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Synthesis, Structure, and Reactivity of a Dimeric Zinc(I) Compound Stabilized by a Sterically Demanding Diiminophosphinate Ligand

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Dedicated to Professor Cameron Jones on the occasion of his 50th birthday

Abstract: The new sterically demanding aminoiminophosphorane Ph_2P(=NDip)(NHDip) (Dip = C_6H_3-2,6-$i$$Pr_2$; LH, **1**) has been prepared as a precursor to the potassium complex [LK] (**2**) and a series of heteroleptic zinc(II) complexes, namely [$(LZnBr)_2$] (**3**), [LZnMe] (**4**), [LZnEt] (**5**), and [$(LZnI)_2$] (**6**). The products have been obtained either through a salt metathesis route by using complex **2** and $ZnBr_2$ to give compound **3**, through a direct reaction of ligand precursor **1** and ZnR_2 (R = Me or Et) yielding complexes **4** or **5**, respectively, or through iodination of complexes **4** or **5** by using I_2 to afford compound **6**. Reduction of the heteroleptic zinc(II) halide complexes **3** or **6** by using a dimeric magnesium(I) compound as a selective, stoichiometric, and soluble reducing agent afforded the new zinc(I) dimer [$(LZn)_2$] (**7**) in good yield. Compounds **1**–**7** were crystallographically and spectroscopically characterized and the coordination behavior of the diiminophosphinate ligand has been investigated and compared with related CN-based ligands. An initial reactivity study has been carried out on [$(LZn)_2$] (**7**) by using small-scale reactions and the oxidative addition of small alkyl halides across the Zn–Zn bond has been found to generate equimolar amounts of the alkyl complexes **4** or **5** and the halide complexes **3** or **6**, respectively.

Keywords: magnesium · N,P ligands · reduction · subvalent compounds · zinc

Introduction

Dimeric zinc(I) compounds of the general formula [RZnZnR] (R = monoanionic ligand) are known as stable compounds since Carmona and co-workers presented the synthesis and structure of [Cp*ZnZnCp*] (Cp* = C_5Me_5) in 2004.[1] Initially, this complex was obtained by the reaction of [$Cp*_2Zn$] with $ZnEt_2$ and subsequently, an improved synthesis from [Cp*K], KH, and $ZnCl_2$ was reported.[2] Since then, a range of ligands were successfully employed to yield stable complexes of the Zn_2^{2+} ion with a Zn–Zn single bond.[3] These complexes are typically obtained by reduction of zinc(II) precursor complexes with strong reducing agents such as Na, K, KC_8, and so on, or by ligand substitution reactions on [Cp*ZnZnCp*]. Notable examples of Zn–Zn-bonded complexes include the terphenyl-stabilized complex [Ar′ZnZnAr′] (Ar′ = C_6H_3-2,6-Dip_2) (Dip = C_6H_3-2,6-$i$$Pr_2$) as part of a series of dimeric Group 12 metal(I) complexes with two-coordinated linear metal atoms,[3o] and a complex featuring the isolated dication [$Zn_2(dmap)_6$]$^{2+}$ (DMAP = C_5H_4N-4-NMe_2) in where the Zn atoms are solely coordinated by neutral substituted pyridines.[3f] The majority of Zn–Zn-bonded complexes however feature a range of sterically demanding anionic N,N'-chelating ligands such as the β-diketiminate examples [{(^{Dip}nacnac)Zn}$_2$] (^{Dip}nacnac = HC{MeCN(Dip)}$_2$)[3s] and [{(^{Mes}nacnac)Zn}$_2$] (^{Mes}nacnac = HC{MeCN(Mes)}$_2$, Mes = C_6H_2-2,4,6-Me_3).[3i] Recently, a range of unusual metal cluster compounds having a central transition metal that are rich in zinc have been investigated[4] and first examples with Zn–Zn-bonded fragments in the coordination sphere of transition metal ions have been prepared.[5] The chemistry of Zn–Zn-bonded complexes has already been reviewed[6] and a limited account of their further reactivity has already been forthcoming.[6,7] An exciting development is furthermore the first catalytic use of a zinc(I) dimer in hydroamination reactions.[8] Here, we report on the synthesis of some heteroleptic zinc(II) complexes, a new zinc(I) dimer, stabilized by a new sterically demanding diiminophosphinate ligand, and an initial investigation of its reactivity.

Results and Discussion

The new diiminophosphinate ligand [$Ph_2P(NDip)_2$]$^-$ (i.e., L^-) was prepared with the target of introducing a new sterically demanding N,N'-chelating ligand with favorable properties such as good solubility and crystallizing properties to the fields of complexes with rare oxidation states and coordination modes, and unusually bonded molecular fragments.

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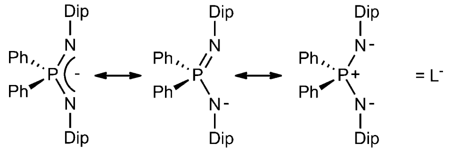
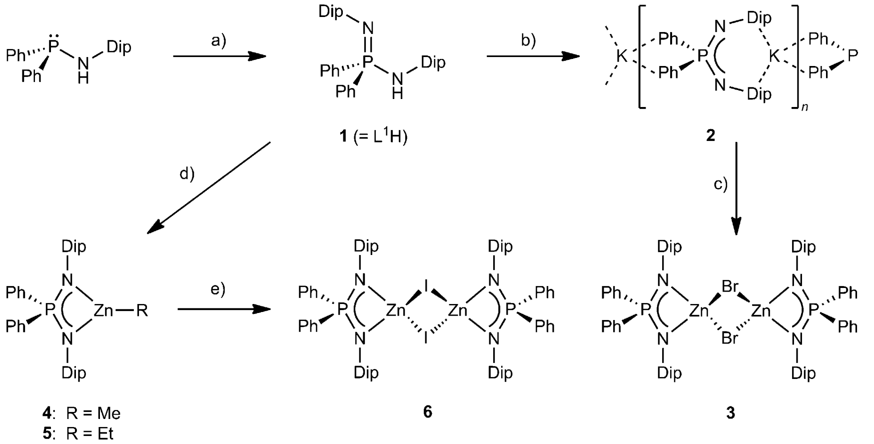


A central phosphorus atom was desirable to allow additional reaction monitoring by ^{31}P NMR spectroscopy on small scale reactions. The overall geometry of the diiminophosphinate unit is comparable to the related sterically demanding amidinate and guanidinate class of ligands[9] and is expected to show some similarities with the chemistry of those and related CN-based ligand systems.

The target aminoiminophosphorane **1** (LH) is prepared by a Staudinger reaction[10] of a phosphinoamine[11] with $DipN_3$[12] in a straightforward manner (see Scheme 1) in good yield, similar to closely related diiminophosphinate ligand precursors.[13,14] The compound is a crystalline solid that is well soluble in hydrocarbons including hexane. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra display resonances for two different Dip substituents and suggest a localized aminoimino configuration at room temperature or at 60 °C in solution. The crystal structure of compound **1** (see Figure 1) shows localized P=N (≈1.54 Å) and P–N(H) (≈1.68 Å) bonds in **1′** (see Table 1) although a polymorph (**1″**) has been characterized (see the Supporting Information for an image) that contains two P–N distances that average (≈1.61 Å) the P=N and P–N(H) bonds in the localized polymorph **1′** (see Table 1). The central phosphorus(V) center shows a distorted tetrahedral arrangement with a determined N-P-N angle range of approximately 108–117° (see Table 1). This geometry contrasts with the large range of anionic ligands that are based on predominantly planar unsaturated C–N systems, such as related amidinates and guanidinates.[9] However, related isoelectronic sila-bisamido ligands with the general formula $R_2Si(NAr)_2^{2-}$ (e.g., R = Me, Ph Ar = Dip) are known and have previously been successfully employed to stabilize Zn–Zn-bonded complexes.[31] Direct comparisons in here are mainly made with complexes carrying ligands of similar steric bulk (i.e., with NDip groups).

