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Reactions of dizincocene with sterically demanding bis(iminodi(phenyl)phosphorano)methanes†

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Reactions of 

\[ \text{Cp}^* \text{Zn}_2 \] 

with sterically demanding bis(iminodi-phenylphosphorano)methanes \( \text{LH} \) (\( \text{LH} = \text{CH}_2(\text{Ph}_2\text{P}=\text{NR})_2 \) \( \text{R} = \text{Ph} \) \( \text{L}^1\text{H} \), \( \text{SiMe}_3 \) \( \text{L}^2\text{H} \), \( 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3 \) (Dipp) \( \text{L}^3\text{H} \)) at ambient temperature occurred with elimination of \( \text{Cp}^*\text{H} \) and subsequent formation of the homoletic complex \( \text{L}_2\text{Zn}_2 \) \( 1 \) and the heteroleptic complexes \( \text{LZnZnCp}^* \) (\( \text{L} = \text{L}^1 \) \( 2 \), \( \text{L}^2 \) \( 3 \), \( \text{L}^3 \) \( 4 \)). \( 3 \) is the first structurally characterized heteroleptic organozinc complex with the zinc atoms in the formal oxidation state +1.

The synthesis of decamethyldizincocene \( \text{Cp}^*\text{Zn}_2 \), the first stable molecular compound containing a direct \( \text{Zn} \)-\( \text{Zn} \) bond with the \( \text{Zn} \) atoms in the formal oxidation state +1, by Carmona et al. in 2004 has very much intensified research activities on group 2 and 12 metal complexes containing metal-metal bonds. Since then, a large number of \( \text{Zn}(\text{I}) \) activities on group 2 and 12 metal complexes containing Mg–Mg \( 4 \) bonds have been synthesized, most of them by Wurtz-analogous coupling reaction of the corresponding halide-substituted compounds \( \text{RMX} \). In addition, the nature of the \( \text{Zn} \)-\( \text{Zn} \) bond has been theoretically investigated in detail.5

The \( \text{Zn} \)-\( \text{Zn} \) bonded complexes are typically stabilized by sterically bulky (often chelating) organic ligands. While these ligands have been shown in the past to be extremely useful for the stabilization of metal-metal bonded complexes, they rather inhibit studies concerning the chemical reactivity of these complexes due to the effective shielding of the metal centers. As a consequence, only a handful of reports concerning the chemical reactivity of such compounds is available. Carmona et al. already mentioned in their initial publication on reactions of \( \text{Cp}^*\text{Zn}_2 \), which typically proceeded with disproportionation and formation of elemental zinc and the corresponding \( \text{Zn}(\text{I}) \) complexes. This reaction pattern turned out to be the most prominent pathway for \( \text{Zn}(\text{I}) \) complexes until we reported on the reaction of \( \text{Cp}^*\text{Zn}_2 \) with the Lewis base 4-dimethylaminopyridine (dmap), yielding \( \text{Cp}^*\text{Zn} \)–\( \text{Zn} \) (dmap)\( \text{Cp}^* \), the first Lewis acid–base adduct of dizincocene.6 In addition, the reaction with \( \text{N} \)-\( \text{H} \) acidic \([\{(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\text{N} \text{(Me)C}_2\text{CH}\}_\text{H} \) (MesnaacnacH) was found to proceed with preservation of the \( \text{Zn} \)-\( \text{Zn} \) bond. Protonation of the \( \text{Cp}^* \) substituent yielded the \( \text{Zn}(\text{I}) \) complex MesnaacnacZn2.7 Recently, \([\text{Zn}_2\text{(dmap)}_6]\text{[Al(O(CF}_3)_3\text{J}_2 \) containing the first base-stabilized \([\text{Zn}_2]^{2+} \) dication was synthesized by reaction of \( \text{Cp}^*\text{Zn}_2 \) with \([\text{H(OEt}_2]_2\text{Al(O(CF}_3)_3\text{J}_2 \).8 In contrast, the reaction of Dipp–BIAN\( \text{Zn}_2 \) with \( \text{C} \)-\( \text{H} \) acidic phenylacetylene rather occurred with \( \text{H} \)-elimination and formation of a binuclear acetylene bridged \( \text{Zn}(\text{II}) \) complex (redox reaction) than with protonation of the Dipp–BIAN substituent.9

In order to elucidate the general applicability of protonation reactions for the synthesis of \( \text{Zn} \)-\( \text{Zn} \) bonded complexes, we studied reactions of \( \text{Cp}^*\text{Zn}_2 \) with \( \text{H} \)-acidic bis(iminophosphorano)methanes \( \text{H}_2\text{C} \) (\( \text{Ph}_2\text{P} \)NR)\( 2 \), which are easily accessible by the Staudinger reaction. These were expected to be promising reagents since reactions with metal alkyls such as \( \text{LiMe} \), \( \text{AlMe}_3 \) and \( \text{ZnMe}_2 \) have previously been shown to proceed with alkane elimination and formation of the corresponding bis(iminodi(phenyl)phosphorano)methane complexes, exhibiting a singly deprotonated, monoanionic ligand.10 In addition, these ligands are able to bind also as neutral and dianionic ligands toward a large variety of main group and transition metals as well as lanthanides.11 Herein, we report on our results obtained from reactions of \( \text{Cp}^*\text{Zn}_2 \) with three bis(iminodi(phenyl)phosphorano)methanes.

