# Reactions of Dizincocene with sterically demanding Bis(iminodi(phenyl)-phosphorano)methanes

**Stephan Schulz,**[a,*] **Sebastian Gondzik,**[a] **Daniella Schuchmann,**[a] **Ulrich Westphal,**[a] **Lukasz Dobrzycki,**[a] **Roland Boese**[a] and **Sjoerd Harder**[b]

**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 complex L¹₂Zn₂ 1 and the heteroleptic complexes LZnZnCp\* (L = L² 2, L³ 3). 3 is the first structurally characterized heteroleptic organozinc complex with the zinc atoms in the formal oxidation state +1.**

The synthesis of decamethyldizincocene Cp\*₂Zn₂,[1] the first stable molecular compound containing a direct Zn-Zn bond with the Zn atoms in the formal oxidation state +1,[2] 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 [3] and Mg(I) complexes containing Mg-Mg [4] bonds have been synthesized, most of them by Wurtz-analogous coupling reaction of the corresponding halide-substituted compounds RMX. 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(II) complexes. This reaction pattern turned out to be the most prominent pathway for Zn(I) 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 Mesnacnac₂Zn₂.[7] Recently, [Zn₂(dmap)₆][Al(OC(CF₃)₃)₄]₂ containing the first base-stabilized [Zn₂]²⁺ dication, was synthesized by reaction of Cp\*₂Zn₂ with [H(OEt₂)][Al(OC(CF₃)₃)₄]₂.[8] 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)methanide 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 LZn-ZnCp\* (L² **2**, L³ **3**) were formed with the sterically more demanding bis(iminodi(phenyl)phosphorano)methanes, respectively.[12]
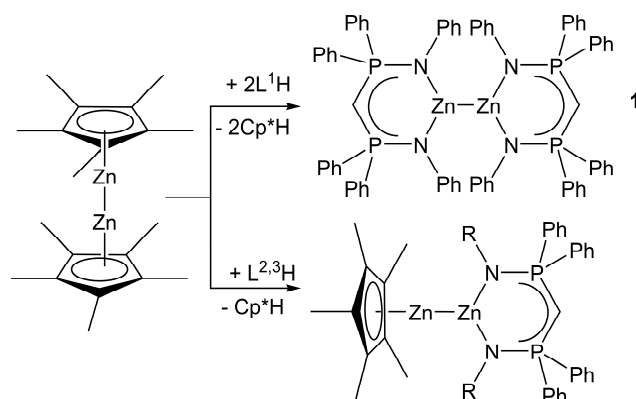


L = L¹ (R = Ph) **4**, L² (R = SiMe₃) **2**, L³ (R = 2,6-i-Pr₂-C₆H₃) **3**
**Scheme 1** Synthesis of **1 - 4**

**2** and **3** as well as L¹Zn-ZnCp\* **4** were also obtained by reactions of equimolar amounts of Cp\*₂Zn₂ and CH₂(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 $^{13}C$ 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 ($C_6D_6$) 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 ppm **3**) indicates $\eta^5$-bonded Cp* groups in solution. *In situ* $^{31}P$ NMR spectroscopy showed the quantitative conversion of the free ligand L-H into the new complexes **1 - 4**. The $^{31}P$ 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 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 $C_6D_6$ (**3**), respectively.
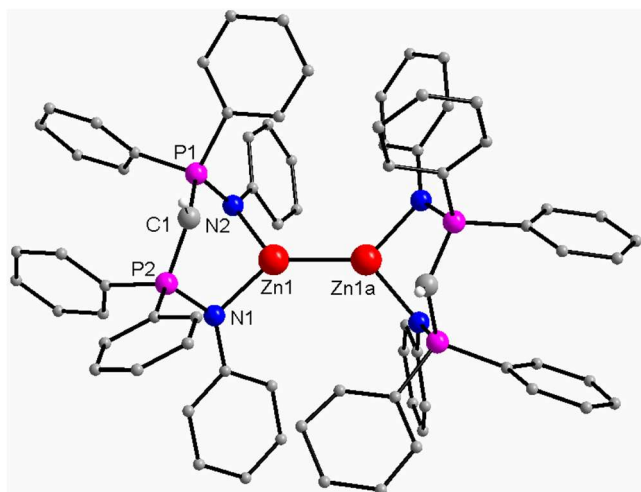