Compound **1** is readily deprotonated with standard reagents to give complexes of the anion L⁻. For example, the reaction of equimolar LH (**1**) and $[K\{N(SiMe_3)_2\}]$ cleanly affords the potassium salt [LK] (**2**), in very good yield (see Scheme 1). The compound has a good solubility in THF, but shows only poor solubility in aromatic solvents such as benzene and toluene and crystallizes from the latter as a solvent-free complex in one-dimensional polymeric chains, see Figure 1 for an excerpt of the polymer. Notable is the coordination of the potassi-



Scheme 1. Synthesis of compounds **1**–**6**. a) $DipN_3$, $-N_2$; b) $[K\{N(SiMe_3)_2\}]$, $-HN(SiMe_3)_2$; c) $ZnBr_2$, −KBr; d) ZnR_2, −RH; e) I_2, −RI.

Table 1. Selected interatomic distances [Å] and angles [°] for compounds **1**–**8**.

	1′	**1″**	**2**	**3**·C_7H_8	**4**·0.5 C_6H_{14}	**5**	**6**·C_6H_6	**7**·0.5 C_6H_6 (**7′**)	**7**·1.5 C_6H_{14} (**7″**)	**8**
P–N	1.6842(15) 1.5428(16) 1.6855(14)[a] 1.5446(16)[a]	1.6068(14) 1.6169(14)	1.5681(19) 1.5703(17)	1.6187(19) 1.6266(19)	1.612(3) 1.619(3) 1.613(3)[a] 1.616(4)[a]	1.6110(14) 1.6154(14)	1.623(2) 1.627(2)	1.6099(17) 1.6017(19) 1.6061(18) 1.6133(18)	1.6051(16) 1.6086(16) 1.6129(16) 1.6127(16)	1.627(3) 1.630(3)
Zn–N	–	–	–	1.9980(18) 2.0133(19)	2.014(3) 2.041(3) 2.031(4)[a] 2.009(3)[a]	2.0292(14) 2.0197(14)	2.015(2) 2.022(2)	2.0163(18) 2.0517(17) 2.0270(17) 2.0383(18)	2.0489(15) 2.0287(15) 2.0410(15) 2.0267(15)	–
Zn–E	–	–	–	2.4052(6) 2.5018(6) (E=Br)	1.941(4) 1.932(5)[a] (E=C)	1.950(2) (E=C)	2.6668(6) 2.6021(6) (E=I)	2.3132(9) (E=Zn)	2.3147(6) (E=Zn)	2.5325(7)[b] 2.5776(6)[b] 2.6869(7)[c] 2.6640(6)[c] (E=I)
N-P-N	117.34(9) 111.40(8)[a]	108.08(7)	125.29(10)	98.68(10)	99.08(18) 98.80(18)[a]	98.51(7)	97.94(11)	99.07(9) 99.21(9)	99.15(8) 99.13(8)	108.04(13)
N···N	2.757 2.670[a]	2.609	2.787	2.462	2.458 2.452[a]	2.444	2.451	2.443 2.452	2.446 2.455	2.636

[a] From a second independent molecule in the asymmetric unit. [b] Terminal. [c] Bridging.

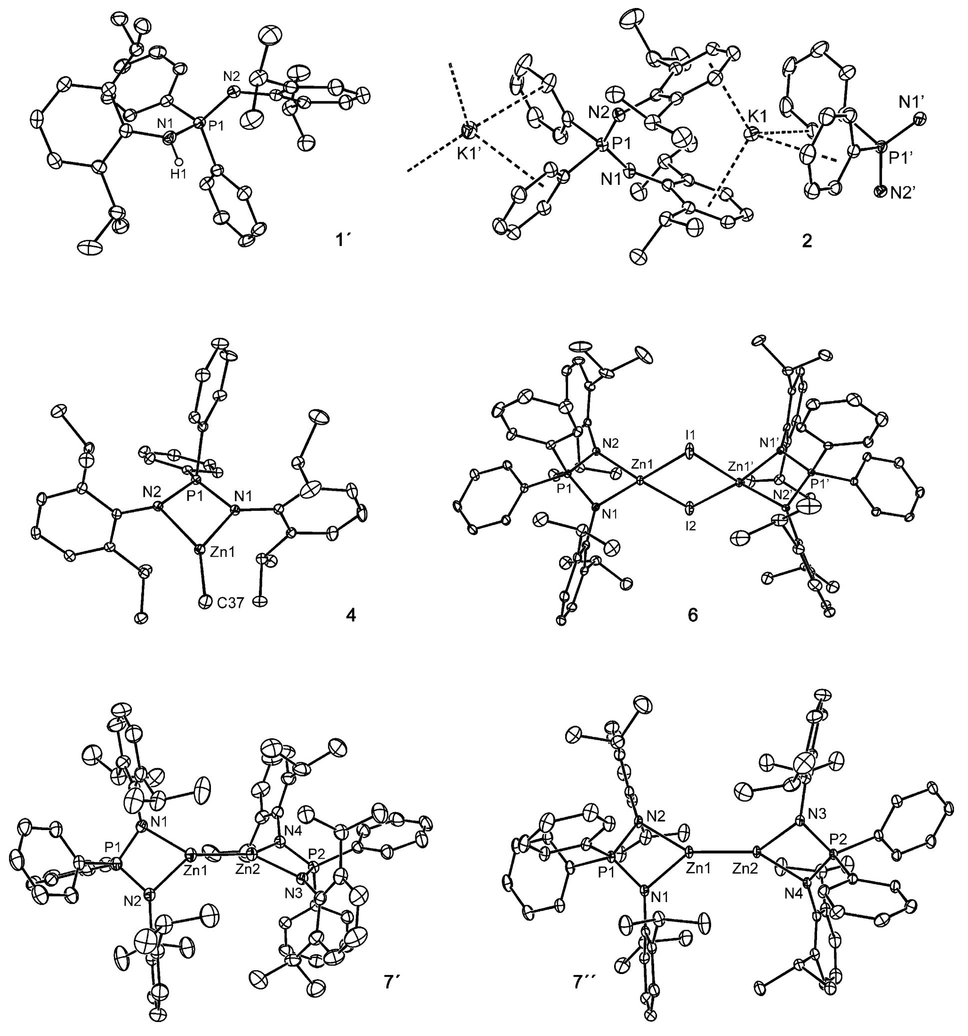


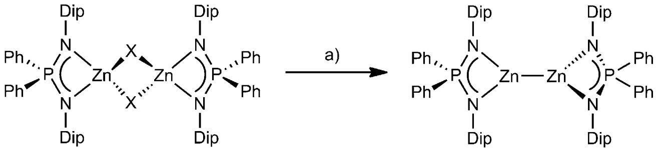
Figure 1. Molecular structures of compounds **1′**, **2**, **4**, **6**, **7′**, and **7″** (30% thermal ellipsoids). Hydrogen atoms (except NH in **1′**) and solvent molecules are omitted for clarity.

um ion to the anionic ligand. It involves no P···N contacts and the K^+ is entirely coordinated by arene···K interactions from two Dip substituents and two phenyl groups from a neighboring ligand. The only other crystallographically characterized diiminophosphinato potassium complex features an *N,N′*-coordination mode and additional THF complexation.[15] For comparison, some homoleptic (solvent-free) potassium complexes of related monoanionic *N,N′*-chelating ligands bearing the Dip substituent have been crystallographically characterized and all show at least one K···N contact.[16] The coordination mode in compound **2** can be described as approximately η^4 and η^6 to Dip and η^1 and η^6 to Ph arene rings with the K···Dip interactions generally being shorter presumably due to a more negative charge accumulation on the Dip groups. Complex **2** is suitable for salt metathesis chemistry and reacts with $ZnBr_2$ to form the heteroleptic complex $[(LZnBr)_2]$ (**3**) with a *N,N′*-chelating diiminophosphinate ligand. The reaction has been carried out in THF and work-up with toluene afforded a THF-free dimeric complex with bridging bromide ligands, see Figure 1 and Table 1 for metrical data. For comparison, closely related heteroleptic zinc halide complexes with Zn^{II} in four-membered chelates are known in $[\{(Piso)ZnX\}_2]$ complexes (Piso = *t*BuC(NDip)$_2$, X = Cl, Br, I)[17] that are broadly isostructural and show very comparable Zn–N and Zn–halide distances though their N···N separations are significantly smaller (see below).