Reactions of \( \text{Cp}^*\text{Zn}_2 \) with two equivalents of \( \text{CH}_2(\text{Ph}_2\text{P}=\text{NR})_2 \) \( \text{R} = \text{Ph} \) \( \text{L}^1\text{H} \), \( \text{SiMe}_3 \) \( \text{L}^2\text{H} \), \( 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3 \) (Dipp) \( \text{L}^3\text{H} \) yielded the expected homoletic complex \( \text{Zn}_2\text{L}_2 \) only in case of the sterically less demanding \( \text{Ph} \)-substituted substituent \( \text{L}^1\text{H} \), whereas heteroleptic complexes \( \text{LZnZnCp}^* \) (\( \text{L}^2 \) \( 2 \), \( \text{L}^3 \) \( 3 \)) were formed with the sterically

Scheme 1

**Synthesis of 1–4.**

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† Electronic supplementary information (ESI) available: Experimental details and characterization of 1–4 including single crystal structure (1, 3) as well as computational details on homo- and heteroleptic complexes are given. CCDC 785388 (1) and 780366 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc02859b

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[^3]: Electronic supplementary information (ESI) available: Experimental details and characterization of 1–4 including single crystal structure (1, 3) as well as computational details on homo- and heteroleptic complexes are given. CCDC 785388 (1) and 780366 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc02859b

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more demanding bis(iminodi(phenyl)phosphorano)methanes, respectively (Scheme 1).

2 and 3 as well as L′1Zn–ZnCp* 4 were also obtained by reactions of equimolar amounts of Cp*2Zn2 and CH3(Ph2P–NR)2. The formation of H2 (redox reaction) or elemental zinc (disproportionation reaction) was not observed in any case. 1–4 are soluble in organic solvents such as toluene and THF, respectively. 1H and 13C NMR spectra of both complexes show the resonances due to the organic groups of the bis(iminodi(phenyl)phosphorano)methane (1) and the Cp* substituent in a 1 : 1 ratio (2, 3, 4). Signals at 3.28 (2) and 3.71 ppm (3) in the 1H NMR spectra (C6D6) due to the presence of a methanide unit in the backbone clearly reveal the monoanionic character of the ligand, whereas no resonance of the C–H moiety was observed for 1 and 4. A single resonance of the Cp* substituent (2.35 2, 2.07 3, 1.91 4 ppm) indicates η3-bonded Cp* groups in solution. In situ 31P NMR spectroscopy showed the quantitative conversion of the free ligand L–H into the new complexes 1–4. The 31P NMR spectra of the isolated complexes each exhibit one sharp singlet, indicating two equivalent phosphorus atoms. The resonances (22.3 1, 24.4 2, 27.4 3, 21.9 4 ppm) are shifted downfield compared to the free ligands (L–H). The IR spectra of 1–4 show strong absorptions due to the P–N moiety between 1250 and 1260 cm−1. Heating of 1–4 in sealed capillaries yielded greyish solids (135 °C 1, 110 °C 2, 150 °C 3, 105 °C 4) due to disproportionation reactions with subsequent formation of elemental Zn.

Single crystals of 1 and 3 suitable for X-ray structure determinations were obtained from solutions in toluene (1) and C6D6 (3), respectively (Fig. 1 and 2).

1 and 3 are both monomeric complexes. 1 contains two threefold-coordinated Zn atoms in an almost ideal trigonal-planar coordination sphere whereas the Zn atoms in the heteroleptic complex 3 show different coordination modes. Zn1 atom adopts a trigonal-planar coordination sphere (sum of the bond angles 359.8(4)°) whereas Zn2 is almost linearly coordinated (Zn1–Zn2–Cp*centr. bond angle 175.4°). The six-membered Cp*2N2Zn metallacycles in 1 and 3 adopt distorted boat conformations as was observed for the monomeric Zn(n)

complex L′1ZnMe. The Zn–N bond lengths of 1 (N1–Zn1 2.042(2), N2–Zn1 2.075(2) Å) are comparable to those observed for L′1ZnMe (N1–Zn1 2.083(3), N2–Zn1 2.042(3) Å), whereas those of 3 (N1–Zn1 1.989(1), N2–Zn1 1.979(1) Å) are significantly shorter, resulting from the reduced steric demand of the Cp* substituent. The P–N and P–C bond lengths in 1–4 are reduced in size for clarity except for C1.

