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Novel phosphonated bicyclic frameworks from Diels–Alder reaction as chelating agents of di- and trivalent metal cations

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ABSTRACT

The synthesis of novel [4+2] cycloadducts by Diels–Alder (DA) reaction between diethyl 1-phosphono-1,3-butadiene and cyclic C=C and N=N dienophiles, such as maleimide and 1,2,4-triazole-3,5-dione derivatives, is described. These phosphonated bicyclic frameworks feature a cage shape enabling metal chelation. Indeed, stable complexes were formed in solution with M^{2+} and M^{3+} metal cations, as evidenced by HRMS in the ESI mode (electrospray ionization). L₁:M (one ligand–one metal) and L₂:M (two ligands–one metal) complexes were identified depending on the nature of the cation.

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Introduction

Phosphonated compounds are widely described in the literature as chelating agents for different metals.¹ In most cases, only phosphonic acids are considered.² Neutral phosphonate alkyl esters are however also able to form complexes. They are used as ancillary functions on macrocyclic ligands,³ or incorporated as α -, β - or γ -substituents on carbonyl derivatives to make small bidentate chelating agents, such as **A**, **B** and **C** (Fig. 1).⁴ Recently, diethyl (phthalimidomethyl)phosphonate (DPIP) was shown to bind lanthanide cations with a stronger affinity than diethyl (2-oxopropyl)phosphonate (OPP).^{4c} Interestingly, the chelating motif of DPIP can be recognized in the (bi)cyclic framework **D** (Fig. 1) which could be accessible via the [4+2] cycloaddition strategy (Diels–Alder reaction, DA and hetero-Diels–Alder reaction, HDA) that we elaborated a few years ago for the preparation of various aminophosphonic derivatives.⁵

Although the DA/HDA reactions of carboxylated dienes are extensively studied to generate functionalized six-membered (hetero)cyclic compounds, with high regio- and stereocontrol,⁶ similar reactions of the phosphonated dienes are much less developed. Indeed, the phosphonate substituent interacts weakly with neutral organic patterns, such as vinyl and butadienyl moieties, and thus brings about a poor activation for [4+2] cycloadditions.⁷ A way to



Figure 1. Diethyl phosphonate bidentate chelating agents.

overcome the low reactivity of phosphono dienes (dienophiles) in the DA/HDA reactions is to allow them to react with highly reactive dienophiles (dienes). We successfully illustrated this strategy in the case of diethyl 1-phopshono-1,3-butadiene (1) which reacts well with tetracyanoethylene,^{5b} acylnitroso derivatives,^{5c} and dialkyl azodicarboxylates.^{5e} Cycloadditions with cyclic partners have not been explored; however such configurationally cis-fixed dienophiles should be more reactive and should lead in principle to cis-fused bicycles with the phosphonate group in the relative *endo*-configuration, endowing the molecules with a cage shape.

In this Letter, we report on the DA and HDA reactions of **1** with *N*-maleimide derivatives or cyclic azo compounds, respectively. The resulting bicyclic cycloadducts have been fully characterized and tested for their chelating properties of bi- and trivalent metal cations in solution, using high resolution mass spectrometry (HRMS) in the electrospray ionization (ESI) mode as an analytical tool.⁸ As evidenced by X-ray crystallography data and theoretical

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investigations, the phosphonated ligands presented in this study display specific structural features that enable the metal chelation.

Results and discussion

Synthesis and characterization of the cycloadducts

Diethyl 1-phosphono-1,3-butadiene (**1**) was obtained from 1,4*trans*-dichlorobutene according to a known procedure.⁹ This diene was previously shown to react exclusively with highly activated aliphatic dienophiles and to produce low yields of cycloadducts. Recent improvement using microwave (MW) activation provided a significant increase of yields.⁵

In the present case, we tested the reactivity of a series of commercially available cyclic C=C dienophiles, activated with electron-withdrawing groups (EWG), under classical heating or MW activation in dichloroethane solution (DCE) or without solvent (neat). Equimolar amounts of diene **1** and dienophiles were used and the conversion was followed by ³¹P NMR and ¹H NMR using the dienyl protons as internal reference. 1,4-Benzoquinone and naphtho-1,4-quinone (dienophiles (a) in Scheme 1) gave only traces of cycloadducts (<10%), while maleic anhydride, maleimide, *N*-methyl-, and *N*-phenyl-maleimides reacted well to furnish the corresponding bicycles **2–5** in 42–75% isolated yields (Scheme 1).¹⁰