The heteroleptic diiminophosphinato zinc alkyl complexes [LZnR] (R = Me (**4**), Et (**5**)) can be obtained in good yields by treating the phosphorane **1** with ZnR_2 (R = Me or Et, respectively). The complexes are monomeric with three-coordinate Zn^{II} centers in the solid state, see Figure 1 and the Supporting information for pictures of compounds **4** and **5**, respectively, and Table 1 for metrical data. The overall structures as well as the Zn–N and Zn–C bond lengths compare well with related sterically demanding complexes with a similar ligand environment,[17,18] though it is worth to point out that [(Piso)ZnMe][17a] shows a N,C-(arene)-complexation mode, likely due to the smaller N···N separation in the amidinate ligand (≈2.19–2.20 Å in Zn^{II} complexes) compared with the diiminophosphinate Zn complexes of this work (≈2.44–2.46 Å). The latter values are still considerably shorter than those for comparable five- or six-membered *N,N′*-chelating Zn complexes,[18] and slightly shorter than those in comparable related dianionic $Me_2Si(NDip)_2^{2-}$ ligands (≈2.54–2.56 Å) as measured from their Zn complexes.[31]

Treatment of the alkyl complexes **4** and **5** with iodine in an aromatic solvent affords the diiminophosphinato zinc iodide complex $[(LZnI)_2]$ (**6**) in good yields. Small-scale experiments followed by multinuclear NMR spectroscopy show that this reaction is facile, high yielding, and produces RI (R = Me or Et) as the expected volatile byproduct. The reaction has been carried out on a preparative scale in good yield by using [LZnEt] (**5**). This reaction provides a second convenient access to a mixed diiminophosphinato zinc halide complex and the desired precursors for reduction reactions. Generally, the heteroleptic zinc(II) complexes **3**–**6** are stable in solution and show no signs of ligand redistributions to a homoleptic complex, that is, $[L_2Zn]$.

Reduction reactions of [(LZnX)$_2$] (X = Br (**3**), I (**6**)) with an excess of K or KC$_8$ largely afforded the potassium salt [LK] (**2**). Dimeric magnesium(I) complexes[19] have previously been successfully used as hydrocarbon-soluble, selective, and stoichiometric reducing agents towards a range of inorganic/organometallic substrates.[19a,20] The reaction of complexes **3** or **6** with [{(^{Mes}nacnac)Mg}$_2$][21] afforded the dimeric zinc(I) compound [(LZn)$_2$] (**7**) in good yield (see Scheme 2). When the reaction is followed by multinuclear NMR spectroscopy at room temperature in deuterated benzene, it is evident that the reaction proceeds rapidly and in good yield (≈85–90 %). Small amounts of the free ligand **1** and Zn metal are also formed. The formation of these byproducts can be suppressed by carrying out the reaction in toluene at low temperatures with slow warming to room temperature. Work up and recrystallization from benzene afforded colorless blocks of [(LZn)$_2$] (**7**) in up to 76 % yield of the isolated product. For this reduction, even the more sterically demanding magnesium(I) dimer [{(^{Dip}nacnac)Mg}$_2$][19b,22] can be used with the precursors **3** or **6** and the reaction proceeds slowly at room temperature and faster at elevated temperatures to yield complex **7**. Attempts to prepare related zinc(I) dimers with sterically demanding amidinate or guanidinate ligands through reduction of zinc(II) halide complexes have failed so far,[17a,b] even despite the use of dimeric magnesium(I) compounds as reducing agents, and the degradation of the ligand systems has been observed in one case.[17b]



3: X = Br
6: X = I

7

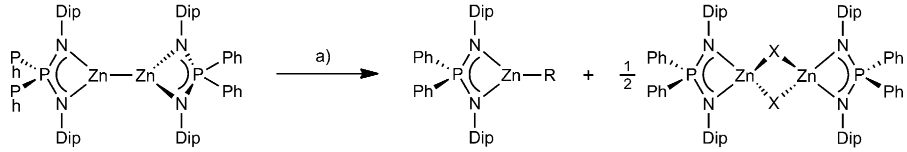
Scheme 2. Synthesis of compound **7**. a) [{Mg(^{Mes}nacnac)}$_2$], −[{Mg(^{Mes}nacnac)(μ-X)}$_2$].

Compound **7** crystallizes with a full molecule in the asymmetric unit for two structurally characterized solvates, **7′** from benzene and **7″** from hexane, respectively, that are very similar in their overall geometry (see Figure 1). Two diiminophosphinate ligands *N,N′*-coordinate the Zn_2^{2+} ion with a Zn−Zn bond length of 2.3132(9) (**7′**) or 2.3147(6) Å (**7″**). This is in the range (≈2.29–2.44 Å) of previously characterized zinc(I) dimers,[1–3,6] but is slightly shorter than those of other *N,N′*-chelating examples (≈2.33–2.44 Å).[3,6] Some Zn_2^{2+} complexes bearing *N,N′*-chelating ligands containing P=N fragments have recently been prepared from [Cp*ZnZnCp*] as a starting material.[3e] The least-square planes of the two NPNZn four-membered chelate rings in complex **7** are twisted by 56.3 (**7′**) or 54.1° (**7″**) relative to each other and thus are oriented between an orthogonal and a co-planar arrangement. As expected, no resonance that could be assigned to a Zn−H moiety for a possible [(LZnH)$_2$] complex formulation was found in the ^{1}H NMR spectrum[23] and a molecular ion peak for compound **7** was observed in the EI mass spectrum and supports the composition as a metal–metal-bonded species.

The metal complexes of the diiminophosphinate ligand presented here, compounds **2**–**7**, all show one doublet and one septet only for the protons of the isopropyl groups at room temperature in their solution ^{1}H NMR spectra. This contrasts with related complexes of comparable sterically demanding *N,N′*-chelating ligands with Dip substituents.[3,6,18] To investigate this, we have chosen [LZnEt] (**5**) as the most soluble compound of this series for a low-temperature ^{1}H NMR study. [LZnEt] shows one sharp doublet for the methyl protons of the isopropyl groups at room temperature that starts to broaden below −30 to −50 °C and splits into two broad resonances (at $\delta = 0.76$ and 1.34 ppm) below the coalescence temperature of approximately −70 °C that are not fully resolved at −85 °C, the limit of this experiment, but were well separated. This splitting of the doublet resonances at very low temperature for PN-based species compared with related CN-based ligands suggest a more flexible coordination behavior compared to the former class and implies a low energy process for the rotation of the *i*Pr groups or another fluxional process of the anionic ligand. This suggests that the ligand in compounds **2**–**7** behaves more like a true anion compared with a more "heterocycle"-like behavior found for CN-based ligands. This difference in the coordination behavior of the diiminophosphinate ligand likely impacts on the further chemistry of the metal complexes. It is possible that this flexibility allows reduction of the precursor complexes **3** and **6** with sterically demanding magnesium(I) dimers at relatively low temperatures and thus facilitates the formation of complex **7**.

