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Diamidophosphines with six-membered chelates and their coordination chemistry with group 4 metals: development of a trimethylene-methane-tethered [PN_2]-type "molecular claw"†

S. Batke,‡ T. Kothe,‡ M. Haas, H. Wadepohl and J. Ballmann*

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The coordination chemistry of the phosphine-tethered diamidophosphine ligands $PhP(CH_2CH_2CH_2NHPh)_2$ ($^{pr}[NPN]H_2$) and $PhP(1,2\text{-}CH_2\text{-}C_6H_4\text{-}NHSiMe_3)_2$ ($^{bn}[NPN]H_2$) featuring six-membered N–C_3–P chelates was explored with group 4 metals, which allowed for the consecutive development of a new trimethylene-methane-tethered [PN_2] scaffold. In the case of the propylene-linked system $^{pr}[NPN]H_2$, access to the sparingly soluble dibenzyl derivative $^{pr}[NPN]ZrBn_2$ (**3-Zr**) was gained, while thermally sensitive zirconium and hafnium diiodo complexes $^{bn}[NPN]MI_2$ (**5-M**, M = Zr, Hf) were isolated in the case of the benzylene-linked derivative $^{bn}[NPN]H_2$. Despite the related phosphine-tethered backbone architectures of both of these ligands, their group 4 complexes were found to exhibit either C_1-symmetric ($^{bn}[NPN]MX_2$) or averaged C_S-symmetric ($^{pr}[NPN]MX_2$) structures in solution. To restrain the overall flexibility of these systems and thereby control the properties of the resulting complexes without disrupting the six-membered chelates, the new trimethylene-methane-tethered *N*,*N*′-di-(*tert*-butyl)-substituted $[PN_2]H_2$ protioligand was designed. This tripodal ligand system was prepared on a gram scale and its C_S-symmetric dichloro complexes $[PN_2]MCl_2$ (**6-M**, M = Ti, Zr, Hf) were isolated subsequently. The benzene-soluble dibenzyl derivative $[PN_2]ZrBn_2$ (**7-Zr**) was synthesised as well and characterised by X-ray diffraction. These results are discussed not only in conjunction with the known [NPN]-coordinated group 4 complexes incorporating five-membered chelates, but also in the context of "molecular claws" that are related to the new [PN_2] tripod.

Introduction

Monoanionic amidodiphosphines (commonly abbreviated as [PNP] ligands) are particularly well-studied hybrid ligands[1–4] and numerous amidodiphosphine complexes with the central metals embedded in five-[5–15] or six-membered chelates[16–18] have been prepared over the past decades.[19] Novel stoichiometric transformations and applications in catalysis have been discovered for these complexes, not only for late[20–29] but also for early transition metals.[30–35] For the related dianionic diamidophosphines (commonly abbreviated as [NPN] ligands), complexes of the early transition metals are dominating the field,[36] possibly due to their unique reactivities towards small molecules.[37–43] Zirconium halides in an [NPN] coordination environment, for example, were shown to react with gaseous dinitrogen upon reduction, although particularly fine-tuned ligands are required for these challenging transformations.[44–47] Chronologically, the first silyl-substituted and silylmethylene-linked [NPN] systems **A** and **B** (see Chart 1) have been prepared almost simultaneously by Schrock[48] and Fryzuk[49] more than 15 years ago. Considering that related silylmethylene- and ethylene-linked [PNP] ligands were already well-established at the time,[3,50,51] it is not surprising that [NPN] ligands are still not as well developed as their [PNP] counterparts. Over the past years, however, the original systems **A** and **B** have been optimised by Fryzuk and coworkers in order to circumvent silylamide bond cleavage reactions and other undesired decomposition pathways.[52,53] Following an iterative approach, the phenylene-, thiophenylene- and cyclopentenylene-linked systems **C**, **D** and **E** (see Chart 1) were prepared and their zirconium complexes isolated and examined subsequently.[54–56]

Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 276, 69120 Heidelberg, Germany.
E-mail: Joachim.ballmann@uni-heidelberg.de

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‡These authors contributed equally to this work.

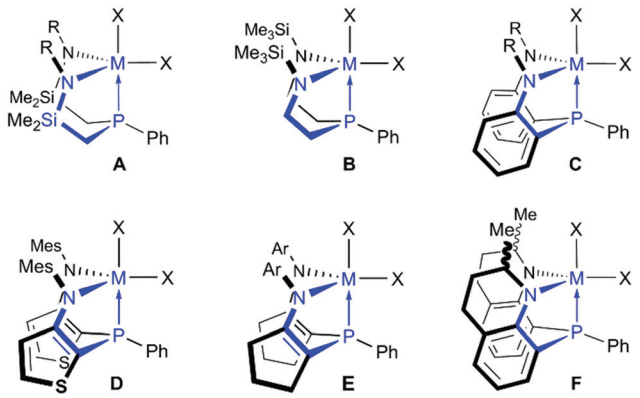


Chart 1 Monomeric [NPN] complexes of the group 4 metals incorporating five-membered chelates (highlighted in blue). **A**: R = ^{t}Bu, Ph, 2,6-$Me_2C_6H_3$; **C**: R = Mes, *p*-Tol, Et; **E**: Ar = 2,6-$Me_2C_6H_3$, 2,6-$^{i}Pr_2C_6H_3$; **A**–**F**: M = Zr (Ti or Hf only in case of **A**, **C** and **F**); X = monoanionic ligand (*e.g.* Cl, I, NMe_2, Bn, Me).

System **C** was found to be well-suited for the preparation of dinitrogen complexes[46] and for the stabilization of a reactive dimethyl zirconium species.[56] A derivative of system **C**, the 2-methyl-tetrahydroquinoline-derived system **F** (see Chart 1),[57] seems noteworthy as well, as it might open up an avenue for the introduction of chirality. What emerges from the inspection of systems **A**–**F** is that each ligand was designed to form five-membered chelates upon complexation of a metal ion. Indeed, diamidophosphines with six-membered chelates have not been explored so far, while [PNP] scaffolds with six-membered chelates are known since 1988.[4]

Thus, an exploration of [NPN] systems with six-membered chelates seemed essential to close the "development gap" between [PNP] and [NPN] systems. In view of the above mentioned iterative optimization that was required to fine-tune [NPN] scaffolds with five-membered chelates, a similar approach was planned to access and optimise the corresponding systems with six-membered chelates.

Expecting that the propylene- and the benzylene-linked ligands, ^{pr}[NPN] and ^{bn}[NPN] (see Chart 2), can be prepared easily, an exploration of their group 4 chemistry was initially pursued. The findings that we made with these complexes allowed for a consecutive ligand optimization, which led to the development of a new tripodal trimethylene-methane-tethered diamidophosphine scaffold. This system was then investigated with respect to its coordination chemistry with group 4 metals. The results, which were attained in this two-step development process are discussed in the following.

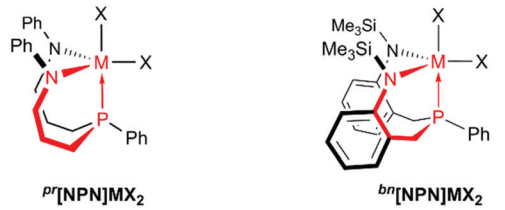


Chart 2 Diamidophosphine complexes of the group 4 metals incorporating six-membered chelates (highlighted in red).

