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

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Reactions of Cp* 2Zn2 with sterically demanding bis(iminodi(phenyl)phosphorano)methanes LH (LH = CH2(Ph2P=NR)2 (R = Ph L1H, SiMe3 L2H, 2,6-i-Pr2C6H3 (Dipp) L3H) at ambient temperature occurred with elimination of Cp*H and subsequent formation of the homoleptic L3Zn 2 and the heteroleptic complexes L 2Zn 2Cp* (L = L12, L23, L14). 3 is the first structurally characterized heteroleptic organozinc complex with the zinc atoms in the formal oxidation state +1.

The synthesis of deamethyldizincocene Cp* 2Zn2, the first stable molecular compound containing a direct Zn–Zn bond with the 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 Zn(i) complexes and Mg(i) complexes containing Mg–Mg bonds have been synthesized, mostly of them by Wurtz-analogous coupling reaction of the corresponding halide-substituted compounds RX. In addition, the nature of the Zn–Zn bond has been theoretically investigated in detail.5

The Zn–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 Cp* 2Zn2, which typically proceeded with disproportionation and formation of elemental zinc and the corresponding Zn(n) complexes. This reaction pattern turned out to be the most prominent pathway for Zn(n) complexes until we reported on the reaction of Cp* 2Zn2 with the Lewis base 4-dimethylaminopyridine (dmap), yielding Cp*Zn–Zn(dmap)2Cp*, the first Lewis acid–base adduct of dizincocene.6 In addition, the reaction with N–H acidic [(2,4,6-Me3C6H2)N(Me)C]2CH]H (MesnacnacH) was found to proceed with preservation of the Zn–Zn bond. Protonation of the Cp* substituent yielded the Zn(i) complex MesnacnacZn2. Recently, [Zn2(dmap)3][Al(O(CF3)3)3]2 containing the first base-stabilized [Zn3]+ cation was synthesized by reaction of Cp* 2Zn2 with [H(OEt2)2][Al(O(CF3)3)3]. In contrast, the reaction of Dipp–BIAN2Zn2 with C–H acidic phenylacetylene rather occurred with H2-elimination and formation of a binuclear acetylene bridged Zn(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 Zn–Zn bonded complexes, we studied reactions of Cp* 2Zn2 with H-acidic bis(iminophosphorano)methanes H2C(P(Ph2)NR)2, which are easily accessible by the Staudinger reaction. These were expected to be promising reagents since reactions with metal alkyls such as LiMe, AlMe3 and ZnMe2 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 Cp* 2Zn2 with three bis(iminodi(phenyl)phosphorano)methanes.

Reactions of Cp* 2Zn2 with two equivalents of CH2(Ph2P=NR)2 (R = Ph L1H, SiMe3 L2H, 2,6-i-Pr2C6H3 (Dipp) L3H) yielded the expected homoleptic complex Zn2L2 only in case of the sterically less demanding Ph-substituted substituent L1H, whereas heteroleptic complexes L 2Zn 2Cp* (L12, L23, L14) were formed with the sterically

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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

Scheme 1  Synthesis of 1–4.
more demanding bis(iminodi(phenyl)phosphorano)methanes, respectively (Scheme 1). \(^\text{12}\)

2 and 3 as well as \(\text{L}^1\text{Zn–ZnCp}^*\) 4 were also obtained by reactions of equimolar amounts of \(\text{Cp}^*\text{Zn}_2\) and \(\text{CH}_3\text{(Ph}_2\text{P=NR)}_2\). The formation of \(\text{H}_2\) (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. \(^\text{1}^\text{H}\) and \(^{13}\text{C}\) NMR spectra of both complexes show the resonances due to the organic groups of the bis(iminodi(phenyl)phosphorano)methane (1) and the \(\text{Cp}^*\) substituent in a 1 : 1 ratio (2, 3, 4). Signals at 3.28 (2) and 3.71 ppm (3) in the \(^1\text{H}\) NMR spectra (\(\text{C}^6\text{D}_6\)) due to the presence of a methanide unit in the backbone clearly reveal the monoanionic character of the ligand, whereas no 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 the monoanionic character of the ligand, whereas no resonance of the C–H moiety was observed for 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 \(\text{Cp}^*\) substituent (2.35 2, 2.07 3, 1.91 4 ppm) indicates \(\eta^3\)-bonded \(\text{Cp}^*\) groups in solution. In situ \(^{31}\text{P}\) NMR spectroscopy showed the quantitative conversion of the free ligand \(\text{L–H}\) into the new complexes 1–4. The \(^{31}\text{P}\) 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 \(\text{P}==\text{N}\) moiety between 1250 and 1260 cm\(^{-1}\). Heating of 1–4 in sealed capillaries yielded greyish solids (135 \(\mp 1\), 110 \(\mp 2\), 150 \(\mp 3\), 105 \(\mp 4\) 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 \(\text{C}^6\text{D}_6\) (3), respectively (Fig. 1 and 2).