Access to the soluble zinc(I) dimer **7** with a central P atom in its ligand framework has allowed an initial investigation of its reactivity by small-scale reactions followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The addition of the strong pyridine donor DMAP to **7** led to no changes of the ^{1}H and ^{31}P{^{1}H} NMR spectra at room temperature nor to any color change. For comparison, DMAP addition to [Cp*ZnZnCp*] gave the unsymmetrically substituted complex [η^5-Cp*ZnZn(dmap)$_2$(η^1-Cp*)][3j] and DMAP forms the adducts [(^{Ar}nacnac)Mg(dmap)Mg(dmap)(^{Ar}nacnac)] (^{Ar}nacnac = ^{Mes}nacnac or ^{Dip}nacnac)[21,22] with the dimeric magnesium(I) compounds [{(^{Ar}nacnac)Mg}$_2$] with lengthened M−M bond lengths and a color change for the coordinated complexes compared with the uncoordinated ones.

The reaction of the zinc(I) dimer **7** with a stoichiometric amount of iodine in deuterated benzene afforded the expected zinc(II) iodide complex **6** at room temperature. A small-scale reaction of **7** with an excess of iodine led to a product mixture and the formation of a few crystals of a salt of the doubly protonated ligand [LH$_2$]$_2$[I$_2$Zn(μ-I)$_2$ZnI$_2$] (**8**) that was crystallographically characterized. Metrical parameters of compound **8** are included in Table 1 and an image can be found in the Supporting Information. Treating complex **7** with an excess of the small alkyl halides RX (MeI, EtI, or EtBr) in deuterated benzene led to an oxidative addition reaction at the Zn$_2$ fragment with an umpolung of the alkyl group from electrophilic to nucleophilic character. This reaction forms both the zinc alkyl complexes **4** or **5** and the zinc halide complexes **3** or **6**, respectively, as shown in Scheme 3. This reaction is reminiscent of the first generation of air-sensitive organometallics by Frankland in 1849.[24] The reaction of **7** proceeds slowly at room temperature or more rapidly at elevated temperatures (50–70 °C) and appears faster for iodides over bromides and methyl- over ethyl-substituted halides. Temperatures of up to approximately 75 °C in sealed NMR tubes can be employed though long reaction times and higher temperatures will eventually lead to partial decomposition of complex **7** and the formation of some finely divided zinc metal, which is expected to have an influence on the activation reaction of RX. Compound **7** also reacts with diiodomethane, CH$_2$I$_2$, and initially after partial conversion at room temperature, some [(LZnI)$_2$] (**6**) and another complex, which shows a resonance at $\delta = 16.6$ ppm (^{31}P NMR spectrum), presumably [LZnCH$_2$I], is formed, but over time converts to a product mixture with a main product having a resonance at $\delta = 14.2$ ppm. This type of activation may potentially be of interest for Zn–carbenoid reactivity, for example, the Simmons–Smith reaction.[25] A product mixture was also found for the reaction of **7** with CBr$_4$. No reaction of compound **7** has been observed with PhF and PhI, even at elevated temperatures. Treatment of complex **7** with the secondary halide 2-bromobutane or the tertiary halide 1-bromoadamantane (AdBr) showed no reaction at room temperature as judged by ^{1}H and ^{31}P NMR spectroscopy. However, after heating to approximately 70 °C (in case of 2-bromobutane) or about 80 °C (in case of AdBr) for several hours, the formation of [(LZnBr)$_2$] (**3**) and another product ($\delta = 13.6$ or 13.1 ppm for 2-bromobutane or AdBr, respectively), likely LZnR, has been observed by ^{31}P{^{1}H} NMR spectroscopy after some decomposition of **7** with zinc metal formation had occurred in both cases. It is possible that freshly generated and highly active zinc metal, known to react with the bromoalkanes (RBr) to form RZnBr,[18,25–27] activates the RBr and subsequently reacts with compound **7** to form the products.



7 **4**: R = Me or **5**: R = Et **3**: X = Br or **6**: X = I

Scheme 3. Reaction of compound **7** with alkyl halides. a) MeI, EtI, or EtBr.

The reaction of activated zinc metal (e.g., Rieke zinc) with organic halides (RX) to form organozinc halides has been investigated as a useful synthetic tool capable of differentiating between unsymmetrical dibromides.[25–27] A pronounced structure–reactivity relationship has been found for the formation of organozinc bromides from activated zinc metal and the reaction rate for the insertion of activated zinc metal into organic bromides can be faster for tertiary over secondary over primary organic bromides. A one-electron transfer process is involved in the rate-determining step.[25–27] In contrast, the reaction of the diamagnetic complex **7** with alkyl halides may not be dominated by radical-type mechanisms and may be largely dependent upon the steric profile of the reagents. A similar general trend has been found for the reactivity of substrates with related dimeric magnesium(I) compounds.[19a] For reactions involving compound **7**, traces of activated zinc metal, for example, formed during partial decomposition of **7** (as well as possible traces of Lewis acids, e.g., Zn^{II} species), may likely have an influence on the activation chemistry of the alkyl halides, especially at elevated temperatures. The apparent different selectivity between activated zinc metal and complex **7**, and presumably other dimeric zinc(I) compounds, with organic halides could be harnessed for their selective activation and may lead to complementary synthetic methods. We are currently investigating the further chemistry of compound **7** and related species towards this goal.

Conclusion

We have synthesized and characterized a potassium complex and a series of heteroleptic zinc(II) complexes of the new diiminophosphinate ligand [Ph$_2$P(NDip)$_2$]$^-$ and compared the coordination behavior with related CN-based ligand systems. The reduction of zinc(II) halide complexes with stoichiometric amounts of dimeric magnesium(I) reagents afforded a new dimeric zinc(I) complex with a Zn–Zn bond in good yield. We performed an initial investigation of the reactivity of the zinc(I) dimer by using small-scale reactions and found an activation of small alkyl halides with an umpolung of the alkyl groups yielding 1:1 mixtures of heteroleptic zinc alkyl and zinc halide complex fragments.

Experimental Section

General considerations: All manipulations were carried out by using standard Schlenk and glove box techniques under an atmosphere of high purity nitrogen. Benzene, toluene, hexane, and THF were dried and distilled over molten potassium whereas pentane was dried and distilled from Na/K alloy. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX 300 or Bruker Avance 400 spectrometer in deuterated benzene, toluene, and/or tetrahydrofuran and were referenced to the residual ^{1}H or ^{13}C{^{1}H} resonances of the solvent used, or external aqueous H$_3$PO$_4$ solutions. IR spectra were recorded by using a Perkin–Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected. Elemental analyses were performed by the Elemental Analysis Service at London Metropolitan University. $DipN_3$,[12] $DipNHPPh_2$,[11] and $[\{(^{Mes}nacnac)Mg\}_2]$[21] were prepared according to literature procedures. All other reagents were used as received (Aldrich chemical company). Small-scale reactions (typically on ≈15 mg complex samples) were carried out in 5 mm NMR tubes with J. Young stopcock in dried deuterated benzene (≈0.55 mL). The reactivity is qualitatively described in the main text. A few small crystals of $[LH_2]_2[I_2Zn(\mu\text{-}I)_2ZnI_2]$ (**8**) were obtained from the reaction of $[(LZn)_2]$ (**7**) with an excess of I_2.

