1)-Nd-N(2)	118.40 (5)
Nd–C(52)	2.754 (2)	N(1)-Nd-C(1)	60.50 (5)
Nd–C(53)	2.761 (2)	P(1)-C(1)-P(2)	142.06 (11)
Nd–C(54)			2.778 (2)
Nd–C(55)			2.797 (3)
Nd–C(56)			2.776 (2)
Nd–C(57)			2.763 (2)
Nd–C(58)			2.783 (2)
Nd–C(59)			2.810 (2)

result did not yield the desired compound of carbene metal bond (M = C) because the deprotonated dilithium salt is very active and can be easily protonated in situ. Both of the green colored crystals of **2** and **3** quickly changed to dark-red as they were exposed in the air, which indicated that neither were stable in the open atmosphere.

The molecular structures of $[Nd\{C(Ph_2P=NSiMe_3)_2\}_2Li(THF)_n]$ (**2**) and $[Cp_2Nd\{CH(Ph_2P=NSiMe_3)_2\}_2]$ (**3**) were determined by X–ray crystallography [8]. An ORTEP view of the anion of **2** with selected bond lengths and bond angles is shown in Fig. 1and Table 2. The two tridentate chelated PCP carbene ligands clamp a central Nd metal to form a six-coordinated geometry. The bond angle of C(1)–Nd–C(2) is essentially linear (178.21(10)°) with identical bond distances (Nd–C(1) = 2.585(3) and Nd–C(2) = 2.583(3) Å respectively), indicating that the two coordinated carbenes are symmetrically situated on either side of the neodymium metal center. Two sets of six atoms, N(1), P(1), C(1), P(2), N(2) and Nd, and N(3), Nd, N(4), P(4), C(2) and P(3) each define two individual co-joined four-membered metallocyclic rings which are in a nearly



Scheme 1. Preparation routes.

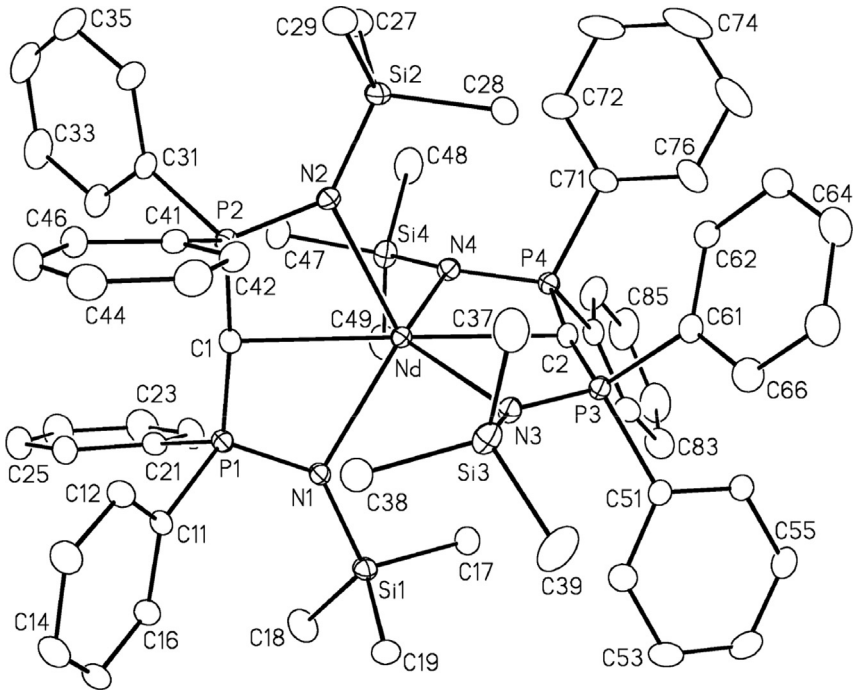


Fig. 1. Perspective view of anion of the $[Nd\{C(Ph_2P=NSiMe_3)_2\}_2]$ (**2**) molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