Results and discussion

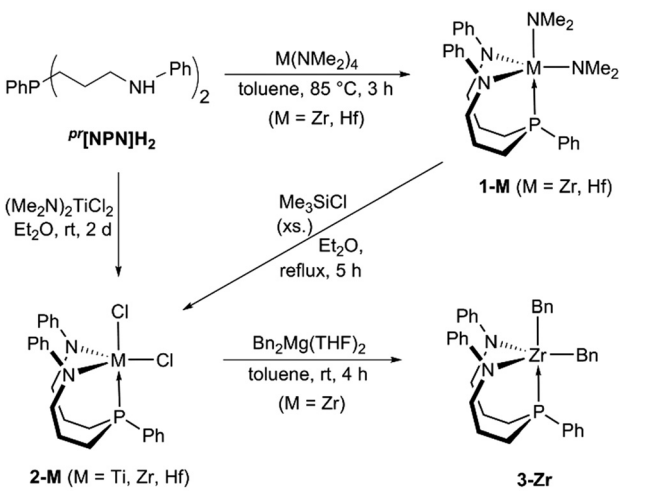
Step 1: group 4 complexes of ^{pr}[NPN]H_2 and ^{bn}[NPN]H_2

In agreement with the above mentioned expectation, the propylene- and benzylene-linked ligands, ^{pr}[NPN]H_2 and ^{bn}[NPN]H_2, were readily synthesised following an adaption of our previously reported experimental procedure for the preparation of related triamidophosphine scaffolds (see Scheme S1 in the ESI†).[58,59] Both ligands were obtained in gram quantities and high purities, which allowed for their direct use to prepare the envisioned group 4 complexes shown in Chart 2.

In the case of ^{pr}[NPN]H_2, the bis-dimethylamido complexes ^{pr}[NPN]M$(NMe_2)_2$ (**1-M**, M = Zr, Hf, see Scheme 1) were obtained *via* protonolysis with M$(NMe_2)_4$ (M = Zr, Hf) and isolated in good yields (**1-Zr**: 70% with $\delta(^{31}P) = -28.0$ ppm; **1-Hf**: 67% with $\delta(^{31}P) = -20.2$ ppm).

In the ^{1}H NMR spectra of complexes **1-M** (M = Zr, Hf), two signals each were detected for the dimethylamides, indicative of trigonal bipyramidal complex geometries. At room temperature, only one set of signals was detected for the equivalent ligand sidearms and significant signal broadening was observed at −80 °C. Whether the *fac*- or the *mer*-isomers of complexes **1-M** (M = Zr, Hf) were present in solution could not be distinguished by NMR spectroscopy, although the facial coordination mode shown in Scheme 1 seems more likely in view of the solution structure of **3-Zr** (*vide infra*).

Following a frequently used synthetic pathway, complexes **1-M** were converted to the corresponding dichlorides ^{pr}[NPN]MCl_2 (**2-M**, M = Zr, Hf) *via* reaction with Me_3SiCl. In the present case, these reactions were only successful when carried out in boiling diethylether, which led to the precipi-



Scheme 1 Synthesis of complexes **1-M**, **2-M** and **3-Zr**.

tation of the desired products in yields of 62% (**2-Zr**) and 51% (**2-Hf**), respectively. A similar procedure relying on the precipitation of the product was found to be effective for titanium as well. Upon reaction of ^{Pr}[NPN]H$_2$ with (Me$_2$N)$_2$TiCl$_2$ in diethylether, a brick-red precipitate of ^{Pr}[NPN]TiCl$_2$ (**2-Ti**) formed over the course of two days at room temperature and was isolated in modest yields of 35% (see Scheme 1).

In the ^{31}P{^{1}H} NMR spectra of **2-M** (M = Ti, Zr, Hf), uninformative singlets were observed at 8.0 ppm (**2-Ti**), −13.1 ppm (**2-Zr**) and −4.0 ppm (**2-Hf**) in dichloromethane-d_2, while rapid decomposition was noticed in THF-d_8. In the respective ^{1}H NMR spectra of these complexes, partially overlapping methylene resonances were detected at room temperature in addition to three well-resolved signals for the *N*-phenyl substituents. On basis of these NMR data, an overall C_S-symmetry was deduced for all three complexes **2-M** (M = Ti, Zr, Hf) in solution. To elucidate their corresponding solid state structures, single crystals suitable for X-ray diffraction were grown from pentane-layered dichloromethane solutions (**2-Ti**: see Fig. 1, **2-Zr**, **2-Hf**: see Fig. S21 and S22 in the ESI,† *cf.* Table 1 for selected metrical parameters). In each case, a trigonal bipyramidal complex geometry with the ligand binding in a facial coordination mode was found, but the expected C_S-symmetry was not observed in the solid state molecular structures.

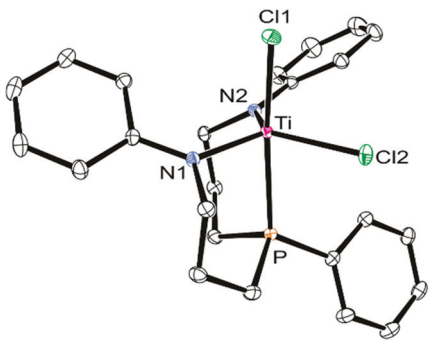
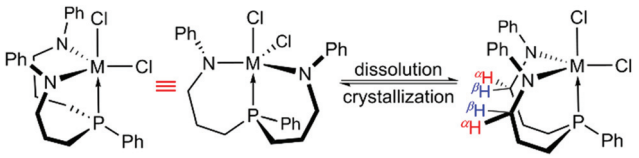


Fig. 1 ORTEP diagram of the molecular structure of **2-Ti** (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50% probability). Selected bond lengths and angles are summarised in Table 1.

Table 1 Selected metrical parameters and ^{31}P NMR shifts (recorded in CD_2Cl_2 at room temperature) of complexes **2-M** (M = Ti, Zr, Hf; X = Cl)

	2-Ti	**2-Zr**	**2-Hf**
M–P (Å)	2.5431(10)	2.7481(11)	2.7262(6)
M–N (Å)	1.9132(11)	2.0503(12)	2.0432(18)
	1.9181(11)	2.0654(12)	2.0545(18)
M–X (Å)	2.3345(9)	2.4555(9)	2.4293(6)
	2.3476(11)	2.4038(7)	2.3835(6)
P–M–X (°)	169.895(14)	174.441(11)	174.694(18)
	82.802(17)	87.20(2)	87.41(2)
N–M–N (°)	111.90(5)	115.61(4)	115.79(8)
δ(^{31}P) (ppm)	8.0	−13.1	−4.0



Scheme 2 Structures of complexes **2-M** (M = Ti, Zr, Hf) in the solid state (left) and in solution (right).

Instead, both ligand sidearms were found in a mutually twisted arrangement with the *N*-phenyl substituents pointing in opposite directions. In solution, these *N*-phenyl substituents were found to be equivalent, although broadened resonances were recorded in the respective proton NMR spectra at −80 °C. In the ^{1}H NMR spectrum of **2-Ti**, for example, two sets of geminally coupled signals centred at approximately 4.3 ppm were detected at −80 °C and assigned to the *N*-methylene protons ($^{\alpha}$H and $^{\beta}$H, see Scheme 2). Thus, these protons were identified as symmetry-related even at low temperatures, indicating that the averaged C_S-symmetry was retained in solution over a wide temperature range. The virtually temperature independent ^{31}P{^{1}H} NMR chemical shifts implied that the facial coordination mode of the ligand (analogous to **3-Zr**) is unaffected over this temperature range, although a meridional coordination mode cannot be ruled out merely by NMR spectroscopy (precipitation of the complexes from dichloromethane-d_2 hampered NMR experiments at lower temperatures). Based on these findings, the averaged C_S-symmetry in solution was interpreted as a consequence of a dynamic twist of the ligand sidearms, which renders them identical on the NMR timescale. For complexes **1-M** (M = Zr, Hf) practically identical observations were made upon analysis of their variable temperature NMR spectra, but no single crystals suitable for X-ray diffraction were obtained for these derivatives.

With the dichlorides **2-M** (M = Ti, Zr, Hf) in hand, the synthesis of alkyl complexes was pursued and **3-Zr** was generated upon reaction of **2-Zr** with Bn$_2$Mg(THF)$_2$ [60] in toluene suspension (see Scheme 1). Over the course of this reaction, gradual dissolution of **2-Zr** was observed along with precipitation of the product as a bright yellow powder, which was separated from magnesium salt by-products by extraction with dichloromethane. In case of titanium and hafnium, similar reactions met with failure, although it remains unclear whether sparingly soluble dibenzyl derivatives were actually formed. This uncertainty is mainly due to the required extraction with polar chlorinated solvents, which might result in decomposition of the products prior to analysis by NMR spectroscopy.