LH ($Ph_2P(=NDip)(NHDip)$) (1): A solution of $DipN_3$ (4.59 g, 22.6 mmol, 1.15 equiv) in toluene (30 mL) was slowly added to a cooled (−80 °C) solution of $Ph_2PNHDip$ (7.09 g, 19.6 mmol, 1.0 equiv) in toluene (20 mL). The mixture was stirred and slowly warmed to room temperature overnight and nitrogen evolved. The mixture was further stirred for another day at room temperature, stirred for 3 h at approximately 60 °C and subsequently all volatiles were removed under reduced pressure. The residue was dried under vacuum at approximately 50 °C yielding a honey-like paste. Recrystallization from pentane (≈40 mL, 30 to −30 °C) afforded colorless crystals of ligand **1**. A second crop was obtained after further concentrating and cooling. Yield: 7.48 g (71 %); m.p. 102–104 °C (melts), liquid >340 °C; ^1H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=0.97$ (d, $J(H,H)=6.8$ Hz, 12 H; $CH(CH_3)_2$), 1.07 (d, $J(H,H)=6.8$ Hz, 12 H; $CH(CH_3)_2$), 3.32 (sept, $J(H,H)=6.8$ Hz, 2 H; $CH(CH_3)_2$), 3.62 (sept, $J(H,H)=6.8$ Hz, 2 H; $CH(CH_3)_2$), 4.32 (d, $^2J(H,P)=3.2$ Hz, 1 H; NH), 6.92–7.18 (m, 12 H; Ar-H), 7.61–7.68 ppm (m, 4 H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=23.8$ ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 120.0 (Ar-C), 123.2 (Ar-C), 123.9 (Ar-C), 127.3 (Ar-C), 128.2 (d, $J(C,P)=12.5$ Hz, Ar-C), 131.1 (d, $J(C,P)=2.7$ Hz, Ar-C), 132.2 (d, $J(C,P)=9.5$ Hz, Ar-C), 134.3 (d, $J(C,P)=122.7$ Hz, Ar-C), 134.7 (br d, $J(C,P)\approx5.4$ Hz, Ar-C), 141.7 (d, $J(C,P)=6.1$ Hz, Ar-C), 143.8 (Ar-C), 147.5 ppm (Ar-C); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=-15.7$ ppm (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 303 K): $\delta=-13.5$ ppm (s); IR (nujol): $\tilde{\nu}=3373$ (m, NH), 1654 (w, br), 1588 (m), 1455 (s), 1436 (s), 1366 (s,), 1330 (m), 1298 (m), 1258 (m), 1189 (m), 1116 (s), 1062 (m), 1029 (m), 906 (m), 795 (m), 754 (s), 696 cm^{-1} (s); elemental analysis calcd (%) for $C_{36}H_{45}N_2P$ (536.73 $g\,mol^{-1}$): C 80.56, H 8.45, N 5.22; found: C 79.93, H 8.38, N 5.17.

N.B.: Compound preparation and storage was carried under inert conditions under nitrogen, but the crystallized product may be stored in a closed vial in air.

[LK] (2): Toluene (20 mL) was added to a mixture of **1** (2.01 g, 3.74 mmol, 1.0 equiv) and $[K\{N(SiMe_3)_2\}]$ (0.784 g, 3.93 mmol, 1.05 equiv) and the mixture was vigorously stirred for 2 h and a precipitate formed. The mixture was concentrated to approximately 10 mL under reduced pressure and hexane (15 mL) was added. The precipitate of **2** was filtered off, dried under vacuum and the solution was cooled to −30 °C yielding a small second crop of **2**. Yield: 2.02 g (94 %); m.p. slow decomp. above approximately 270 °C; full decomp. around 298–302 °C; ^1H NMR (C_6D_6, $[D_8]$THF (≈4:1), 400.1 MHz, 303 K): $\delta=1.27$ (d, $J(H,H)=6.8$ Hz, 24 H; $CH(CH_3)_2$), 4.24 (sept, $J(H,H)=6.8$ Hz, 4 H; $CH(CH_3)_2$), 6.94–7.00 (m, 2 H; Ar-H), 7.18–7.37 (m, 10 H; Ar-H), 7.98–8.06 ppm (m, 4 H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, $[D_8]$THF (≈4:1), 100.6 MHz, 303 K): $\delta=24.0$ ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 116.7 (d, $J(C,P)=2.1$ Hz, Ar-C), 122.7 (Ar-C), 127.0 (d, $J(C,P)=11.2$ Hz, Ar-C), 131.5 (Ar-C), 142.7 (d, $J(C,P)=7.0$ Hz, Ar-C), 144.2 (d, $J(C,P)=111.0$ Hz, Ar-C), 148.7 ppm (d, $J(C,P)=1.7$ Hz, Ar-C) (N.B.: one resonance is missing and is believed to be hidden by the strong residual solvent peak at around $\delta=128$ ppm); $^{31}P\{^1H\}$ NMR (C_6D_6, $[D_8]$THF (≈4:1), 162.0 MHz, 303 K): $\delta=-25.7$ ppm (s); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=-21.9$ (s); IR (nujol): $\tilde{\nu}=1577$ (m), 1460 (s), 1427 (s), 1376 (s), 1362 (s), 1351 (s), 1298 (m), 1289 (m), 1259 (s), 1173 (m), 1153 (m), 1135 (m), 1114 (m), 1103 (s), 1072 (m), 1057 (m), 1045 (m), 1030 (m), 994 (m), 792 (m), 778 (m), 764 (m), 756 (s), 749 (s), 709 (s), 690 (m), 587 cm^{-1} (m); elemental analysis calcd (%) for $C_{36}H_{44}KN_2P$ (574.82 $g\,mol^{-1}$): C 75.22, H 7.72, N 4.87; found: C 75.19, H 7.83, N 4.91.

$[(LZnBr)_2]$ (3): THF (15 mL) was added to a cooled (−80 °C) mixture of **2** (0.500 g, 0.870 mmol, 1.0 equiv) and $ZnBr_2$ (0.207 g, 0.919 mmol, 1.06 equiv). The mixture was stirred briefly at −80 °C then with slow warming to room temperature overnight. Toluene (4 mL) was added, all volatiles removed, and the residue was dried under vacuum. The residue was extracted into warm (≈50 °C) toluene (20 mL) and filtered. Concentration (to ≈10 mL) and cooling to 4 °C yielded compound **3** as a colorless crystalline material that was dried under vacuum. A second crop was obtained after further concentrating (to ≈4 mL) and cooling of the solution. Yield: 0.38 g (64 %); m.p. 278–282 °C (melts); ^1H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=1.00$ (d, $J(H,H)=6.8$ Hz, 48 H; $CH(CH_3)_2$), 3.98 (sept, $J(H,H)=6.8$ Hz, 8 H; $CH(CH_3)_2$), 6.71–7.71 ppm (m, 32 H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=24.6$ ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 124.1 (d, $J(C,P)=1.5$ Hz, Ar-C), 124.4 (d, $J(C,P)=2.0$ Hz, Ar-C), 131.0 (d, $J(C,P)=2.0$ Hz, Ar-C), 132.4 (d, $J(C,P)=6.6$ Hz, Ar-C), 134.6 (d, $J(C,P)=73.1$ Hz, Ar-C), 139.8 (Ar-C), 146.9 ppm (d, $J(C,P)=3.9$ Hz, Ar-C) (N.B.: one resonance is missing and is believed to be hidden by the strong residual solvent peak at around $\delta=128$ ppm); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=14.4$ ppm(s); IR (nujol): $\tilde{\nu}=1620$ (w, br), 1589 (w), 1460 (s), 1436 (s), 1377 (s), 1365 (m), 1260 (s), 1185 (m), 1111 (s), 1024 (s), 797 (s), 750 (m), 695 cm^{-1} (m); elemental analysis calcd (%) for $C_{72}H_{88}Br_2N_4P_2Zn_2$ (1362.03 $g\,mol^{-1}$, vacuum dried sample): C 63.49, H 6.51, N 4.11; found: C 62.87, H 6.40, N 4.09.