Pyridazine-3,6-dione and phthalazine-1,4-dione (N=N dienophiles (a) in Scheme 2) were prepared by the oxidation of diaza precursors with lead tetraacetate¹¹ and directly engaged in the reaction with **1** at low temperature. The first heterodienophile failed to give a cycloadduct (because it rapidly polymerized), but the latter could be trapped by the diene at 0 °C and led to the hetero-bicycle 6 in 38% vield after chromatography. 4-Methyl- and 4phenyl-1.2.3-triazole-3.5-diones (commercially available N=N dienophiles (b)) reacted also to furnish cycloadducts 7 and 8, respectively, in 75% and 83% yields after purification.¹² It is worth mentioning that these cycloadducts with N-N cyclic junction are preferably obtained under MW conditions, whereas the previous compounds with C-C cyclic junction are prepared upon heating the partners without a solvent. Indeed, in this case, only slight microwave activation was observed (decrease of reaction time by a factor of 2).

The novel compounds **2–8** have been unambiguously characterized using ¹H, ¹³C and ³¹P NMR, IR and HRMS data (see Supplementary data). In particular, all the *cis* relative stereochemistry of the



Scheme 1. DA reaction of diethyl 1-phosphono-1,3-butadiene (1) with cyclic dienophiles.



Scheme 2. HDA reaction of diethyl 1-phosphono-1,3-butadiene (1) with cyclic azo dienophiles.

C–C fused bicycles **2–5** has been established on the basis of typical H, H and H, P coupling constants,¹³ as illustrated for compound **4** in Figure 2. The observation of a single peak in ³¹P NMR (at 25.70 ppm) confirmed the complete selectivity of the [4+2] cyclo-addition (*endo-* and *cis-*stereoselectivity). Only one compound (from the N–N fused bicycle series) could be crystallized for single crystal X-ray analysis. The 3D structure of compound **8** (Fig. 3)¹⁴ allowed measuring the pyramidalization degree of the nitrogen atoms at the bicyclic junction, using either the Bruton parameter (*P*)¹⁵ or the Woodward parameter (*h*)¹⁶ (see Table 1).

The structure **8**, along with the *endo*- and *exo*-stereoisomers of structure 5, has been fully optimized using the B3LYP hybrid density functional as implemented in the JAGUAR 7.5 program package.¹⁷ The optimized structures of the three compounds are depicted in Figure 4. In the case of endo-5 and exo-5, the lowest energy conformer presents systematically the phosphonate group in a pseudo-axial position. For 8. no pseudo-axial/pseudo-equatorial position could be defined. Interestingly, in all the cases, the low relative energy of the different conformers around the C-P bond (within 4–5 kcal mol⁻¹) indicated a rather facile rotation around this bond. The calculated structure endo-5 in the pseudo-axial conformation is in excellent agreement with the NMR data. The cage shape of the potential ligands 5 and 8 has been estimated from their optimized structures and the X-ray data (when available). Results in Table 1 clearly indicate that 5 (C-C bicyclic junction) is less flat than 8 (N–N bicyclic junction).

ESI-HRMS study of metal complexation

Using two representative ligands, namely **5** and **8**, we have looked for a complex formation in EtOH and CH_3CN using High

	EtC EtC $2 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ $	$\mathbf{p} = \mathbf{O}_{O}$ 0_{O}	
³ J (Hz)		Dihedral angl	e (°)
H ₆ , P	22.1	H ₆ -C ₆ -C ₁ -P	131
H_1, H_6	8.8	H1-C1-C6- H6	30
H ₅ , H ₆	7.0	H ₅ -C ₅ -C ₆ - H ₆	43

Figure 2. Typical coupling constants of compound **4** and dihedral angles deduced from the related Karplus' curves.¹³



Figure 3. X-ray structure of compound 8 with displacement ellipsoids drawn at the 50% probability level.