In the proton NMR spectrum of **3-Zr**, two sets of signals were observed for the inequivalent benzyl groups and significantly different $^3J_{H,P}$ coupling constants of 2.6 and 7.9 Hz were determined. Thus, a facial coordination mode of the ligand with one of the benzyl substituents located in *trans*- and the other in *cis*-position to the phosphine is in agreement[48] with the solution structure proposed for **3-Zr** (see Scheme 1). The

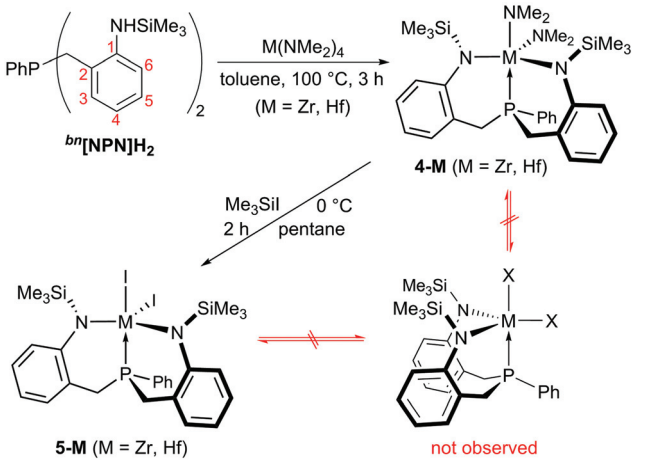
$^{31}P\{^{1}H\}$ NMR signal was found at −19.1 ppm and only one set of ^{1}H NMR signals was detected for the ligand sidearms, indicative of a close structural relationship between **3-Zr** and complexes **2-M** in solution.

As the low solubility of **3-Zr** hampered further conversions (*e.g.* in attempted hydrogenations or ethylene polymerization reactions), we turned our attention to the *N*,*N*′-bis-(trimethylsilyl)-substituted benzylene-linked system $^{bn}[NPN]H_2$ expecting that this ligand scaffold might form adequately soluble group 4 complexes. Following a synthetic strategy similar to the one used for the propylene-linked ligand, the tetrakis-(dimethylamido) precursors $M(NMe_2)_4$ (M = Ti, Zr, Hf) were reacted with $^{bn}[NPN]H_2$ and clean conversions were observed in the case of zirconium and hafnium. The resulting dimethylamido complexes $^{bn}[NPN]M(NMe_2)_2$ (M = Zr, Hf) (**4-M**, see Scheme 3) were isolated (**4-Zr**: 52% yield with $\delta(^{31}P)$ = 8.2 ppm; **4-Hf**: 72% yield with $\delta(^{31}P)$ = 15.6 ppm), but only ill-defined product mixtures were obtained in the case of titanium. In contrast to the protio-ligand $^{bn}[NPN]H_2$, inequivalent sets of ^{1}H and $^{13}C\{^{1}H\}$ NMR signals for the ligand sidearms were detected for each complex **4-M** (M = Zr, Hf). In the proton NMR spectra of **4-Zr**, for example, two singlet resonances for the different trimethylsilyl units (δ = −0.06 ppm and 0.33 ppm) and four sets of signals for the different methylene protons (δ = 2.60 ppm, 2.69 ppm, 3.04 ppm and 3.07 ppm) were observed in addition to partially overlapping aromatic signals. For the dimethylamides, two singlet resonances were detected at δ = 2.65 ppm and 3.30 ppm, indicative of a trigonal bipyramidal complex geometry with the two dimethylamides either in *cis*- and *trans*-position to the phosphine (*fac*-isomer) or in a *syn*- and *anti*-alignment with respect to the phosphine-bound phenyl substituent (*mer*-isomer).

Although these isomers cannot be distinguished easily by NMR spectroscopy in solution, it was clearly shown that complexes **4-M** are C_1-symmetric in solution at room temperature, while averaged C_S-symmetric solution structures were observed for complexes **1-M**, **2-M** and **3-Zr**. Even at +80 °C, no signs of a beginning coalescence of the ligand resonances were detected, indicating that complexes **4-M** are configurationally stable within this temperature range. Single crystals suitable for X-ray diffraction were obtained by cooling saturated solutions of complexes **4-M** (M = Zr, Hf) in Et_2O to −40 °C (**4-Zr**: see Fig. 2, **4-Hf**: see Fig. S23 in the ESI,† for selected metrical parameters see Table 2).

Inspection of the refined molecular structure of **4-Zr** revealed that the central zirconium ion is situated in a trigonal–bipyramidal coordination polyhedron with N1, N2 and N4 occupying the equatorial positions. The phosphine donor atom and N3 were found in axial positions and only a diminutive deviation from an ideal geometry (*fac*-isomer) was noticed. Accordingly, an averaged N_{eq}–Zr–N_{eq} angle of 118° and a practically linear principal axis (P–Zr–N3 = 170°) was found in the solid state structure.

The important insight gained from this molecular structure is that both ligand sidearms are inequivalent with the trimethylsilyl substituents pointing in different directions, which agrees well with the structure of **4-Zr** in solution. This is also the case for the isostructural hafnium derivative **4-Hf**.



Scheme 3 Synthesis of C_1-symmetric complexes **4-M** and **5-M** (M = Zr, Hf). Arabic numbers printed in red are used in the experimental part for the NMR signal assignment of $^{bn}[NPN]H_2$, **4-M** and **5-M**.

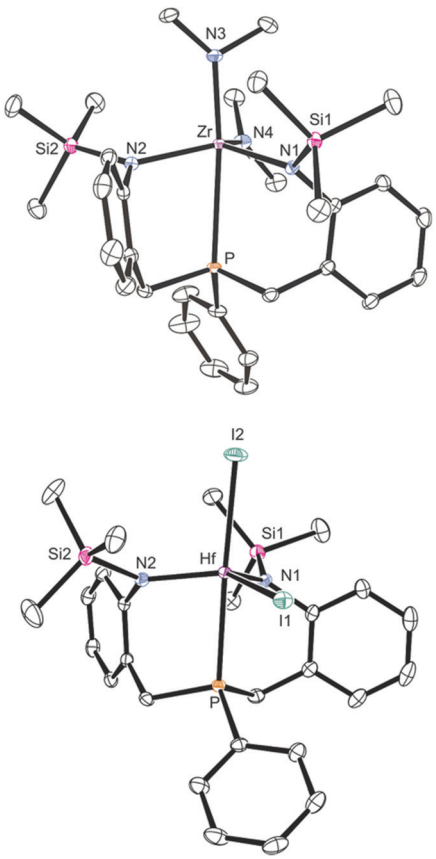


Fig. 2 ORTEP diagrams of **4-Zr** (top) and **5-Hf** (bottom) (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50% probability). Selected bond lengths are summarised in Table 2.

Table 2 Selected metrical parameters and ^{31}P NMR shifts (recorded in C_6D_6 at room temperature) of complexes **4-M** (M = Zr, Hf; X = NMe_2) and **5-Hf** (X = I)

	4-Zr	4-Hf	5-Hf
M–P (Å)	2.8922(13)	2.8725(16)	2.7560(9)
M–N (Å)	2.1223(13)	2.1004(18)	2.0064(15)
	2.1343(12)	2.1176(16)	2.0363(15)
M–X (Å)	2.0561(13)	2.0437(18)	2.8264(8)
	2.0574(14)	2.0430(18)	2.8043(8)
P–M–X (°)	169.95(3)	170.52(4)	176.376(9)
	92.00(3)	91.67(5)	83.33(2)
N–M–N (°)	121.75(5)	121.85(7)	109.57(6)
$\delta(^{31}P)$ (ppm)	8.2	15.6	13.4

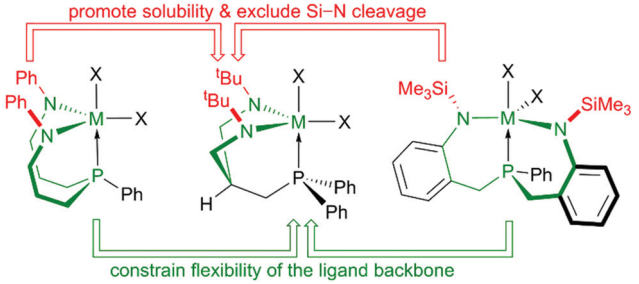


Chart 3 Design of the tripodal diamidophosphine $[PN_2]H_2$.