coplanar relationship. The two planes are perpendicular to each other (dihedral angle of 84.62(4)°). The neodymium to carbons bond distances of **2** (Nd–C(1) = 2.585(3) and Nd–C(2) = 2.583(3) Å) are considerably shorter than the Nd-carbene (NHC) distances in literature data (Nd–C 2.669(2) Å [10] and 2.609(3) ~ 2.656 (5) Å [2d]) as well as the Nd-alkyl complex (2.674(5) ~ 2.694(5) Å) [11]. However, it is longer than in the terminal alkyl neodymium compound $\{Nd[(CH_3)_5C_5]_2CH[(Si(CH_3)_3]_2\}$ (Nd–C = 2.517(7) Å) reported in the literature [12]. Additionally, there is only one Nd(III) carbene complex structure reported in literature with $[H_2C(Ph_2P=NSi\text{-}i\text{-}Pr)_2\}_2$ ligand where C–Nd=C structural unit is present, with bond distances of double C=Nd (2.592(3) Å) and single C–Nd (2.864(3) Å) [3e]. Obviously the bond distances of C–Nd (Nd to PCP carbene carbon) in **2** is shorter than the reported data, this indicates the existence of multiple bonding interactions between Nd and C in **2** (C=Nd = C). To the best of our knowledge, compound **2** is the first example wherein the two PCP ligands bond to Nd to form a linear cumulene carbon metal structure (C=Nd = C).

An ORTEP view of the molecular structure of **3** with selected bond lengths and bond angles is shown in Fig. 2 and Table 2. One tridentate PCP spirocyclic chelated ligand is coordinated to Nd with average Nd–N bond distance of 2.576(2) Å and Nd–C (carbon) bond distance of 2.7401(17) Å, which are consistent with the methane structure. There are two five-membered Cp rings coordinated to Nd with average Nd–C bond distances of 2.771(2) Å and 2.786(2) Å respectively. One Cp ring is located above the plane defined by P(1), P(2) and Nd atoms, and the second Cp ring is situated below this plane with dihedral angle of 59.08(9)° between them. Considering that compound **3** has a higher coordination number than **2**, it is reasonable that the average Nd–N bond lengths are slightly longer in **3** (2.5761(15) Å) than in **2** (2.532(3) Å). The bridging carbon is protonated to make the complex a methanide and the Nd–carbon bond distance in compound **3** is appropriate for a single bond in contrast to the Nd-(carbene)carbon link in **3**. Similar crystal structures of lanthanide compounds of $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(Ph_2P=N(SiMe_3)_2\}]$ (Ln = Y, Er and Sm) [13a] and $[(\eta^8\text{-}\{1,4\text{-}(SiMe_3)_2C_8H_6\})Ln\{CH(Ph_2P=N(SiMe_3)_2\}]$ (Ln = Y and Er) [13b] with bis(diphenyliminophosphorane)methanide were reported in the literature. The Y–C = 2.638(3), Sm–C = 2.697(2) and Er–C = 2.621(3) Å (Nd-methanide) bond distances were determined in these three compounds $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(Ph_2P=N(SiMe_3)_2\}]$ (Ln = Y, Er and Sm) [13a], which are slightly shorter than that in **3** (Nd–C = 2.7401(17) Å). However, the bond distances are comparable when effects of metallic ionic radius are taken into consideration. Slightly longer bond distances of Y–C (2.680(2) Å) and Er–C (2.668(2) Å) were found in these two compounds $[(\eta^8\text{-}\{1,4\text{-}(SiMe_3)_2C_8H_6\})Ln\{CH(Ph_2P=N(SiMe_3)_2\}]$ (Ln = Y