**Fig. 1** Solid state structure of **1**; H atoms are omitted for clarity except for that on C1.

**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 $CP_2N_2Zn$ metallacycles in **1** and **3** adopt distorted boat conformations as was observed for the monomeric Zn(II) 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** (P1-N2 1.615(1), P2-N1 1.615(1), C1-P1 1.725(1), C1-P2 1.732 (1) Å) and **3** (P1-N1 1.6277(11), P2-N2 1.6266(11), C1-P1 1.7018(13), C1-P2 1.7163(13) Å) are comparable to those observed in $L^1ZnMe$ (P1-N1 1.585(3), P2-N2 1.600(3), C1-P1 1.728(4), C1-P2 1.739(4) Å).
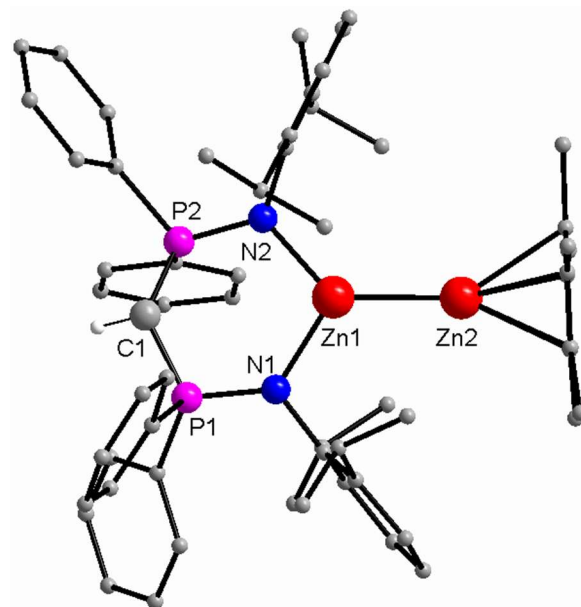


**Fig. 2** Solid state structure of **3**; H atoms are omitted and C atoms are reduced in size for clarity except for C1.

The endocyclic bond angles within the metallacycles of **1** (N1-Zn1-N2 98.82(1), C1-P1-N2 104.14(1), C1-P2-N1 106.95(1), Zn1-N2-P1 102.72(1), Zn1-N1-P2 103.87(1), P1-C1-P2 122.20(1)°) are comparable to those of $L^1ZnMe$ (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 107.47(4), C1-P1-N1 110.43(6), C1-P2-N2 114.56(6), Zn1-N1-P1 127.25(6), Zn1-N2-P2 118.01(6), P1-C1-P2 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(2) Å) is only slightly elongated compared to that observed for Cp*$_2$Zn$_2$ (2.305(3) Å),[1] but shorter than those observed in **1** (2.3490(1) Å) as well as in the homoleptic $\beta$-diketiminato-stabilized Zn(I) complexes Mesnacnac$_2$Zn$_2$ (2.3813(8) Å)[7] and Dippnacnac$_2$Zn$_2$ (2.3586(7) Å),[3] respectively. This 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 $\eta^5$-coordinated Cp* substituent (Zn2-Cp*$_{centr.}$ 1.944 Å) is significantly shorter compared to those observed in Cp*$_2$Zn$_2$ (2.04 Å) and dmap$_2$Zn$_2$Cp*$_2$ (2.033 Å), respectively.

DFT calculations (B3LYP/SVP) of homoleptic LZnZnL ($L^1$ **1**, $L^2$) and heteroleptic complexes LZnZnCp* ($L^1$ **4**, $L^2$ **2**, $L^3$ **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$_2$N$_2$Zn ring (Zn-N 2.099, 2.102; P-N 1.639, 1.646; P-C 1.736, 1.740 Å **1**; Zn-N 2.048, 2.042; P-N 1.657, 1.653; P-C 1.722, 1.731 Å **3**) agree very well with the experimental values. The Zn-Zn bond lengths in the heteroleptic complexes LZnZnCp* only slightly increase with increasing steric bulk of the substituents (L$^1$ 2.369 **4**, L$^2$ 2.376 **2**, L$^3$2.381 Å **3**), whereas those of the homoleptic complexes differ significantly (L$^1$ 2.396 **1**, L$^2$ 2.438 Å **5**).[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* substituent is less electropositive (0.55 (**2**), 0.57 (**3**, **4**)) 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*(dmap)$_2$Zn-ZnCp*.[6]

**Conclusion.** Cp*$_2$Zn$_2$ 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 LZn-ZnCp*.[15]

## Notes and references

$^a$ *University of Duisburg-Essen, Universitätsstr. 5-7, S07 S03 C30, 45117 Essen, Germany. Fax: Int (+)201 1833830; Phone: Int (+)201 1834635; E-mail: stephan.schulz@uni-due.de;* $^b$ *University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. Phone: (+)31 50 3634322; E-mail: s.harder@rug.nl.*

† 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 in the suppporting information file. See DOI: 10.1039/b000000x/

‡ CCDC 785388 (**1**) and 780366 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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