Table 1

Shape of molecules from calculations and X-ray data



Entry ^a	Х	Angles formed by two bonds (three atoms) ($^{\circ}$)				P (°) ^b		h (Å) ^c			
		1-6-7	1-6-5	7-6-5	4-5-9	4-5-6	6-5-9	X ₆	X5	X ₆	X5
1	N (8)	120.7	111.1	107.1	125.5	113.4	108.9	21.10	12.20	0.384	0.288
2		120.27	114.85	107.66	126.43	117.10	110.02	17.23	6.45	0.345	0.208
3	C (5) ^d	113.02	116.75	104.80	114.27	115.15	104.59	25.99	25.43	0.457	0.464

^a Entry 1 = values from X-ray diffraction; entry 2-3 = values from calculations.

^b P = pyramidality calculated as $360^{\circ} - (\Sigma \text{ of } 3 \text{ angles around } X)^{\circ}$.

 c h = height of atom X from the plane formed by the three surrounding atoms.

^d Calculated **5** refers to *endo*-stereoisomer with P substituent in pseudo-axial conformation.



Figure 4. Optimized structures of compounds 5 and 8.

Resolution Mass Spectrometry (HRMS) coupled to Electrospray Ionization (ESI). ESI has been shown to be a very useful technique to study the formation of non-covalent complexes between organic ligands and metallic cations.⁸ This technique also allows for the stoichiometric determination of the complexes formed in the solution that is the number of ligands surrounding the metallic core. It should be mentioned that a careful tuning of the ESI parameters is required to avoid, on the one hand, the destruction of the complexes during the ionization process and the transfer into the gas phase and, on the other hand, the detection of adducts not present in the solution but formed in the ion source. To ensure the detection of stable complexes formed in the solution, a systematic variation of the most important ESI parameters was performed with 5 and: (i) La(NO₃)₃ in CH₃CN and EtOH and (ii) Mn(ClO₄)₂ in CH₃CN. The tube lens voltage varied between 20 and 160 V, capillary temperature between 125 and 325 °C and capillary voltage between 20 and 160 V. Moreover, fragmentation in the source was also tested between 0 and 100 (maximum value) a relative unit to check the stability of the complexes. Even at the highest value of source CID, the L₁:M and L₂:M complexes are the dominant species. This clearly shows the inherent stability of these complexes and the fact that they are not adducts formed during the ESI process.

To investigate complex formation in the solution, we have added defined quantities of metallic salts (either nitrate or perchlorate salts) to a solution of **5** and **8** in EtOH or CH₃CN. Different cations have been screened, either divalent (Mg^{2+} , Ca^{2+} , Mn^{2+} and Zn^{2+}) or trivalent (La^{3+} , Ce^{3+} , Pr^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Er^{3+} , Tm^{3+} and

Relative abundance of complexes formed with 5 in EtOH	Table 2	
	Relative abundance of complexes formed with 5	in EtOH

Cations	$[LM(ClO_4)]^+$	[LM(ClO ₄)·EtOH] ⁺	$[L_2M(ClO_4)]^+$	$%L_2M^a$
Zn ²⁺	100	18	30	20.3
^b Mn ²⁺	100	16	31	21.1
Ca ²⁺	100	19	73	38.0
Mg ²⁺	100	80	74	29.1
Cations	$[LM(NO_3)_2]^+$	$[LM(NO_3)_2 \cdot EtOH]^+$	$[L_2M(NO_3)_2]^+$	%L ₂ M ^c
Lu ³⁺	100	65	44	21.0
Tm ³⁺	100	60	30	15.8
Er ³⁺	100	66	45	21.3
Gd ³⁺	49	33	100	54.9
Eu ³⁺	100	51	92	37.7
Sm ³⁺	100	50	92	38.0
Pr ³⁺	100	37	28	16.9
Ce ³⁺	36	13	100	67.1
La ³⁺	15	5	100	83.3
3				

 a % L_2M = [L_2M(ClO_4)]^*/([LM(ClO_4)]^* + [LM(ClO_4)-EtOH]^* + [L_2M(ClO_4)]^*) \times 100. b [LH*] = 25.