Attempts to convert complexes **4-M** (M = Zr, Hf) to the corresponding halides or triflates *via* treatment with Me_3SiCl or Et_3SiOTf led to unidentified mixtures of products. The reactions of **4-M** (M = Zr, Hf) with Me_3SiI, however, resulted in clean conversions to the corresponding iodides ^{bn}[NPN]MI_2 (**5-M**, M = Zr, Hf), which were isolated in acceptable yields (**5-Zr**: 47% with $\delta(^{31}P)$ = 8.5 ppm; **5-Hf**: 59% with $\delta(^{31}P)$ = 13.4 ppm; see Scheme 3). Particularly noteworthy is the fact that these reactions need to be carried out at low temperatures as the products were found to be thermally sensitive. Interestingly, decomposition of **5-Zr** (purified sample) set in within a few hours at room temperature (in C_6D_6 solution), while purified samples of **5-Hf** could be kept at room temperature for approximately two days (in C_6D_6 solution). Solid samples of both complexes were found to be stable at −40 °C for more than one month. In the ^1H NMR spectra of **5-M** two different singlet resonances for the trimethylsilyl units were found for each complex and two signals detected in the corresponding $^{13}C\{^1H\}$ NMR spectra as well. As in the case of **4-M**, overall C_1-symmetries were deduced from these NMR data and no cross-peaks were observed in the EXSY NMR spectra at room temperature. A crystallographic analysis revealed that complex **5-Hf** is C_1-symmetric in the solid state as well (see Fig. 2, *cf.* Table 2 for selected metrical parameters).

With the iodides **5-M** available, the focus was once again set on the isolation of alkyl derivatives. Unfortunately, no clean conversions to the desired dialkyl species were observed in the reactions of **5-M** with $LiCH_2SiMe_3$, $Bn_2Mg(THF)_2$ or MeMgBr, not even in the presence of excess of the alky transfer reagent.

In view of these findings, the first step of our ligand screening and optimization procedure was considered complete and three particularly noteworthy observations were made:

(i) Group 4 complexes of both ligands (^{pr}[NPN] and ^{bn}[NPN]) were found to adopt C_1-symmetric structures in the solid state. This observation was ascribed to the highly flexible phosphine-tethered ligand backbones. Note that this interpretation applies to the solid state structures only, while higher ligand flexibilities might facilitate dynamic processes in solution and thus lead to the observation of higher averaged symmetries in solution.

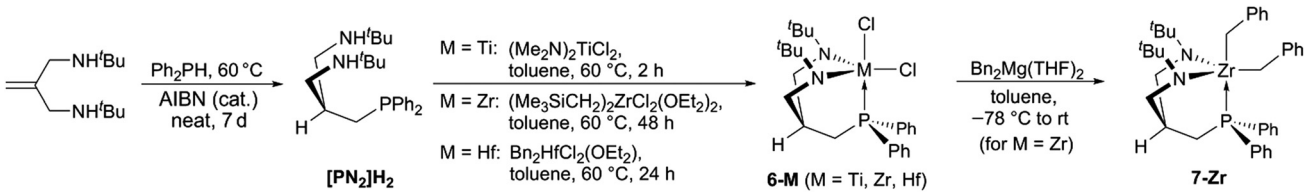
(ii) In solution, averaged C_S-symmetric structures, reminiscent to the C_S-symmetric structures of systems **A–F** (*cf.* Chart 1), were observed only for the complexes of the *N*,*N*′-diphenyl-substituted ^{pr}[NPN] ligand and ascribed to a dynamic process that renders both ligand sidearms equivalent on the NMR timescale. Therefore, the hypothesis that the sterically demanding *N*-trimethylsilyl groups in ^{bn}[NPN]MX_2 effectively prevent a dynamic equilibration was considered reasonable.

(iii) The low solubilities of complexes **2-M** and **3-Zr** (bearing the *N*,*N*′-diphenyl-substituted ^{pr}[NPN] ligand) and the thermal sensitivity of **5-Zr** (bearing the *N*,*N*′-bis-(trimethylsilyl)-substituted ^{bn}[NPN] ligand) were identified as major drawbacks of the individual systems.

Based on these findings we concluded that a control over the overall flexibility of these systems was required to allow for a more predictable fine-tuning. One possibility to achieve this goal without disrupting the six-membered N–C_3–P chelates, was to restrain the exceedingly flexible central 10-membered N–C_3PC_3–N chelate within these systems by crosslinking the sidearms. Out of the several theoretical possibilities to interconnect both sidearms, an implementation of a central six-membered N–C_3–N-chelate was considered practical and a system with overall three six-membered chelates was envisioned (see Chart 3). To enhance solubilities, *N*-*tert*-butyl and *N*-$SiMe_3$ substituents were considered and the former chosen in order to exclude Si–N bond cleavage reactions, which might be related to the thermal sensitivities of complexes **5-M** (M = Zr, Hf). Thus, the geometrically rigid C_S-symmetric "molecular claw"[61] shown in Chart 3 was identified as target molecule for the second step of our study.

Step 2: $[PN_2]H_2$ and its group 4 complexes

For the synthesis of the desired $[PN_2]H_2$ ligand scaffold, a radical hydrophosphination pathway starting from diphenyl phosphine and *N*,*N*′-bis-(*tert*-butyl)-substituted 2-(aminomethyl)-allylamine[62] was pursued. In order to achieve acceptable reaction rates, the latter amine was used as a solvent and the radical initiator (AIBN) only added in small portions over the period of 7 days (see Scheme 4). Using this methodology, the desired protioligand $[PN_2]H_2$ was obtained in >95% purity on a 5 g scale. Slow addition of AIBN was found to be of par-



Scheme 4 Synthesis of the tripodal protioligand $[PN_2]H_2$ and its group 4 complexes **6-M** (M = Ti, Zr, Hf) and **7-Zr**.

ticular importance in order to effectively suppress homocoupling of Ph_2PH and avoid a contamination of the product with Ph_4P_2.[63,64]

With $[PN_2]H_2$ available in adequate quantities, the synthesis of the group 4 dichloro complexes **6-M** (M = Ti, Zr, Hf) was targeted (see Scheme 4). For M = Zr, $(Me_3SiCH_2)_2ZrCl_2(OEt_2)_2$ [65] was identified as the most convenient precursor, while the use of $Bn_2ZrCl_2(OEt_2)$[66] resulted in lower yields of the target complex (**6-Zr**). Both precursors $(Me_3SiCH_2)_2HfCl_2(OEt_2)_2$ [65] and $Bn_2HfCl_2(OEt_2)$[66] were suitable for the preparation of **6-Hf**, although the use of the former starting material is not recommended due to the difficulties associated with its isolation.[67] Complexes $(Me_2N)_2MCl_2(L)_2$ (M = Zr, Hf, L = THF, DME)[68–70] were found to be unsuitable for the preparation of **6-Zr** and **6-Hf**. Interestingly, the titanium homologue $[PN_2]TiCl_2$ (**6-Ti**) can be prepared starting from $(Me_2N)_2TiCl_2$,[71] albeit in modest yields of only 27%. In the proton NMR spectra of each complex **6-M**, only one sharp singlet for the *tert*-butyl groups was found in addition to two geminally coupled signals for the NCH_2 units. In the aliphatic region, a phosphorus-coupled signal for the CH_2P unit and a multiplet for the central methine-bridgehead was detected for each complex.