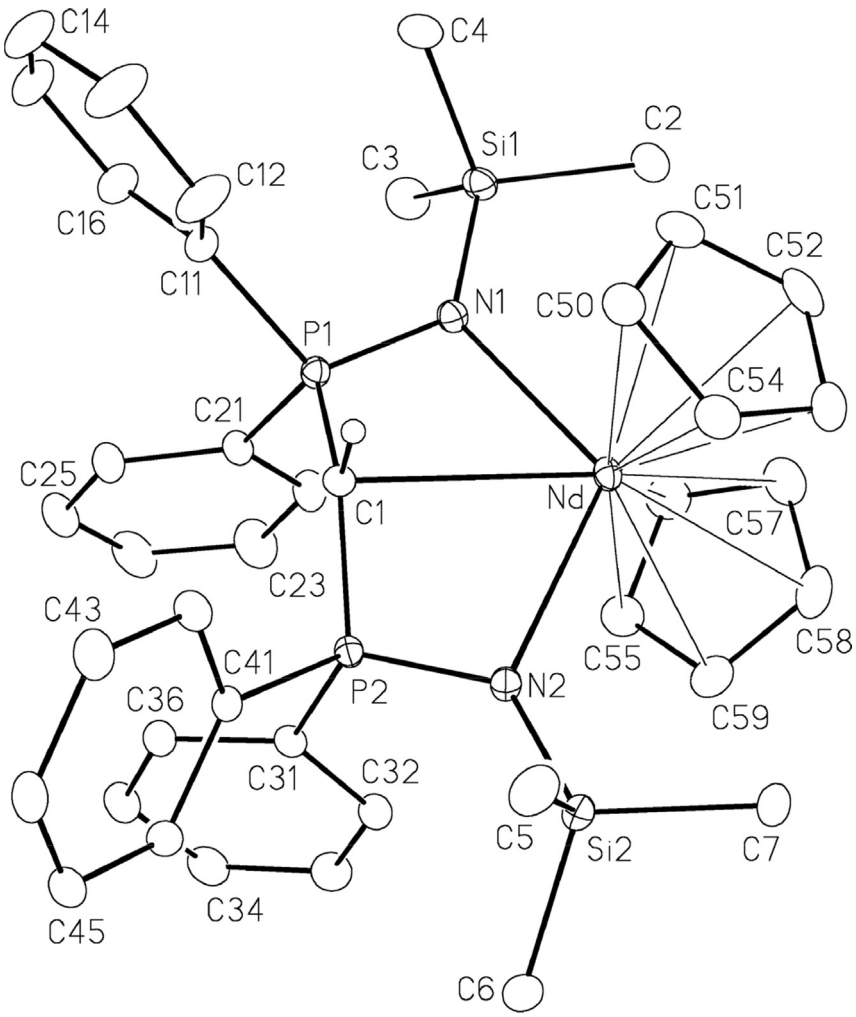


Fig. 2. Perspective view of the $[Cp_2Nd\{CH(Ph_2P=NSiMe_3)_2\}_2]$ (**3**) molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

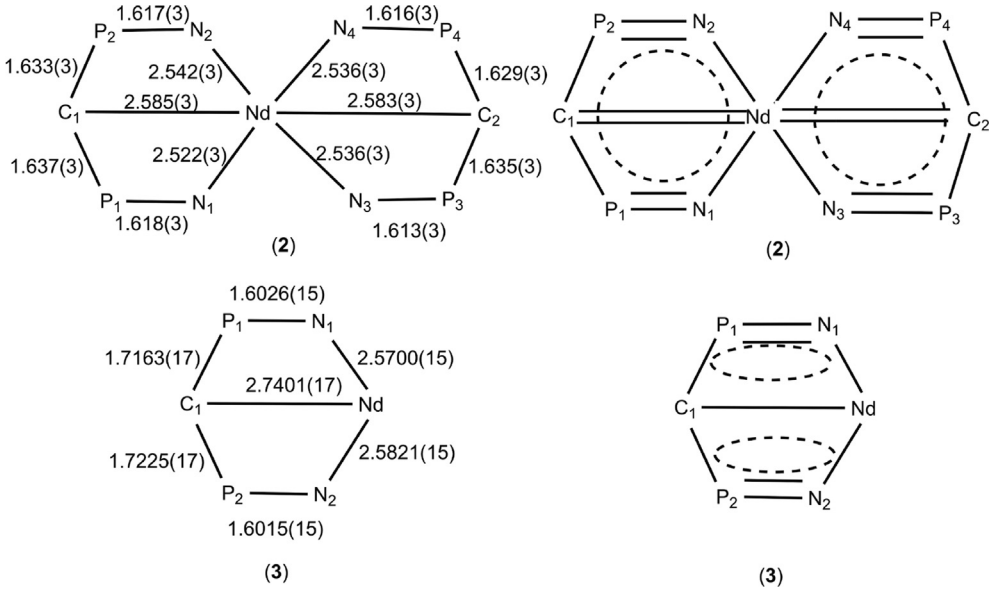
and Er) [13b], indicating that different ligands also has an effect on bond lengths.