The endocyclic bond angles within the metallacycles of 1 (N1–Zn1–N2 98.82(1), C1–P1–N2 106.14(1), C1–P2–N1 106.96(1), N1–Zn1–P2 104.13(1), P1–C1–P2 122.20(1)°) are comparable to those of L′1ZnMe (N1–Zn1–N2 99.4(1), C1–P1–N2 106.8(2), C1–P2–N1 108.9(2), Zn1–N1–P1 97.8(2), Zn1–N2–P1 99.5(2), P1–C1–P2 120.1(2)°), whereas those of 3 (N1–Zn1–N2 107.47(4), P1–C1–P2 110.43(6), C1–P2–N2 114.56(6), Zn1–N1–P1 127.25(6), Zn1–N2–P2 118.01(6), C1–P1–C2 128.02(8)°) differ significantly. However, a CCDC structural database search revealed that these bond angles typically span a wide range and that the endocyclic angles observed for 1 and 3 are within the typical range previously described for metal complexes of bis(iminodi(phenyl)phosphorano)methanides.13 The Zn–Zn bond (2.3272(1) Å) is only slightly elongated compared to that observed for Cp*2Zn2 (2.305(3) Å),1 but shorter than those observed in 1 (2.3490(1) Å) as well as in the homoleptic β-diketiminato-stabilized Zn(n) complexes Mesnacnac2Zn2 (2.3813(8) Å)15 and Dippnacnac2Zn2 (2.3586(7) Å),13 respectively. These findings clearly reflect the influence of the increasing coordination number at the Zn atom due to the use of an N,N′-chelating ligand. The Zn–C bond length toward the η3-coordinated Cp* substituent (Zn2–Cp*centr. 1.944 Å) is significantly shorter compared to those observed in Cp*2Zn2 (2.04 Å) and dnapZn2Cp*2 (2.033 Å), respectively.

Fig. 1 Solid state structure of 1; H atoms are omitted for clarity except for that on C1.

Fig. 2 Solid state structure of 3; H atoms are omitted and C atoms are reduced in size for clarity except for C1.
DFT calculations (B3LYP/SVP) of homoleptic L\textsubscript{1} ZnZnL\textsubscript{1} (L\textsubscript{1} 1, 2 \textsuperscript{3}) and heteroleptic complexes L\textsubscript{1} ZnZnCp\textsuperscript{*} (L\textsubscript{1} 4, L\textsubscript{2} 2, L\textsubscript{3} 3) were performed to investigate the influence of steric bulk of the substituents on the Zn–Zn bond lengths. The structural parameters of the calculated structures of 1 and 3 such as the Zn–Zn (2.396 1, 2.381 Å 3) bond length and the distances within the CP\textsubscript{2}N\textsubscript{2}Zn ring (Zn–N 2.099, 2.102; P–N 1.639, 1.646; P–C 1.722, 1.731 Å) agree very well with the experimental values. The Zn–Zn bond lengths in the heteroleptic complexes L\textsubscript{1} ZnZnCp\textsuperscript{*} only slightly increase with increasing steric bulk of the substituents (L\textsubscript{1} 2.369 4, L\textsubscript{2} 2.376 2, L\textsubscript{3} 2.381 Å 3), whereas those of the homoleptic complexes differ significantly (L\textsubscript{1} 2.396 1, L\textsubscript{2} 2.438 Å 5).\textsuperscript{14} The Zn atoms in 3 carry different partial charges as was expected due to the different coordination sphere. The Zn atom in 2–4 bound to the Cp\textsuperscript{*} substituent is less electropositive (0.55 (3), 0.57 (3)), compared to the Zn atom bound to two electronegative N atoms (0.79 (2), 0.76 (3, 4)). Comparable findings have been previously observed for the dmap-stabilized dizincocene Cp\textsuperscript{*}(dmap)\textsubscript{2}Zn–ZnCp\textsuperscript{*}.\textsuperscript{6}

Cp\textsuperscript{*}Zn\textsubscript{2}\textsuperscript{14} is a promising starting reagent for the synthesis of novel low-valent organozinc complexes by reaction with organic substituents containing acidic H atoms including a C–H moiety as shown here, yielding so far unknown base-free, heteroleptic Zn(i) complexes of the type L\textsubscript{1} Zn–ZnCp\textsuperscript{*}.\textsuperscript{15} Schulz is grateful for financial support by the DFG and L.D. acknowledges the Foundation for Polish Science for the Kolumb fellowship.

Notes and references
12 Experimental details are given in the ESL.\textsuperscript{14} In situ NMR studies clearly showed the formation of Cp\textsuperscript{*}H during the reaction.
14 The structure of the homoleptic complex L\textsubscript{1} Zn\textsubscript{2} couldn’t be calculated within these studies due to limited computing time.