^c $^{\times}$ $L_2M = [L_2M(NO_3)_2]^+/([LM(NO_3)_2]^+ + [LM(NO_3)_2 \cdot EtOH]^+ + [L_2M(NO_3)_2]^+) \times 100.$

 Table 3

 Relative abundance of complexes formed with 8 in EtOH

Cations	$[LM(ClO_4)]^+$	$[LM(ClO_4) \cdot EtOH]^+$	$\left[L_2M(ClO_4)\right]^+$	$%L_2M^a$
Zn ²⁺	100	16	13	10.1
^b Mn ²⁺	100	52	13	7.9
Ca ²⁺	93	100	63	24.6
^c Mg ²⁺	100	87	27	12.6
Cations	$[LM(NO_3)_2]^+$	$[LM(NO_3)_2 \cdot EtOH]^+$	$[L_2M(NO_3)_2]^*$	$%L_2M^a$
Lu ³⁺	100	86	13	6.5
Tm ³⁺	100	71	9	5.0
Er ³⁺	100	72	6	3.4
Gd ³⁺	100	86	79	29.8
Eu ³⁺	100	73	27	13.5
Sm ³⁺	100	71	24	12.3
Pr ³⁺	100	45	22	13.2
Ce ³⁺	83	37	100	45.4
La ³⁺	31	13	100	69.4

^a See Table 2.

^b $[LMn_2(ClO_4)_3 \cdot EtOH]^+ = 77.$

^c $[LH]^+ = 10$.

Lu³⁺). Tables 2 and 3 gather the results obtained for the two ligands tested in EtOH. Similar results are obtained in CH₃CN (see Supplementary data).¹⁸

In all cases, only single charged complexes were detected due to the presence of one perchlorate counter-anion in the case of divalent cations or two nitrate anions for the trivalent lanthanides. Species with a residual solvent molecule were observed for the L₁:M complexes. This solvent molecule is certainly present to fulfill the coordination sphere of the metallic cation. Upon increasing the tube lens voltage we observed the disappearance of these species in favor of the corresponding L₁:M complexes. Interestingly, the predominant species for all tested cations is a monochelated complex (i.e., L₁:M) except for the trivalent cations La³⁺ and Ce³⁺ for which a bischelated complex is observed (i.e., L2:M). Although a detailed structural investigation would be required to explain this observation, it is likely that the size of the metallic core plays an important role. Indeed, the ionic radius for La³⁺ and Ce³⁺ is somewhat larger $(\sim 120 \text{ pm})$ than that of the other metals $(\sim 110 \text{ pm})$. The same observation is made when comparing complexes with Ca²⁺ $(\sim 110 \text{ pm})$ to the other divalent complexes $(\sim 90 \text{ pm})$. The larger the metal cation, the easier it is to add a second ligand to the coordination sphere. The nature of the ligand should also play a role. since globally, the percentages of L₂:M complexes versus L₁:M are systematically higher for 5 as compared to 8.

We have performed competition experiments considering either two ligands versus one given cation or two cations versus one given ligand. First, a mixture of **5** (0.25 mM) and **8** (0.25 mM) in EtOH with 5 equiv of Mn^{2+} or Zn^{2+} was analyzed as above (see Supplementary data). The selectivity of ligands toward each metal is measured by the ratio of respective complexes detected by ESI-HRMS. We found for Mn^{2+} and Zn^{2+} , a selectivity of 7.4 and 5.9, respectively, in favor of ligand **5**, meaning that the cage shape allowed better complexation properties. Ligand **5** (0.5 mM) in EtOH with a mixture of Eu³⁺ (2.5 equiv) and La³⁺ (2.5 equiv) was studied; the selectivity of metals toward the best ligand **5** was 27.5 in favor of Eu³⁺. This suggests that the hardest metal is complexed, as expected in the case of 0,0-bidentate ligands.

Conclusion

Using the stereoselective (H)DA strategy, we have obtained new phosphonated ligands that are structurally related to DPIP (see Fig. 1). Their bicyclic framework orientates adequately the P=O motif (from diene **1**) and the neighboring C=O function (from dienophiles) to enable metal complexation.

As evidenced by ESI-HRMS, both ligands **5** and **8** are able to make L_1 :M and L_2 :M complexes with a large variety of di- and tri-valent cations. However **5** (bicycle with C–C junction) appeared 6- to 7-fold more powerful than **8** (bicycle with N–N junction), and selective toward hard M⁺³ cations.

Work is in progress for the development of N-functionalized derivatives of **3** featuring additional chelating functions.

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Supplementary data

Supplementary data (synthetic protocols for the preparation of **2**, **3**, **4**, **6** and **7** and related spectroscopic analyses, X-ray data of **8**, ESI-HRMS spectra of representative complexes of *endo*-**5**, *exo*-**5** and

8, and computational details) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.116.