[LZnMe] (4): Me_2Zn (0.440 mL of a 1.0 M solution in heptane, 0.440 mmol, 1.07 equiv) was added to a cooled (−80 °C) solution of **1** (0.220 g, 0.410 mmol, 1.0 equiv) in hexane (8 mL). The mixture was warmed to room temperature and stirred for 30 min. The mixture was warmed to 40 °C and concentrated under reduced pressure at this temperature to approximately 4 mL. Slow cooling to room temperature afforded a crop of colorless crystals of compound **4**. Further concentrating (to ≈2 mL) and cooling of the supernatant solution to 4 °C gave a second crop of **4**. Crystals suitable for X-ray diffraction were obtained from cyclohexane. Yield: 0.20 g (79 %); m.p. slow decomp. above about 150 °C, full decomp. above about 200 °C; ^1H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=-0.04$ (s, 3 H; $ZnCH_3$), 1.01 (d, $J(H,H)=6.8$ Hz, 24 H; $CH(CH_3)_2$), 3.81 (sept, $J(H,H)=6.8$ Hz, 4 H; $CH(CH_3)_2$), 6.74–7.34 ppm (m, 16 H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=-13.4$ ($ZnCH_3$), 24.1 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 124.0 (d, $J(C,P)=2.3$ Hz, Ar-C), 124.2 (d, $J(C,P)=3.1$ Hz, Ar-C), 127.9 (d, $J(C,P)=11.7$ Hz, Ar-C), 131.1 (d, $J(C,P)=2.9$ Hz, Ar-C), 131.9 (d, $J(C,P)=8.6$ Hz, Ar-C), 135.2 (d, $J(C,P)=95.9$ Hz, Ar-C), 141.1 (Ar-C), 146.2 ppm (d, $J(C,P)=5.1$ Hz, Ar-C); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=14.8$ ppm (s); IR (nujol): $\tilde{\nu}=1588$ (m), 1573 (w), 1461 (s), 1432 (s), 1380 (s), 1360 (s), 1318 (s), 1283 (m), 1258 (s), 1239 (m), 1211 (s), 1188 (m), 1158 (m), 1115 (s), 1056 (m), 1043 (s), 995 (s), 932 (m), 813 (m), 803 (m), 784 (s), 753 (m), 743 (m), 715 (m), 696 (s), 666 (s), 648 (m), 616 (m), 598 cm^{-1} (s); elemental analysis calcd (%) for $C_{37}H_{47}N_2PZn$ (616.15 $g\,mol^{-1}$): C 72.13, H 7.69, N 4.55; found: C 72.04, H 7.73, N 4.44.

[LZnEt] (5): Et_2Zn (2.0 mL of a 1.0 M solution in hexane, 2.0 mmol, 1.15 equiv) was added to a cooled (−80 °C) solution of **1** (0.93 g, 1.73 mmol, 1.0 equiv) in hexane (30 mL). The mixture was warmed to room temperature and stirred for 1 h. The mixture was stirred at 40 °C for 20 min and concentrated under reduced pressure at this temperature to approximately 6 mL. Cooling to 4 °C afforded a crop of colorless crystals of complex **5**. Further concentrating (to ≈2–3 mL) and cooling of the supernatant solution gave a second smaller crop of **5**. Yield: 0.78 g (71 %); m.p. slow decomp. above 200 °C; full decomp. around 300 °C; ^1H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=0.89$ (q, $J(H,H)=8.0$ Hz, 2 H; $ZnCH_2CH_3$), 0.97 (d, $J(H,H)=6.8$ Hz, 24 H; $CH(CH_3)_2$), 1.45 (t, $J(H,H)=8.0$ Hz, 3 H; $ZnCH_2CH_3$), 3.84 (sept, $J(H,H)=6.8$ Hz, 4 H; $CH(CH_3)_2$), 6.68–7.36 ppm (m, 16 H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=1.5$ ($ZnCH_2CH_3$), 12.5 ($ZnCH_2CH_3$), 24.0 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 124.0 (d, $J(C,P)=2.3$ Hz, Ar-C), 124.2 (d, $J(C,P)=3.0$ Hz, Ar-C), 127.9 (d, $J(C,P)=11.6$ Hz, Ar-C), 131.1 (d, $J(C,P)=2.7$ Hz, Ar-C), 131.9 (d, $J(C,P)=8.6$ Hz, Ar-C), 135.3 (d, $J(C,P)=96.0$ Hz, Ar-C), 141.2 (Ar-C), 146.2 ppm (d, $J(C,P)=5.2$ Hz, Ar-C); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=14.2$ ppm (s); IR (nujol): $\tilde{\nu}=1588$ (m), 1574 (w), 1462 (s), 1454 (s), 1434 (s), 1378 (s), 1360 (s), 1333 (m), 1317 (s), 1260 (s), 1187 (m), 1115 (s), 1098 (m), 1043 (m), 996 (s), 952 (m), 931 (m), 814 (m), 791 (s), 773 (m), 754 (m), 742 (m), 717 (m), 697 (s), 666 (m), 616 (m), 594 cm^{-1} (s); elemental analysis calcd (%) for $C_{38}H_{49}N_2PZn$ (630.17 $g\,mol^{-1}$): C 72.43, H 7.84, N 4.45; found: C 72.62, H 7.69, N 4.51.

[(LZnI)$_2$] (6): A solution of I_2 (0.370 g, 1.46 mmol, 1.22 equiv) in toluene (15 mL) was added dropwise to a cooled (0 °C) solution of **5** (0.75 g, 1.19 mmol, 1.0 equiv) in toluene (8 mL) until the iodine color does not disappear any more upon addition (or the process is slowed considerably). The mixture was stirred briefly at room temperature, concentrated under reduced pressure to approximately 12 mL and hexane (10 mL) was added. After cooling to −30 °C, a crop of colorless crystalline material of compound **6** was obtained and dried under vacuum. The supernatant solution was concentrated at approximately 40 °C to about 1–2 mL and hexane (3 mL) was added. Cooling afforded a smaller second crop of **6**. Crystals suitable for X-ray diffraction were obtained from benzene. Yield: 0.74 g (85 %); m.p. about 235–241 °C (melts); decomp. above 310 °C; ^{1}H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=1.01$ (d, $J(H,H)=6.8$ Hz, 48H; $CH(CH_3)_2$), 3.83 (sept, $J(H,H)=6.8$ Hz, 8H; $CH(CH_3)_2$), 6.69–7.70 ppm (m, 32H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=$ 24.7 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 124.2 (d, $J(C,P)=2.1$ Hz, Ar-C), 124.9 (d, $J(C,P)=2.8$ Hz, Ar-C), 131.4 (d, $J(C,P)=2.7$ Hz, Ar-C), 132.3 (d, $J(C,P)=8.8$ Hz, Ar-C), 134.1 (d, $J(C,P)=97.0$ Hz, Ar-C), 139.7 (Ar-C), 146.7 ppm (d, $J(C,P)=5.1$ Hz, Ar-C) (N.B.: one resonance is missing and is believed to be hidden by the strong residual solvent peak at around $\delta=128$ ppm); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=$ 17.1 ppm (s); IR (nujol): $\tilde{\nu}=1630$ (w, br), 1587 (w), 1573 (m), 1462 (s), 1384 (s), 1366 (s), 1316 (m), 1256 (m), 1233 (m), 1202 (m), 1106 (s), 1043 (m), 984 (m), 930 (m), 822 (m), 795 (s), 745 (m), 716 (m), 698 (s), 670 cm^{-1} (m); elemental analysis calcd (%) for $C_{78}H_{94}I_2N_4P_2Zn_2$ ($C_{72}H_{88}I_2N_4P_2Zn_2{\cdot}C_6H_6$, 1534.14 $g\,mol^{-1}$): C 61.07, H 6.18, N 3.65; found: C 60.95, H 6.22, N 3.73.