1 and 3 are both mononuclear 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)\(^{\circ}\)) whereas Zn2 is almost linearly coordinated (Zn1–Zn2–Cp*centr. bond angle 175.4\(^{\circ}\)). The six-membered \(\text{CP}_2\text{N}_2\text{Zn}\) metallacycles in 1 and 3 adopt distorted boat conformations as was observed for the mononeric \(\text{Zn(II)}\) complex \(\text{L}^1\text{ZnMe}\). The Zn–N bond lengths of 1 (N1–Zn1 2.042(2), N2–Zn1 2.075(2) \(\text{Å}\)) are comparable to those observed for \(\text{L}^1\text{ZnMe}\) (N1–Zn1 2.083(3), N2–Zn1 2.042(3) \(\text{Å}\)), whereas those of 3 (N1–Zn1 1.989(1), N2–Zn1 1.979(1) \(\text{Å}\)) are significantly shorter, resulting from the reduced steric demand of the \(\text{Cp}^*\) substituent. The P–N and P–C bond lengths in 1–4 and those of \(\text{L}^1\text{ZnMe}\) (P1–N1 1.585(3), P2–N2 1.600(3), C1–P1 1.725(1), C1–P2 1.732(1) \(\text{Å}\)) are comparable to those observed in \(\text{L}^1\text{ZnMe}\) (P1–N1 1.585(3), P2–N2 1.600(3), C1–P1 1.728(4), C1–P2 1.739(4) \(\text{Å}\)).

The endocyclic bond angles within the metallacycles of 1 (N1–Zn1–N2 98.8(2), C1–P1–N1 106.4(1), C1–P2–N2 106.9(1), Zn1–N1–P1 102.7(1), Zn1–N2–P2 103.8(1), P1–C1–P2 122.0(1)) are comparable to those of \(\text{L}^1\text{ZnMe}\) (N1–Zn1–N2 99.4(1), C1–P1–N1 106.8(2), C1–P2–N2 108.9(2), Zn1–N1–P1 97.8(2), Zn1–N2–P2 99.5(2), P1–C1–P2 120.1(2)), whereas those of 3 (N1–Zn1–N2 107.4(7), C1–P1–N1 110.4(3), C1–P2–N2 114.5(6), Zn1–N1–P1 127.25(6), Zn1–N2–P2 118.0(1), P1–C1–P2 128.0(2)) 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. \(^\text{13}\) The \(\text{Zn}–\text{Zn}\) bond (2.327(2) \(\text{Å}\)) is slightly elongated compared to that observed for \(\text{Cp}^*\text{Zn}_2\) (2.305(3) \(\text{Å}\)),\(^{1}\) but shorter than those observed in 1 (2.349(0) \(\text{Å}\)) as well as in the homoleptic \(\beta\)-diketiminato-stabilized Zn(II) complexes Mesnacnac2Zn2 (2.3813(8) \(\text{Å}\))\(^{1}\) and DippnacnacZn2 (2.3586(7) \(\text{Å}\)), respectively. These findings clearly reflect the influence of the increasing coordination number at the Zn atom due to the use of an \(\text{N}^1\text{N}^2\)-chelating ligand. The Zn–C bond length toward the \(\eta^3\)-coordinated \(\text{Cp}^*\) substituent (Zn2–\(\text{Cp}^*\)centr. 1.944 \(\text{Å}\)) is significantly shorter compared to those observed in \(\text{Cp}^*\text{Zn}_2\) (2.04 \(\text{Å}\)) and \(\text{dmap}_2\text{Zn}_2\text{Cp}^*\text{Zn}_2\text{Cp}^*\) (2.033 \(\text{Å}\)), respectively.
DFT calculations (B3LYP/SVP) of homoletic \( \text{L}^1 \, \text{ZnZnL} \) (\( L^1 \, 1, \, L^2 \)) and heteroleptic complexes \( \text{L}^1 \text{ZnZnCp}^* \) (\( L^1 \, 4, \, L^2 \, L^3 \)) were performed to investigate the influence of steric bulk of the substituents on the \( \text{Zn} \text{–Zn} \) bond lengths. The structural parameters of the calculated structures of 1 and 3 such as the \( \text{Zn} \text{–Zn} \) (2.396 \( 1, \, 2.381 \, \text{Å} \)) bond length and the distances within the \( \text{CP}^* \text{NiZn} \) ring (\( \text{Zn} \text{–N} \) 2.099, 2.102; \( \text{P} \text{–N} \) 1.639, 1.646; \( \text{P} \text{–C} \) 1.736, 1.740 \( \text{Å} \); \( \text{N} \text{–Zn} \) 2.048, 2.042; \( \text{P} \text{–N} \) 1.657, 1.653; \( \text{P} \text{–C} \) 1.722, 1.731 \( \text{Å} \)) agree very well with the experimental values.

The \( \text{Zn} \text{–Zn} \) bond lengths in the heteroleptic complexes \( \text{L}^2 \text{ZnZnCp}^* \) only slightly increase with increasing steric bulk of the substituents (\( L^2 \, 2.369, \, 2.376, \, 2.376 \text{Å} \)), whereas those of the homoletic complexes differ significantly (\( L^1 \, 2.396, \, 2.438 \text{Å} \)).

The \( \text{Zn} \) atoms in 3 carry different partial charges as was expected due to the different coordination sphere. The \( \text{Zn} \) atom in 2–4 bound to the \( \text{Cp}^* \) substituent is less electronegative (0.55 (2), 0.57 (3, 4)) compared to the \( \text{Zn} \) atom bound to two electro-negative \( \text{N} \) atoms (0.79 (2), 0.83 (3, 4)). Comparable findings were previously observed for the dmap-stabilized dizincocene \( \text{Cp}^*(\text{dmap})\text{Zn–ZnCp}^* \).

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Notes and references


12 Experimental details are given in the ESL.\(^\dagger\) In situ NMR studies clearly showed the formation of \( \text{Cp}^* \text{H} \) during the reaction.


14 The structure of the homoleptic complex \( \text{L}^1 \, \text{ZnZnCp}^* \) couldn’t be calculated within these studies due to limited computing time.