In agreement with their C_S-symmetric structures in solution, one set of signals was found for the symmetry-related Ph_2P-groups in each complex. For titanium and hafnium, single crystals suitable for X-ray diffraction were grown by slowly cooling a boiling toluene solution of **6-Ti** or **6-Hf** to room temperature (**6-Ti**: see Fig. 3, **6-Hf**: see Fig. S24 in the ESI,† *cf.* Table 3 for selected metrical parameters). Inspection of the refined molecular structures of **6-Ti** and **6-Hf** confirmed that the complexes adopt the expected C_S-symmetric geometries, although a crystallographic plane of symmetry is only found in the case of titanium. The central metals in both structures were found in trigonal bipyramidal coordination polyhedra with the ligand binding in a facial coordination mode. In both cases, the axial positions of the trigonal bipyramids are occupied by the phosphine and one chloride, while both amides and the second chloride were found in the equatorial positions. The unexceptional bond distances and angles (see Table 3) indicated that both virtually isostructural assemblies are free of strains.

The reaction of $Bn_2Mg(THF)_2$ with complexes **6-M** proceeded cleanly in the case of zirconium and led to the isolation of the corresponding dibenzyl complex **7-Zr** as a benzene-soluble pale yellow powder. Thus, our approach to employ *tert*-butyl groups to promote solubilities was considered successful.

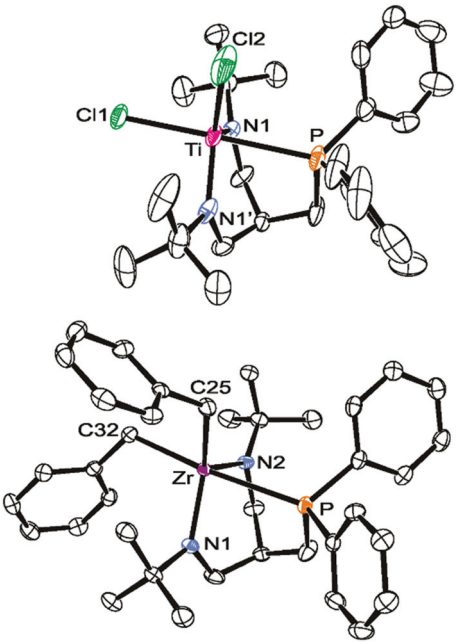


Fig. 3 ORTEP diagrams of **6-Ti** (top) and **7-Zr** (bottom) (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50% probability). Selected bond lengths and angles are summarised in Table 3.

Table 3 Selected metrical parameters and ^{31}P NMR shifts of complexes **6-M** (M = Ti, Hf) and **7-Zr**

	6-Ti	6-Hf	7-Zr
M–P (Å)	2.597(3)	2.7233(15)	2.8472(4)
M–N (Å)	1.867(5)	2.000(3)	2.0250(12)
	1.867(5)	2.003(3)	2.0489(12)
M–X (Å)	2.394(2)	2.4687(13)	2.3336(15)
	2.327(3)	2.4367(13)	2.3292(15)
P–M–X (°)	179.09(9)	175.78(3)	173.89(4)
	89.95(10)	90.94(4)	87.81(4)
N–M–N (°)	106.7(3)	101.99(14)	103.80(5)
δ ^{31}P (ppm)	−8.4[a]	−1.8[a]	−17.7[b]

[a] Recorded in dichloromethane-d_2 at room temperature. [b] Recorded in C_6D_6 at room temperature.

In the proton NMR spectrum of **7-Zr**, the signals corresponding to the ligand were easily assigned *via* comparison to the proton NMR spectrum of **6-Zr** and the remaining two sets of signals assigned to two inequivalent benzyl ligands. Based on the different $^{3}J_{H,P}$ coupling constants of the benzylic methylene protons (0.4 Hz *vs.* 2.0 Hz),[48] these sets of signals were assigned to a *trans-P* and *cis-P*-positioned benzyl substituent, which is in line with an overall C_S-symmetric structure in solution. In the solid state molecular structure of **7-Zr**, a trigonal bipyramidal geometry around zirconium was found with the phosphine and one of the benzyl ligands occupying the axial positions (see Fig. 3).

A comparison of the molecular structures of **6-Ti** and **7-Zr** (*cf.* Table 3 and Fig. 3) revealed that a certain flexibility of the ligand is retained allowing for variable metal amide distances (**6-Ti**: ~1.85 Å *vs.* **7-Zr**: ~2.03 Å) and different metal phosphine bond lengths (**6-Ti**: ~2.60 Å *vs.* **7-Zr**: ~2.85 Å). Therefore, this ligand might be of use not only for the complexation of group 4 metals, but also for coordinating other transition metals.

In contrast to trianionic C_3-symmetric "molecular claws",[61,73,74] only a few trimethylene-methane-based mono- and dianionic C_1- or C_S-symmetric phosphorus-containing tripods are known,[75] which effectively support a tridentate coordination to a single metal ion. Interestingly, aggregation or incomplete cage-closure has been observed more frequently.[75–78] In view of the "development gap" between [PNP] and [NPN] ligands discussed in the introduction, the new [PN_2] system reported herein, certainly adds to fill this void. Nevertheless, the development of amidodiphosphines still seems to be ahead, as a monoanionic silyl-tethered tripodal [NP_2] scaffold has already been prepared by Peters and co-workers, while similar silyl-tethered diamidophosphines are so far unknown.[79] In view of the trimethylene-methane backbone of the new [PN_2] tripod, however, Rüther's neutral bis-(*N*-methylimidazole-2-yl)-derived phosphine [$P(Im)_2$][80] and Gade's dianionic diamidopyridine [pyN_2][81] seem to represent the most closely related systems (see Chart 4). Employing [pyN_2]-coordinated zirconium hydrazinediido complexes,[82,83] Gade and co-workers have applied their system not only for the stabilization of unusual polyazametallacylces[84] and the assembly of a $(NSN)^{2-}$ unit within the coordination sphere of zirconium,[85] but also for the catalytic formation of indoles from 1,1-disubstituted hydrazines and alkynes.[86–89]

Closely related titanium imido derivatives bearing this ligand and their reactivity towards unsaturated substrates have been studied recently by Mountford,[90,91] while Schrock made use of this ligand backbone to prepare cationic hafnium alkyl complexes as initiators for the living polymerization of 1-hexene.[92,93]

Inspired by this work, our current efforts are directed towards the application of the new [PN_2]-coordinated group 4 complexes in catalysis and towards the synthesis of related [PN_2]-coordinated hydrazinediido complexes.

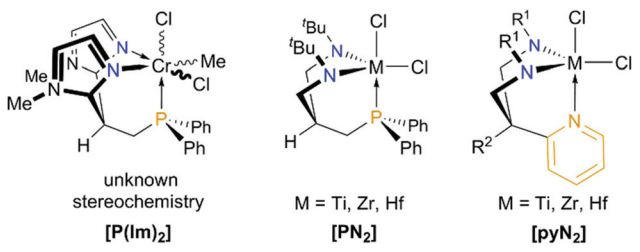


Chart 4 Monomeric complexes of the carbon-tethered C_S-symmetric "molecular claws" [$P(Im)_2$], [PN_2] and [pyN_2] (R^1 = $^{t}BuMe_2Si$, Me_3Si, 3,5-$Me_2C_6H_3$, C_6F_5 for R^2 = Me and R^1 = Me_3Si for R^2 = H). Note that [pyN_2]-coordinated imido complexes of Ti, Zr, Nb, Ta, Mo and W are known as well.[72]