[(LZn)$_2$] (7): Toluene (8 mL) was added to a cooled (−80 °C) mixture of **3** (0.115 g, 84.4 μmol, 1.0 equiv) and [{(^{Mes}nacnac)Mg}$_2$] (65 mg, 90.8 μmol, 1.08 equiv) and the mixture was slowly warmed to room temperature overnight with vigorous stirring. The volatiles were removed under reduced pressure and the residue was extracted with benzene (≈6 mL) and filtered. The solution was slowly concentrated (to ≈1 mL) under reduced pressure at approximately 40 °C and slowly cooled to room temperature until crystallization started. Then the mixture was further stored at 4 °C to afford colorless blocks of complex **7**·$0.5\,C_6H_6$. Crystals of **7**·$1.5\,C_6H_{14}$ were obtained from an extraction into warm hexane. Yield: 80 mg (76 %); m.p. slow decomp. above about 137 °C (turns grey at higher temperatures); ^{1}H NMR (C_6D_6, 400.1 MHz, 303 K): $\delta=1.00$ (d, $J(H,H)=6.8$ Hz, 48H; $CH(CH_3)_2$), 3.79 (sept, $J(H,H)=6.8$, 8H; $CH(CH_3)_2$), 6.77–7.38 ppm (m, 32H; Ar-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 303 K): $\delta=24.3$ (br, $CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 123.4–123.5 (m of two overlapping resonances, Ar-C), 130.6 (d, $J(C,P)=2.0$ Hz, Ar-C), 131.6 (d, $J(C,P)=6.6$ Hz, Ar-C), 135.8 (d, $J(C,P)=71.3$ Hz, Ar-C), 141.3 (Ar-C), 145.7 ppm (d, $J(C,P)=3.9$ Hz, Ar-C) (N.B.: one resonance is missing and is believed hidden by the strong residual solvent peak at around $\delta=$ 128 ppm); $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 303 K): $\delta=12.3$ ppm (s); IR (nujol): $\tilde{\nu}=1620$ (w, br), 1589 (m), 1556 (m), 1459 (s), 1435 (s), 1379 (s), 1366 (s), 1318 (m), 1261 (s), 1233 (m), 1212 (s), 1118 (s), 1101 (m), 1043 (m), 992 (s), 931 (m), 809 (m), 775 (s), 750 (m), 716 (m), 699 (s), 660 cm^{-1} (m); MS (EI): *m/z* (%): 1202.7 $[M]^+$ (8, correct isotope pattern), 536.4 $[Ph_2P(NDip)_2H]^+$ (33), 360.2 $[Ph_2PNDip]^+$ (100); elemental analysis calcd (%) for $C_{72}H_{88}N_4P_2Zn_2$ (1202.22 $g\,mol^{-1}$, vacuum dried sample): C 71.93, H 7.38, N 4.66; found: C 71.87, H 7.46, N 4.73.

X-ray crystallography: Suitable crystals were mounted in silicone oil and were either measured by using a Nonius Kappa CCD diffractometer (**1′**, **2**, **7**·$0.5\,C_6H_6$), a Bruker X8 Apex II diffractometer (**2**), or an Oxford Xcalibur Gemini Ultra diffractometer (**5**, **6**·C_6H_6) with $Mo_{K\alpha}$ radiation ($\lambda=$ 0.71073 Å), or at the MX1 beamline at the Australian Synchrotron (**3**·C_7H_8, **4**·0.5 C_6H_{14}, **7**·$1.5\,C_6H_{14}$, **8**) with synchrotron radiation with a wavelength close to $Mo_{K\alpha}$ radiation. All structures were refined by using SHELX.[28] All non-hydrogen atoms were refined anisotropically. The NH hydrogen atoms in **1′** and **8** were located and refined; all other hydrogen atoms were included in calculated positions. The structures of **1′** and **4**·$0.5\,C_6H_{14}$ contain two crystallographically independent molecules each in the asymmetric unit with very similar geometrical features. Disorder in two isopropyl groups each in **5** and **7**·$0.5\,C_6H_6$ have been modeled with two positions for each carbon atom. Semi-empirical (multi-scan) absorption corrections were performed on all datasets. The relatively low data completeness for **4**·$0.5\,C_6H_{14}$ and **7**·$1.5\,C_6H_{14}$ are due to the limitations of the experimental set-up (one phi scan) at the synchrotron. Two datasets on a crystal of **7**·$1.5\,C_6H_{14}$ in different orientations were merged, but still yield relatively low data values. The Supporting Information contains selected crystallographic details in Table S1 and images of the molecular structures of **1″**, **3**·C_7H_8, **5**, and **8**. CCDC-890439 (**1′**), 890440 (**1″**), 890441 (**2**), 890442 (**3**·C_7H_8), 890443 (**4**·$0.5\,C_6H_{14}$), 890444 (**5**), 890445 (**6**·C_6H_6), 890446 (**7**·$0.5\,C_6H_6$), 890447 (**7**·$1.5\,C_6H_{14}$), and 890448 (**8**) 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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[1] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136–1138.

[2] D. del Rio, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* **2005**, *117*, 1270–1273; *Angew. Chem. Int. Ed.* **2005**, *44*, 1244–1247.

[3] a) J. Gao, S. Li, Y. Zhao, B. Wu, X.-J. Yang, *Organometallics* **2012**, *31*, 2978–2985; b) H. P. Nayek, A. Lühl, S. Schulz, R. Köppe, P. W. Roesky, *Chem. Eur. J.* **2011**, *17*, 1773–1777; c) M. Carrasco, R. Peloso, A. Rodríguez, E. Álvarez, C. Maya, E. Carmona, *Chem. Eur. J.* **2010**, *16*, 9754–9757; d) S. Gondzik, D. Bläser, C. Wölper, S. Schulz, *Chem. Eur. J.* **2010**, *16*, 13599–13602; e) S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese, S. Harder, *Chem. Commun.* **2010**, *46*, 7757–7759; f) S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser, R. Boese, *Angew. Chem.* **2009**, *121*, 5859–5862; *Angew. Chem. Int. Ed.* **2009**, *48*, 5748–5751; g) Y. Liu, S. Li, X.-J. Yang, P. Yang, J. Gao, Y. Xia, B. Wu, *Organometallics* **2009**, *28*, 5270–5272; h) P. Yang, X.-J. Yang, J. Yu, Y. Liu, C. Zhang, Y.-H. Deng, B. Wu, *Dalton Trans.* **2009**, 5773–5779; i) S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics* **2009**, *28*, 1590–1592; j) D. Schuchmann, U. Westphal, S. Schulz, U. Florke, D. Bläser, R. Boese, *Angew. Chem.* **2009**, *121*, 821–824; *Angew. Chem. Int. Ed.* **2009**, *48*, 807–810; k) J. Yu, X.-J. Yang, Y. Liu, Z. Pu, Q.-S. Li, Y. Xie, H. F. Schaefer, B. Wu, *Organometallics* **2008**, *27*, 5800–5805; l) Y.-C. Tsai, D.-Y. Lu, Y.-M. Lin, J.-K. Hwang, J.-S. K. Yu, *Chem. Commun.* **2007**, 4125–4127; m) X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer III, Y. Liang, B. Wu, *Chem. Commun.* **2007**, 2363–2365; n) I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem.* **2007**, *119*, 4380–4383; *Angew. Chem. Int. Ed.* **2007**, *46*, 4302–4305; o) Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2007**, *129*, 10847–10857; p) J. F. Van der Maelen, E. Gutierrez-Puebla, A. Monge, S. Garcia-Granda, I. Resa, E. Carmona, M. T. Fernandez-Diaz, G. J. McIntyre, P. Pattison, H.-P. Weber, *Acta Crystallogr. Sect. B* **2007**, *63*, 862–868; q) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Rio, R. A. Andersen, *J. Am. Chem. Soc.* **2007**, *129*, 693–703; r) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 5939–5942; *Angew. Chem. Int. Ed.* **2006**, *45*, 5807–5810; s) Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. von R. Schleyer, H. F. Schaefer III, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, *127*, 11944–11945.