All bond distances within the ligand frameworks in complexes **2** and **3** are considerably altered in comparison to the relevant values in free bis(iminophosphorano)methane ligands [14]; the P═N bond distances are elongated and the endocyclic P–C bond distances are significantly shortened. However, exocyclic P–C distances are unaffected. In comparison, the endocyclic P–C and P═N bond distances in **3** (average P–C = 1.719(3) and P═N = 1.602(3) Å) are notably different than those of the free ligand. The P–C length is shorter while the P═N length is longer in **2** (average P–C = 1.634(3) and P═N = 1.616(3) Å) than in **3**. The average P–C–P bond angles 172.9(2)°(**2**) and 142.1(2)°(**3**) are wider compared to the corresponding values in the free ligand [$H_2C\{Ph_2P=NSiMe_3\}_2$] (124.94(15)°) [14a]. These values for **3** are comparable to those in the complex [$Sm\{C(Ph_2P=NSiMe_3)_2\}(NCy_2)(THF)$] (138.0(3)°) [6a], in which a very short double metal-carbene Sm═C bond was formed. The P–C–P and C–Nd–C angles in **2** are nearly 180° and the system represents an example of a linear carbene metal cumulene structure. These factors suggest that there is a delocalization of π electron density within each of the four-membered metallocyclic rings. This interaction contributes a π bonding component which strengthens the Nd–carbene bonds in **2** and **3**, thus making these bond distances slightly shorter than those found in other systems where this stabilization is absent [10,11]. The coplanarity of each pair of four-membered metallocylic rings on either side of the Nd and their mutually perpendicular relationship in **2** also enhances the possibility of delocalization of the π electrons. The results in the endometallocyclic P–C and P═N bond distances being essentially equal. The structure of compound **2** provides convincing evidence to support the proposed π electron delocalization interaction model for these systems.

It is interesting to compare the bond distances of four-membered rings formed via the PCP spirocyclic ligand bonding to metal Nd(III) in the two synthesized Nd(III) compounds **2** and **3** (as shown in Scheme 2). It is clearly shown that bond distances of double bond P═N in **2** are longer than in **3**. Conversely, single bond distances of P–C, C–Nd and N–Nd are shorter in **2** than in **3** (Scheme 2). This demonstrates that the bonding electrons are more delocalized in **2** than in **3** within the four-membered rings, which indicate that the ring system is more conjugated in **2** than that in **3** (Scheme 2). This led us to believe that formation of the C═Nd = C cumulene strengthens the carbene Nd(III) carbon metal bond, and delocalizes the bonding electrons, which enhances the system conjugation interaction. This explains why two bis PCP carbene bonded to Nd(III) is significantly more stable than mono PCP carbene bonded, as well as why mono carbene Nd(III) compound was difficult to synthesize and isolate.