Experimental

Materials and methods

All manipulations were performed under an atmosphere of dry and oxygen-free argon by means of standard Schlenk or Glovebox techniques. Toluene, THF, pentanes, hexanes and diethylether were purified by passing the solvents through activated alumina columns (MBraun Solvent Purification System). Toluene-d_8, THF-d_8 and benzene-d_6 were refluxed over sodium and purified by distillation. DMSO-d_6, CD_2Cl_2, $Me_3SiOSiMe_3$ and dichloromethane were dried over CaH_2 and distilled prior to use. Diphenyl phosphine and Me_3SiX (X = Cl, OTf, I) were dried over molecular sieves and purified by distillation. NMR spectra were recorded on a Bruker Avance II 400 MHz or a Bruker Avance III 600 MHz spectrometer at room temperature unless noted otherwise. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual proton signals of the lock solvent.[94] $^{31}P\{^{1}H\}$ NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85%H_3PO_4 at 0.0 ppm). Microanalyses (C, H, N) were performed at the Department of Chemistry at the University of Heidelberg. Compounds $(Me_2N)_2TiCl_2$ [71] and $(Me_2N)_2MCl_2(DME)_2$ (M = Zr, Hf)[68–70] were synthesised according to literature. AIBN and $M(NMe_2)_4$ (M = Ti, Zr, Hf) were purchased from commercial suppliers and used as received. Commercially available solution of Me_3SiCH_2Li (1.0 M in pentane) and BnMgCl (1.0 M in Et_2O) were used for the preparation of $(Me_3SiCH_2)_2MCl_2(OEt_2)_2$ (M = Zr, Hf),[65,67] $Bn_2MCl_2(Et_2O)$ (M = Zr, Hf)[66] and $Bn_2Mg(THF)_2$.[60] Experimental procedures for the synthesis of ^{pr}[NPN]H_2, ^{bn}[NPN]H_2 and *N*,*N*′-bis-(*tert*-butyl)-2-(aminomethyl)-allylamine are provided in the ESI.†

^{pr}[NPN]Zr(NMe$_2$)$_2$ (1-Zr). A solution of $Zr(NMe_2)_4$ (816 mg, 3.07 mmol, 1.00 eq.) in toluene (10 mL) was added to a solution of ^{pr}[NPN]H_2 (1.15 g, 3.07 mmol, 1.00 eq.) in toluene (60 mL) and the resulting clear yellow solution transferred to a teflon-valve ampule. After evacuation of the headspace, the ampule was sealed and heated to 85 °C for 3 h. The bright yellow reaction mixture was then allowed to cool to room temperature and condensed to dryness under reduced pressure. The residue was triturated with pentanes (15 mL) and the resulting pale yellow precipitate collected on a sintered glass

frit and washed with pentane (5 mL). After drying in vacuum, the product was obtained as a pale yellow powder (1.20 g, 2.17 mmol, 70%). Elemental analysis calcd for $C_{28}H_{39}N_4PZr$: C 60.72, H 7.10, N 10.12, found: C 60.51, H 6.97, N 10.29. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.37 (dd, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 7.2 Hz, 4 H, *m*-NPh), 7.24–7.17 (m, 2 H, *m*-PPh), 6.95 (d, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 0.9 Hz, 4 H, *o*-NPh), 6.93–6.89 (m, 3 H, *o*-PPh, *p*-PPh), 6.84 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, *p*-NPh), 3.78–3.71 and 3.62–3.56 (m and m, 2 H each, NCH_2), 3.19 (s, 6 H, NMe_2), 3.10 (s, 6 H, NMe_2), 1.62–1.17 (m, 8 H, PCH_2CH_2); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 153.4 (s, *ipso*-NPh), 133.1 (d, $^3J_{C,P}$ = 14.2 Hz, *m*-PPh), 132.4 (d, $^1J_{C,P}$ = 14.3 Hz, *ipso*-PPh), 130.2 (d, $^4J_{C,P}$ = 1.8 Hz, *p*-PPh), 129.8 (s, *m*-NPh), 128.7 (d, $^2J_{C,P}$ = 8.3 Hz, *o*-PPh), 117.1 (s, *p*-NPh), 115.1 (s, *o*-NPh), 46.5 (d, $^3J_{C,P}$ = 6.0 Hz, NMe_2), 45.0 (d, $^3J_{C,P}$ = 7.5 Hz, NCH_2), 41.9 (s, NMe_2), 27.0 and 22.7 (d and s, $J_{C,P}$ = 6.9 Hz, PCH_2CH_2); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −28.0 (s).

^{pr}[NPN]Hf(NMe$_2$)$_2$ (1-Hf). Following the procedure provided for the zirconium derivative, the title compound was prepared starting from ^{pr}[NPN]H_2 (1.13 g, 3.00 mmol, 1.00 eq.) and Hf$(NMe_2)_4$ (1.07 g, 3.00 mmol, 1.00 eq.). After heating and trituration with pentane (50 mL), the product was isolated as a white powder (1.30 g, 2.02 mmol, 67%). Elemental analysis calcd for $C_{28}H_{39}N_4PHf$: C 52.46, H 6.13, N 8.74, found: C 52.41, H 5.85, N 8.73.^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.38 (t, $^3J_{H,H}$ = 7.8 Hz, 4 H, *m*-NPh), 7.23–7.18 (m, 2 H, *m*-PPh), 7.00 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, *o*-NPh), 6.93–6.89 (m, 3 H, *o*-PPh, *p*-PPh), 6.84 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, *p*-NPh), 3.71–3.57 and 3.56–3.47 (m and m, 2 H each, NCH_2), 3.24 (s, 6 H, NMe_2), 3.16 (s, 6 H, NMe_2), 1.54–1.27 (m, 8 H, PCH_2CH_2); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 153.8 (s, *ipso*-NPh), 133.2 (d, $^3J_{C,P}$ = 13.9 Hz, *m*-PPh), 132.1 (d, $^1J_{C,P}$ = 16.4 Hz, *ipso*-PPh), 130.4 (d, $^4J_{C,P}$ = 1.8 Hz, *p*-PPh), 129.8 (s, *m*-NPh), 128.7 (d, $^2J_{C,P}$ = 8.4 Hz, *o*-PPh), 117.1 (s, *p*-NPh), 115.3 (s, *o*-NPh), 46.6 (d, $^3J_{C,P}$ = 6.1 Hz, NMe_2), 44.6 (d, $^3J_{C,P}$ = 6.7 Hz, NCH_2), 41.5 (s, NMe_2), 27.3 and 22.7 (d, $J_{C,P}$ = 8.2 Hz and s, PCH_2CH_2); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −20.2 (s).

^{pr}[NPN]TiCl$_2$ (2-Ti). Small portions of solid $(Me_2N)_2TiCl_2$ (360 mg, 1.74 mmol, 1.00 eq.) were added within 10 min to a stirred solution of ^{pr}[NPN]H_2 (655 mg, 1.74 mmol, 1.00 eq.) in Et_2O (50 mL) resulting in the formation of a clear dark red reaction mixture. After stirring for 3 h at room temperature, a precipitate appeared in the dark red-brown reaction mixture and stirring was continued for 2 d. The finely divided solids were then isolated *via* filtration and the black filtrate discarded (no addition crops of the product were obtained when the filtrate was kept at room temperature for 7 d). The crude material was washed with Et_2O (5 mL) and dried in vacuum overnight to afford the product as a brick-red powder (300 mg, 0.61 mmol, 35%). Elemental analysis calcd for $C_{24}H_{27}Cl_2N_2PTi$: C 58.44, H 5.52, N 5.68, found: C 58.39, H 5.88, N 5.58. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.42–7.36 (m, 5 H, *m*-NPh, *p*-PPh), 7.36–7.32 (m, 2 H, *o*-PPh), 7.28 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, *o*-NPh), 7.27–7.23 (m, 2 H, *m*-PPh), 7.08 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-NPh), 4.43–4.34 and 4.27–4.18 (m and m, 2 H each, NCH_2), 2.31–2.18 and 2.16–1.89 (m and m, 2 H and 6 H, PCH_2CH_2); $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 152.0 (s, *ipso*-NPh), 132.9 (d, $^2J_{C,P}$ = 10.0 Hz, *o*-PPh), 131.4 (d, $^4J_{C,P}$ = 2.4 Hz, *p*-PPh), 130.6 (d, $^1J_{C,P}$ = 29.4 Hz, *ipso*-PPh), 129.9 (s, *m*-NPh), 129.2 (d, $^3J_{C,P}$ = 9.0 Hz, *m*-PPh), 124.9 (s, *p*-NPh), 116.9 (s, *o*-NPh), 52.4 (d, $^3J_{C,P}$ = 8.0 Hz, NCH_2), 25.5 (s, CH_2), 25.1 (d, $^1J_{C,P}$ = 14.3 Hz, PCH_2); $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = 8.0 (s).