[4] T. Bollermann, C. Gemel, R. A. Fischer, *Coord. Chem. Rev.* **2012**, *256*, 537–555, and references therein.

[5] T. Bollermann, K. Freitag, C. Gemel, R. W. Seidel, M. von Hopffgarten, G. Frenking, R. A. Fischer, *Angew. Chem.* **2011**, *123*, 798–802; *Angew. Chem. Int. Ed.* **2011**, *50*, 772–776.

[6] a) T. Li, S. Schulz, P. W. Roesky, *Chem. Soc. Rev.* **2012**, *41*, 3759–3771; b) S. Schulz, *Chem. Eur. J.* **2010**, *16*, 6416–6428; c) D. L. Kays, S. Aldridge, *Angew. Chem.* **2009**, *121*, 4172–4174; *Angew. Chem. Int. Ed.* **2009**, *48*, 4109–4111; d) E. Carmona, A. Galindo, *Angew. Chem.* **2008**, *120*, 6626–6637; *Angew. Chem. Int. Ed.* **2008**, *47*, 6526–6536; e) A. Grirrane, I. Resa, A. Rodríguez, E. Carmona, *Coord. Chem. Rev.* **2008**, *252*, 1532–1539; f) A. Schnepf, H.-J. Himmel, *Angew. Chem.* **2005**, *117*, 3066–3068; *Angew. Chem. Int. Ed.* **2005**, *44*, 3006–3008; g) G. Parkin, *Science* **2004**, *305*, 1117–1118.

[7] I. L. Fedushkin, O. V. Eremenko, A. A. Skatova, A. V. Piskunov, G. K. Fukin, S. Y. Ketkov, E. Irran, H. Schumann, *Organometallics* **2009**, *28*, 3863–3868.

[8] A. Lühl, H. D. Nayek, S. Blechert, P. W. Roesky, *Chem. Commun.* **2011**, *47*, 8280–8282.

[9] For reviews see, for example: a) C. Jones, *Coord. Chem. Rev.* **2010**, *254*, 1273–1289; b) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, *57*, 183–352; c) P. C. Junk, M. L. Cole, *Chem. Commun.* **2007** 1579–1590; d) M. P. Coles, *Dalton Trans.* **2006**, 985–1001; e) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141; f) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300.

[10] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635–646.

[11] A. Stasch, *Angew. Chem.* **2012**, *124*, 1966–1969; *Angew. Chem. Int. Ed.* **2012**, *51*, 1930–1933.

[12] L. P. Spencer, R. Altwer, P. Wei, L. Gelmini, J. Gauld, D. W. Stephan, *Organometallics* **2003**, *22*, 3841–3854.

[13] For reviews see, for example: a) A. Steiner, S. Zacchini, P. I. Richards, *Coord. Chem. Rev.* **2002**, *227*, 193–216; b) F. Baier, Z. Fei, H. Gornitzka, A. Murso, S. Neufeld, M. Pfeiffer, I. Rüdenauer, A. Steiner, T. Stey, D. Stalke, *J. Organomet. Chem.* **2002**, *661*, 111–127, and references therein.

[14] S. Li, D. Cui, D. Li, Z. Hou, *Organometallics* **2009**, *28*, 4814–4822.

[15] A. Steiner, D. Stalke, *Inorg. Chem.* **1993**, *32*, 1977–1981.

[16] a) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, *Organometallics* **2011**, *30*, 1291–1294; b) G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose, A. Stasch, *New J. Chem.* **2009**, *33*, 64–75; c) S. Yao, H.-S. Chan, C.-K- Lam, H. K. Lee, *Inorg. Chem.* **2009**, *48*, 9936–9946; d) N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304; e) W. Clegg, E. K. Cope, A. J. Edwards, F. S. Mair, *Inorg. Chem.* **1998**, *37*, 2317–2319.

[17] a) S. Schmidt, S. Schulz, D. Bläser, R. Boese, M. Bolte, *Organometallics* **2010**, *29*, 6097–6103; b) C. Jones, L. Furness, S. Nembenna, R. P. Rose, S. Aldridge, A. Stasch, *Dalton Trans.* **2010**, *39*, 8788–8795; c) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, P. Takolpuckdee, A. K. Tomov, A. J. P. White, D. J. Williams, M. R. J. Elsegood, S. H. Dale, *Inorg. Chem.* **2007**, *46*, 9988–9997.

[18] L. Stahl, I. P. Smoliakova in *Comprehensive Organometallic Chemistry III, Vol. 2* (Eds.: D. M. P. Mingos, R. H. Crabtree), Elsevier, Oxford, **2007**, pp. 311–418, and references therein.

[19] a) A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40*, 5659–5672; b) S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757.

[20] a) B. D. Rekken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 6504–6507; b) S. L. Choong, C. Schenk, A. Stasch, D. Dange, C. Jones, *Chem. Commun.* **2012**, *48*, 2504–2506; c) M. Asay, S. Inoue, M. Driess, *Angew. Chem.* **2011**, *123*, 9763–9766; *Angew. Chem. Int. Ed.* **2011**, *50*, 9589–9592; d) C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch, *Inorg. Chem.* **2011**, *50*, 12315–12325; e) J. Li, C. Schenk, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625; f) W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 10074–10077; g) N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517–13525; h) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* **2010**, *2*, 865–869; i) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881–9884; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701–9704.

[21] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955.

[22] S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, *120*, 9219–9223; *Angew. Chem. Int. Ed.* **2008**, *47*, 9079–9083.

[23] a) J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen, S. Harder, *Chem. Commun.* **2009**, 3455–3456; b) S. Schulz, T. Eisenmann, D. Schuchmann, M. Bolte, M. Kirchner, R. Boese, J. Spielmann, S. Harder, *Z. Naturforsch. B* **2009**, *64*, 1397–1400; c) H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt, M. Noltemeyer, *Chem. Commun.* **2001**, 1118–1119; d) W. Kläui, U. Schilde, M. Schmidt, *Inorg. Chem.* **1997**, *36*, 1598–1601.

[24] D. Seyferth, *Organometallics* **2001**, *20*, 2940–2955, and references therein.

[25] P. Knochel, S. Perrone, N. Grenouillat in *Comprehensive Organometallic Chemistry III, Vol. 9* (Eds.: D. M. P. Mingos, R. H. Crabtree), Elsevier, Oxford, **2007**, pp. 81–143, and references therein.

[26] *Active Metals: Preparation, Characterization, Application* (Ed.: A. Fürstner), VCH, Weinheim, **1996**.

[27] a) A. Guijarro, D. M. Rosenberg, R. D. Rieke, *J. Am. Chem. Soc.* **1999**, *121*, 4155–4167; b) A. Guijarro, R. D. Rieke, *Angew. Chem.* **1998**, *110*, 1789–1791; *Angew. Chem. Int. Ed.* **1998**, *37*, 1679–1681.

[28] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

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