DFT calculations on a model compound of [$Nd\{C(Me_2P=NSiH_3)_2\}_2]^-$ (**2a**) and [$Cp_2Nd\{HC(Me_2P=NSiH_3)\}$] (**3a**) were performed using Gaussian 03 based on the crystal structures [9]. DFT optimized structures of model compounds **2a** and **3a** were shown in Fig. 3, the core structural geometry and bond distances of **2a** and **3a** were equivalent when comparing their crystal structural data (Fig. 3). Molecular orbitals of **2a** containing the carbene and Nd bonding interactions are shown for the HOMO (MO-151), HOMO-1 (MO-150) and HOMO-7 (MO-144) (Fig. 4). Two σ bonds are formed with two mutual carbon p_x orbitals from two sides along the x axis overlapping with the Nd $d_{x^2-y^2}$, d_{z^2} atomic orbitals as shown in MO-144. Meanwhile, two π bonds are formed between the two carbons centers using carbon p_y and p_z atomic orbitals and Nd d_{xz}, d_{yz} orbitals interaction as shown in HOMO (MO-151) and HOMO-1 (MO-150) in Fig. 4. These results clearly demonstrate the existence of multiple bonding between the carbene center and the Nd in compound **2**, forming a metal-carbon cumulene structure (C═Nd = C), which is also in agreement with observation of the shortest Nd–C bond distance displayed by **2**. DFT calculations for **3a** showed carbon p_y and Nd d_{yz}, $d_{x^2-y^2}$ interactions which form a σ bond, in addition to the carbon p_z overlapping with the proton s orbital to form a π bond as shown in HOMO (MO-126) and MO-110 (Fig. 4).

In order to fully understand the bond properties of the cumulene structure (C═Nd = C), DFT NBO calculations on a model compound of [$Nd\{C(Me_2P=NSiH_3)_2\}_2]^-$ (**2a**) and [$Cp_2Nd\{HC(Me_2P=NSiH_3)\}$] (**3a**) (as shown in Fig. 3) were performed using Gaussian 03 [9]. The NBO results revealed that bonding contributions mainly originate from molecular orbitals of HOMO (MO-151), HOMO-1 (MO-150) and MO-144 as shown in Fig. 4. The calculated atomic orbital contribution components to the formed cumulene bonds were listed in the caption of Fig. 4. The average



Scheme 2. Bond distances of four-membered rings formed through PCP spirocyclic bonded to Nd(III) in compounds **2** and **3**.

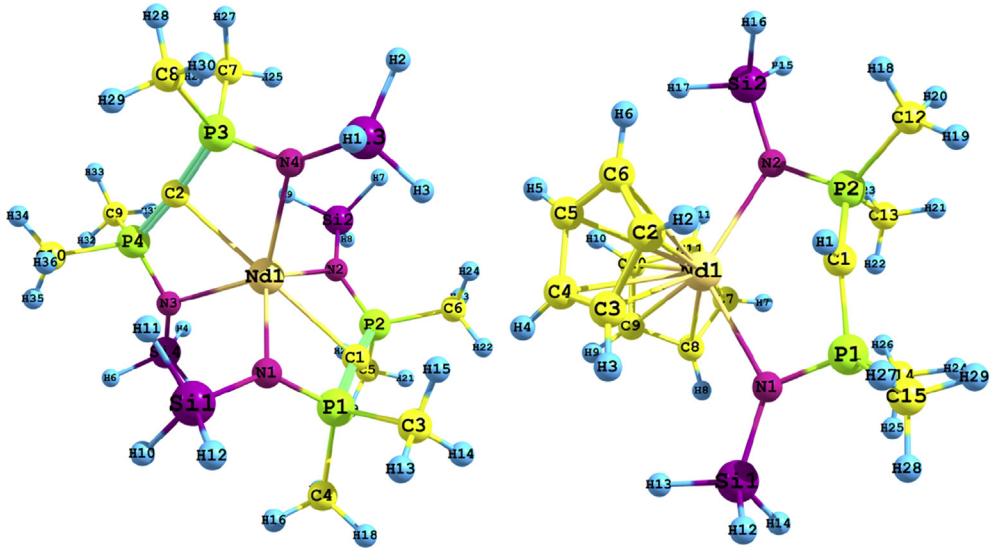


Fig. 3. DFT optimized model structures of **2a** and **3a**. Calculated bond distances: C1-Nd1 = 2.58486 Å and C2-Nd1 = 2.58277 Å (**2a**); C1-Nd1 = 2.74013 Å (**3a**).