^{pr}[NPN]ZrCl$_2$ (2-Zr). A thick-wall ampule was charged with a solution of **1-Zr** (1.00 g, 1.81 mmol, 1.00 eq.) in Et_2O (150 mL) and trimethylsilyl chloride (2.50 mL, 2.14 g, 19.7 mmol, approximately 10 eq.) was added in one portion. The ampule was sealed and the reaction mixture then stirred at 65 °C for 5 h (*caution*: pressurised reaction setup, the use of a blast shied is recommended). Over the course of the reaction, a fine yellow precipitate was deposited on the walls of the ampule. After cooling to room temperature, approximately half of the solvent was removed in vacuum and the precipitate then collected *via* filtration. The crude material was washed with Et_2O (5 mL) and dried in vacuum to afford the product as pale yellow powder (0.60 g, 1.12 mmol, 62%). Elemental analysis calcd for $C_{24}H_{27}Cl_2N_2PZr$: C 53.72, H 5.07, N 5.22, found: C 54.02, H 5.32, N 5.69. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.42–7.33 (m, 7 H, *o*-PPh, *p*-PPh, *m*-NPh), 7.30–7.25 (m, 2 H, *m*-PPh), 7.11 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H, *o*-NPh), 6.97 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, *p*-NPh), 4.05–3.98 and 3.91–3.85 (m and m, 2 H each, NCH_2), 2.15–2.02 (m, 4 H, CH_2), 1.96–1.84 (m, 4 H, PCH_2); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 149.9 (s, *ipso*-NPh), 133.1 (d, $^3J_{C,P}$ = 11.9 Hz, *m*-PPh), 131.5 (d, $^4J_{C,P}$ = 2.2 Hz, *p*-PPh), 130.3 (s, *m*-NPh), 129.9 (d, $^1J_{C,P}$ = 27.8 Hz, *ipso*-PPh), 129.4 (d, $^2J_{C,P}$ = 9.2 Hz, *o*-PPh), 122.2 (s, *p*-NPh), 115.9 (s, *o*-NPh), 47.3 (d, $^3J_{C,P}$ = 7.2 Hz, NCH_2), 25.7 (d, $^1J_{C,P}$ = 13.9 Hz, PCH_2), 23.8 (s, CH_2); $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −13.1 (s).

^{pr}[NPN]HfCl$_2$ (2-Hf). Following the procedure provided for the zirconium derivative, the title compound was prepared starting from **1-Hf** (0.66 g, 1.0 mmol, 1.00 eq.) and trimethylsilyl chloride (1.0 mL, 0.89 g, 8.2 mmol, 8.00 eq.) in Et_2O (80 mL). The product was isolated as a white powder (0.33 g, 0.53 mmol, 51%). Elemental analysis calcd for $C_{24}H_{27}Cl_2N_2PHf$: C 46.21, H 4.36, N 4.49, found: C 46.12, H 4.65, N 4.55. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.43–7.37 (m, 3 H, *o*-PPh, *p*-PPh), 7.35 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 7.5 Hz, 4 H, *m*-NPh), 7.31–7.27 (m, 2 H, *m*-PPh), 7.10 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, *o*-NPh), 6.92 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-NPh), 3.98–3.94 and 3.84–3.78 (m and m, 2 H each, 4 H, NCH_2), 2.17–2.09 (m, 4 H, CH_2), 1.95–1.84 (m, 4 H, PCH_2); $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 150.3 (s, *ipso*-NPh), 133.2 (d, $^2J_{C,P}$ = 11.6 Hz, *o*-PPh), 131.5 (d, $^4J_{C,P}$ = 2.2 Hz, *p*-PPh), 130.1 (two overlapping signals, *ipso*-PPh, *m*-NPh), 129.4 (d, $^3J_{C,P}$ = 9.2 Hz, *m*-PPh), 121.4 (s, *p*-NPh), 116.1 (s, *o*-NPh), 46.5 (d, $^3J_{C,P}$ = 6.7 Hz, NCH_2), 26.2 (d, $^1J_{C,P}$ = 15.3 Hz, PCH_2), 24.0 (s, CH_2); $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −4.0 (s).

^{pr}[NPN]ZrBn$_2$ (3-Zr). A solution of $Bn_2Mg(THF)_2$ (175 mg, 0.50 mmol, 1.00 eq.) in toluene (15 mL) was added to stirred suspension of **2-Zr** (267 mg, 0.50 mmol, 1.00 eq.) in toluene (2 mL) maintained at 0 °C. The pale yellow suspension was

stirred for 4 h at room temperature resulting in gradual dissolution of the starting material and simultaneous formation of a fluorescent yellow precipitate. The reaction mixture was evaporated under reduced pressure and the residual solids dried in vacuum for 4 h. Dichloromethane (20 mL) was then added and the residue and the resulting suspension filtered through Celite. The Celite pad was washed thoroughly with dichloromethane (3 × 10 mL) and the filtrate reduced in volume to approximately 5 mL. A fine bright yellow precipitate of the product formed during reduction of the solvent. The precipitate was filtered off, washed with a minimal amount of dichloromethane and dried in vacuum to afford the product as a bright yellow powder (190 mg, 0.29 mmol, 59%). Despite numerous attempts, carbon values were approx. 1.5% too low upon combustional analysis, possibly indicative of minor amounts of magnesium salt by-products. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.33–7.29 (m, 1 H, *p*-PPh), 7.24 (m, 4 H, *m*-NPh), 7.19 (m, 2 H, *o*-PPh), 7.09 (t, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, *m*-PPh), 6.98 (t, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, *m*-$PhCH_2^{(\alpha)}$), 6.91 (d, $^{3}J_{H,H}$ = 8.2 Hz, 4 H, *o*-NPh), 6.80 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2 H, *p*-NPh), 6.78–6.74 (m, 4 H, *o*-$PhCH_2^{(\alpha)}$, *m*-$PhCH_2^{(\beta)}$), 6.68 (t, $^{3}J_{H,H}$ = 7.3 Hz, 1 H, *p*-$PhCH_2^{(\alpha)}$), 6.58 (t, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, *p*-$PhCH_2^{(\beta)}$), 6.00 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, *o*-$PhCH_2^{(\beta)}$), 3.56–3.48 and 3.43–3.35 (m and m, 2 H each, NCH_2), 2.43 (d, $^{3}J_{H,P}$ = 2.6 Hz, 2 H, $CH_2Ph^{(\alpha)}$), 2.38 (d, $^{3}J_{H,P}$ = 7.9 Hz, 2 H, $CH_2Ph^{(\beta)}$), 1.68–1.54 and 1.49–1.41 (m and m, 8 H total, PCH_2CH_2) with (α) and (β) differentiating the two benzyl substituents; $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 151.0 (s, *ipso*-NPh), 149.6 and 148.9 (s and s, *ipso*-$PhCH_2$), 132.7 (d, $^{3}J_{C,P}$ = 8.1 Hz, *m*-PPh), 132.6 (d, $^{1}J_{C,P}$ = 17.7 Hz, *ipso*-PPh), 130.7 (s, *p*-PPh), 130.2 (s, *m*-NPh), 129.3 (d, $^{2}J_{C,P}$ = 8.6 Hz, *o*-PPh), 128.9 (s, $PhCH_2$), 128.8 (s, $PhCH_2$), 126.2 (two overlapping s, $PhCH_2$), 121.8 (s, $PhCH_2$), 120.4 (s, $PhCH_2$), 120.2 (s, *p*-NPh), 115.1 (s, *o*-NPh), 76.5 (s, $CH_2Ph^{(\alpha)}$), 68.6 (d, $^{2}J_{C,P}$ = 25.8 Hz, $CH_2Ph^{(\beta)}$), 46.3 (d, $^{3}J_{C,P}$ = 7.6 Hz, NCH_2), 25.6 and 23.2 (d and s, $J_{C,P}$ = 9.0 Hz, PCH_2CH_2) with (α) and (β) differentiating the two benzyl substituents; $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −19.1 (s).