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- 0. Protocol for the synthesis of **5** and spectroscopic characterization (see Supplementary data for compounds **2**, **3** and **4**). A neat mixture of diene **1** (0.200 g, 1.052 mmol, 1 equiv) and *N*-phenylmaleimide (0.182 g, 1.052 mmol, 1 equiv) is stirred at 120 °C for 1 h. The reaction is followed by TLC and ³¹P NMR. The oily reaction mixture is directly purified by column chromatography (silica gel: ethyl acetate) to afford a white solid (0.216 g, 56%). *R*_f = 0.2 (ethyl acetate); mp = 73.3-73.° °C; ¹H NMR (500 MHz, CDCl₃): *δ* 7.44 (ddd, ³*J*_{H,H} = 7.5 Hz and ⁴*J*_{H,H} = ⁵*J*_{H,H} = 2.3 Hz, Ph, 2H), 7.37-7.35 (m, Ph, 3H), 6.16-6.15 (m, CH=CH, 1H), 6.01 (dd, ³*J*_{H,H} = 9.7 Hz and ³*J*_{H,H} = 9.4 Hz, CH=CH, 1H), 4.18-4.09 (m, PO(OCH₂CH₃)₂, 2H), 4.10-4.01 (m, PO(OCH₂CH₃)₂, 2H), 3.35 (dtd, ³*J*_{H,P} = 26.2 Hz, ³*J*_{H,H} = 8.6 Hz and ⁴*J*_{H,H} = 3.5 Hz, 1H), 3.27 (td, ³*J*_{H,H} = 9.2, HZ, 3H, H, 9.2 and 3.8 Hz, CH, 1H), 3.20 (dtd, ²*J*_{H,P} = 22.0 Hz, ³*J*_{H,H} = 6.8 Hz and ⁴*J*_{H,H} = 2.7 Hz, CH, 1H), 2.80-2.76 (m, ²*J*_{H,H} = 7.1, Hz, CH₂, 1H), 2.55-2.51 (m, CH₂, 1H), 1.24 (td, ³*J*_{H,H} = 7.0 Hz and ⁴*J*_{H,P} = 3.0 Hz, PO(OCH₂CH₃)₂, 3H), 1.21 (td, ³*J*_{H,H} = 7.0 Hz and ⁴*J*_{H,P} = 3.0 Hz, C=O), 132.18 (s, Ph), 130.46 (d, ³*J*_{C,P} = 7.2 Hz, C=C), 128.99 (s, Ph), 128.43 (s, Ph), 126.55 (s, Ph), 123.23 (d, ²*J*_{C,P} = 7.2 Hz, PO(OCH₂CH₃)₂), 40.66 (d, ³*J*_{C,P} = 5.3 Hz, CH), 34.06 (d, ¹*J*_{C,P} = 4.2 Hz, PO(OCH₂CH₃)₂); ³¹PNMR (121 MHz, CDCl₃): *δ* 25.50; IR: v 3657-3327 (w), 2984 (m), 1782 (C=O, w), 1713 (C=O, s), 1597 (m), 1498 (s), 1442 (w), 1383 (s), 1244 (P=O, s), 1196 (s), 1164 (s), 1049 (s), 1020 (P-O, s), 960 (P-O, s), 750 (s), 692 (s), 659 (s) cm⁻¹; HRMS: *m/z* calcd for C₁₈H₂₁No₅P: 362.1157. Found: 362.1140.
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- 12. Protocol for the synthesis of **8** and spectroscopic characterization (see Supplementary data for compounds **6** and **7**). A solution of 4-phenyl-4H-1,2,4-triazole-3,5-dione (0.46 g, 2.63 mmol, 1 equiv), diene **1** (0.50 g, 2.63 mmol, 1 equiv), and dichloroethane (3.5 mL) is stirred in a microwave oven under 500 W irradiation at 120 °C for 30 min. The reaction mixture is then concentrated under vacuum and purified by column chromatography (silica gel: toluene, then ethyl acetate) to afford a pale yellow gummy solid (0.794 g, 83%). $R_f = 0.4$ (ethyl acetate); mp = 67.5-71.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.54–7.42 (m, Ph, 5H), 6.11 (dtt, ${}^{3}J_{H,H} = 10.3$ Hz, ${}^{3}J_{H,H} = {}^{4}J_{H,H} = 5.2$ Hz and ${}^{4}J_{H,P} = {}^{4}J_{H,H} = 2.2$ Hz, CH=CH, 1H), 6.09–6.03 (m, CH=CH, 1H), 4.97 (dddt, ${}^{2}J_{H,P} = 14.7$ Hz, ${}^{3}J_{H,H} = 4.8$ Hz, ${}^{4}J_{H,H} = 3.1$ Hz and ${}^{5}J_{H,H} = 1.5$ Hz, 1H), 4.29 (dddd, ${}^{2}J_{H,H} = 16.9$ Hz, ${}^{3}J_{H,H} = 6.7$ Hz, ${}^{5}J_{H,P} = 3.7$ Hz and ${}^{4}J_{H,H} = 5.7$ Hz and ${}^{4}J_{H,H} = 5^{4}J_{H,H} = 5.2$ Hz and ${}^{4}J_{H,H} = 5^{4}J_{H,H} = 2.4$ Hz, (H2, 1H), 1.28 (t, ${}^{3}J_{H,H} = 1.5$ Hz, 20 (cddd, ${}^{2}J_{H,H} = 16.8$ Hz, ${}^{3}J_{H,H} = 6.7$ Hz and ${}^{4}J_{H,H} = 5.7$ Hz, 20 (cddz, 2.1), 128.28 (s, Ph), 127.30 (s, Ph), 124.75