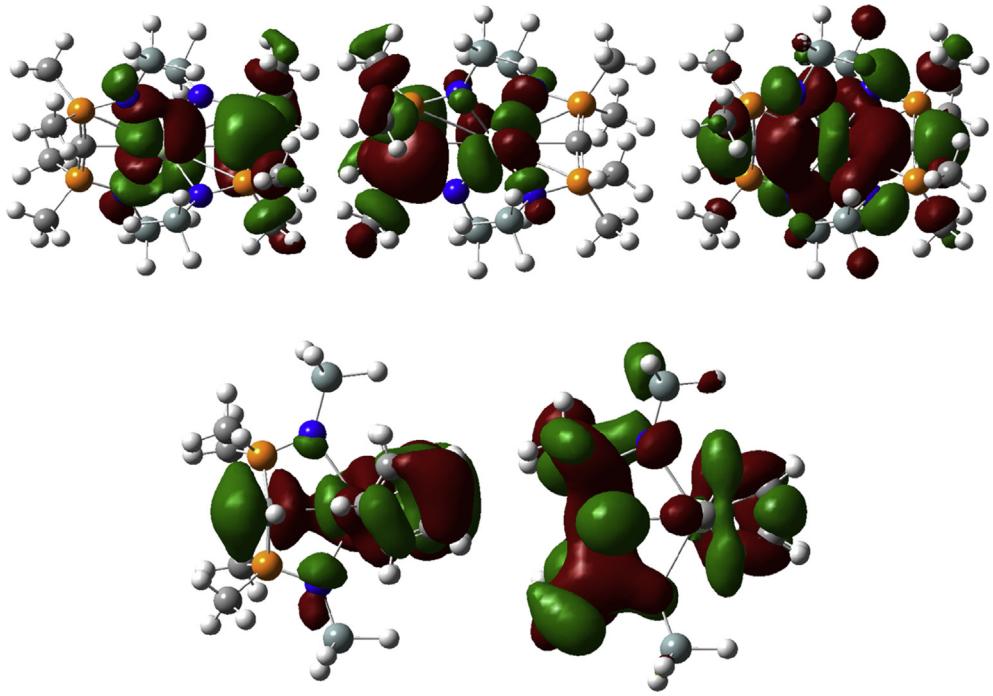


Fig. 4. $[Nd\{C(Me_2P=NSiH_3)_2\}_2]^-$ (**2a**), top (from left to right): HOMO (MO-151 which contains π bonding component), HOMO-1 (MO-150 which contains π bonding component) and MO-144 (which contains σ bonding component); and $[Cp_2Nd\{HC(Me_2P=NSiH_3)\}]$ (**3a**), bottom: (left) HOMO (MO-126) and (right) MO-110. NBO analysis of orbital component: HOMO (Nd 43.50%, C1 0.05% and C2 37.10%), HOMO-1 (Nd 23.40%, C1 54.90% and C2 0.07%), MO-144 (Nd 19.70%, C1 18.70% and C2 16.30%).

overall C═Nd double bond contains 21.19% carbon and 14.43% Nd respectively, indicating the cumulene structure is a conjugated covalent bonding system.

4. Conclusions

In conclusion, treating anhydrate neodymium trichloride with two equivalent of dilithiumbis(iminophosphorano)methandiide (Li_2L (**1**)) formed the neodymium metal carbene complex **2** with a short Nd−carbene multiple bond best described as a Nd═C double bond with metal carbon cumulene structure (C═Nd = C). This description is supported by data from both X-ray crystalline structural and Gaussian 03 DFT calculations. Treating neodymium trichloride with one equivalent of dilithiumbis(iminophosphorano) methandiide gave an intermediate metal carbene complex, which when reacted further with two equivalent of CpTl, yielded complex **3**. DFT Gaussian 03 calculations revealed single bond formation between the (methine) carbon and neodymium in **3**. To the best of our knowledge, compound **2** is the first example of the two PCP ligands bond to Nd to form a linear cumulene carbon metal structure (C═Nd = C). Our results demonstrated that the electron rich PCP carbene ligand reacted with d, f orbital lanthanide metal of

neodymium can form the multiple bonding interaction cumulene linear structure of C═Nd = C. NBO analysis revealed that the cumulene structure is a conjugated covalent multiple bonding system.

Supporting information available

Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-1874122 (**2**) and CCDC-1874123 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) 144–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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