(s, Ph), 122.03 (d, ${}^{3}_{J_{CP}}$ = 9.8 Hz, C=C), 118.36 (d, ${}^{2}_{J_{CP}}$ = 4.1 Hz, C=C), 62.51 (d, ${}^{2}_{J_{CP}}$ = 6.7 Hz, PO(OCH₂CH₃)₂), 62.30 (d, ${}^{2}_{J_{CP}}$ = 6.1 Hz, PO(OCH₂CH₃)₂), 50.59 (d, ${}^{1}_{J_{CP}}$ = 139.2 Hz, CH), 43.43 (s, CH₂), 15.65 (d, ${}^{3}_{J_{CP}}$ = 5.6 Hz, PO(OCH₂CH₃)₂), 15.57 (d, ${}^{3}_{J_{CP}}$ = 5.8 Hz, PO(OCH₂CH₃)₂); 31 P NMR (121 MHz, CDCl₃): δ 18.16; IR: ν 3566 (w), 3485 (w), 2982 (w), 2908 (w), 1776 (C=O, s), 1709 (C=O, s), 1598 (w), 1502 (s), 1416 (s), 1292 (m), 1252 (P=O, s), 1018 (P-O, s), 9.968 (P-O, s), 766 (s) cm⁻¹; HRMS: *m/z* calcd for C₁₆H₂₀O₅PNa: 388.1042. Found: 388.1038.

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- 14. The details of X-ray analysis are given in Supplementary data. The structure has been deposited in the Cambridge crystallography Database with the number CCDC815319.
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- 17. JAGUAR, version 7.5, Schrödinger, LLC, New York, NY, 2008. See Supplementary data for the detailed methods and results of calculations.
- 18. ESI-HRMS analyses were performed on a LTQ-Orbitrap XL hybrid mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). Data were acquired in positive ion mode using full-scan MS with a mass range of 200-2000 m/z. The orbitrap operated at 30,000 resolution (FWHM definition). All experimental data were acquired using daily external calibration prior to data acquisition. Appropriate tuning of the electrospray ion source was done to ensure the preservation of the complexes formed in the solution but to avoid the detection of adducts formed during the ESI process. The following electrospray inlet conditions were applied: flow rate, 200 μ L min⁻¹; spray voltage, 5 kV; sheath gas (N2) flow rate, 20 a.u.; auxiliary gas (N2) flow rate; capillary temperature, 275 °C; capillary voltage, 45 V; tube lens, 80 V. Salts purchased from Aldrich, Alpha or Acros were of the highest quality available and vacuum dried at room temperature on P₂O₅ prior to use. Acetonitrile from Biolsolve (LC-MS grade) and ethanol from Fisher (absolute) were used for MS experiments. For all experiments, the concentration of the ligand was ca.0.5 mM with 5 equiv of cation. For competition experiments between two ligands and one metallic cation, concentration of 0.25 mM of each ligand was used with 5 equiv of cation. 2.5 equiv of each cation with 0.5 mM of ligand was used for the competition experiments for one ligand between two cations.