^{bn}[NPN]Zr(NMe$_2$)$_2$ (4-Zr). A solution of $Zr(NMe_2)_4$ (1.27 g, 4.70 mmol, 1.10 eq.) in toluene (10 mL) was added to a stirred solution of ^{bn}[NPN]H_2 (2.00 g, 4.30 mmol, 1.00 eq.) in toluene (80 mL) at room temperature. The resulting pale yellow solution was heated to 100 °C for 3 h and then allowed to cool to room temperature. All volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (3 × 5 mL). After drying in vacuum, the title compound was obtained as a yellowish powder (1.43 g, 2.20 mmol, 52%). Elemental analysis calcd for $C_{30}H_{47}N_4PSi_2Zr$: C 56.12, H 7.38, N 8.73, found: C 55.96, H 7.47, N 8.69. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.54–7.51 (m, 2 H, *o*-PPh), 7.35 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1 H, 6-ArH), 7.21 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, 5-ArH), 7.11–7.09 (m, 2 H, *m*-PPh), 7.07–6.99 (m, 4 H, 4-ArH/*p*-PPh/3-ArH), 6.96 (t, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, 4-ArH), 6.93–6.89 (m, 1 H, 5-ArH), 6.68 (t, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, 6-ArH), 3.30 (s, 6 H, NMe_2), 3.07 (dd, $^{3}J_{H,P}$ = 4.6 Hz, $^{2}J_{H,H}$ = 13.7 Hz, PCH_2, 1 H), 3.04 (dd, $^{3}J_{H,P}$ = 2.9 Hz, $^{2}J_{H,H}$ = 13.0 Hz, PCH_2, 1 H), 2.69 (t, $^{2}J_{H,H}$ = 11.3 Hz, PCH_2, 1 H), 2.60 (t, $^{2}J_{H,H}$ = 12.8 Hz, PCH_2, 1 H), 2.65 (s, NMe_2, 6 H), 0.33 (s, $SiMe_3$, 9 H), −0.06 (s, $SiMe_3$, 9 H); $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 150.4 (d, $^{3}J_{C,P}$ = 8.9 Hz, 1-ArC), 148.2 (d, $^{3}J_{C,P}$ = 3.4 Hz, 1-ArC), 134.9 (s, 2-ArC), 133.3 (d, $^{2}J_{C,P}$ = 1.3 Hz, 2-ArC), 133.2 (d, $^{1}J_{C,P}$ = 1.7 Hz, *ipso*-PPh), 132.3 (d, $^{2}J_{C,P}$ = 13.4 Hz, *o*-PPh), 132.0 (d, $^{3}J_{C,P}$ = 2.4 Hz, 3-ArC), 131.8 (d, $^{4}J_{C,P}$ = 1.8 Hz, 6-ArC), 131.2 (d, $^{3}J_{C,P}$ = 4.8 Hz, 3-ArC), 130.1 (d, $^{4}J_{C,P}$ = 1.5 Hz, *p*-PPh), 129.9 (d, $^{4}J_{C,P}$ = 5.2 Hz, 6-ArC), 129.0 (d, $^{3}J_{C,P}$ = 9.4 Hz, *m*-PPh), 128.6 (d, $^{5}J_{C,P}$ = 2.4 Hz, 5-ArC), 127.5 (d, $^{4}J_{C,P}$ = 3.2 Hz, 4-ArC), 123.6 (d, $^{4}J_{C,P}$ = 1.2 Hz, 4-ArC), 122.5 (d, $^{5}J_{C,P}$ = 2.2 Hz, 5-ArC), 46.4 (d, $^{3}J_{C,P}$ = 4.1 Hz, NMe_2), 44.4 (s, NMe_2), 36.5 (d, $^{1}J_{C,P}$ = 3.3 Hz, PCH_2), 27.2 (d, $^{1}J_{C,P}$ = 4.4 Hz, PCH_2), 2.4 (s, $SiMe_3$), 2.2 (s, $SiMe_3$); $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 8.2 (s).

^{bn}[NPN]Hf(NMe$_2$)$_2$ (4-Hf). Following the procedure provided for the zirconium derivative, the title compound was prepared starting from ^{bn}[NPN]H_2 (2.00 g, 4.30 mmol, 1.00 eq.) and Hf $(NMe_2)_4$ (1.68 g, 4.70 mmol, 1.10 eq.). The product was obtained as a pale beige powder (2.25 g, 3.10 mmol, 72%). Elemental analysis calcd for $C_{30}H_{47}HfN_4PSi_2$: C 49.40, H 6.50, N 7.68, found: C 49.19, H 6.73, N 7.74. ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.60–7.50 (m, 2 H, *o*-PPh), 7.35 (d, 1 H, $^{3}J_{H,H}$ = 6.5 Hz, 6-ArH), 7.20 (s, 1 H, 5-ArH), 7.14–6.91 (m, 8 H, 6-ArH/4-ArH/3-ArH/*m*-PPh/*p*-PPh), 6.72–6.64 (m, 1 H, 5-ArH), 3.36 (s, 6 H, NMe_2), 3.16 (d, $^{2}J_{H,H}$ = 13.7 Hz, 1 H, PCH_2), 3.08 (d, $^{2}J_{H,H}$ = 12.7 Hz, 1 H, PCH_2), 2.77 (t, $^{2}J_{H,H}$ = 11.3 Hz, 1 H, PCH_2), 2.67 (s, 6 H, NMe_2), 2.65 (t, $^{2}J_{H,H}$ = 12.6 Hz, 1 H, PCH_2), 0.33 (s, 9 H, $SiMe_3$), −0.06 (s, 9 H, $SiMe_3$); $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6): δ [ppm] = 149.9 (d, $^{3}J_{C,P}$ = 8.9 Hz, 1-ArC), 148.0 (d, $^{3}J_{C,P}$ = 3.2 Hz, 1-ArC), 134.6 (s, 2-ArC), 133.3 (d, $^{2}J_{C,P}$ = 1.8 Hz, 2-ArC), 133.1 (d, $^{1}J_{C,P}$ = 3.5 Hz, *ipso*-PPh), 132.5 (d, $^{4}J_{C,P}$ = 2.4 Hz, 6-ArC), 132.2 (d, $^{3}J_{C,P}$ = 12.8 Hz, 3-ArC), 131.1 (d, $^{3}J_{C,P}$ = 4.9 Hz, 3-ArC), 130.1 (d, $^{4}J_{C,P}$ = 1.0 Hz, *p*-PPh), 129.8 (d, $^{4}J_{C,P}$ = 5.2 Hz, 6-ArC), 129.0 (d, $^{3}J_{C,P}$ = 7.6 Hz, *m*-PPh), 128.6 (d, $^{5}J_{C,P}$ = 2.5 Hz, 5-ArC), 127.5 (d, $^{4}J_{C,P}$ = 3.2 Hz, 4-ArC), 123.6 (s, 4-ArC), 122.7 (d, $^{5}J_{C,P}$ = 2.2 Hz, 5-ArC), 46.4 (d, $^{3}J_{C,P}$ = 4.1 Hz, NMe_2), 44.3 (s, NMe_2), 37.0 (d, $^{1}J_{C,P}$ = 5,0 Hz, PCH_2), 26.9 (d, $^{1}J_{C,P}$ = 6.1 Hz, PCH_2), 2.4 (s, $SiMe_3$), 2.3 (s, $SiMe_3$); $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ [ppm] = 15.6 (s).

^{bn}[NPN]ZrI$_2$ (5-Zr). A suspension of **4-Zr** (1.50 g, 2.30 mmol, 1.00 eq.) in *n*-pentane (20 mL) was cooled to 0 °C and a solution of trimethylsilyl iodide (732 µl, 1.03 g, 5.10 mmol, 2.20 eq.) in *n*-pentane (5 mL) was added dropwise within 10 min. After stirring of the reaction mixture was continued for 2 h at 0 °C, all volatiles were removed in vacuum and the residue washed with *n*-pentane (3 × 3 mL). The crude material was suspended in diethylether (10 mL) and a minimal amount of toluene was added at room temperature to dissolve all solids. The resulting solution was kept for 24 h at −40 °C and the crystalline product isolated *via* filtration. After drying in vacuum, the product was obtained as a pale yellow crystalline powder (880 mg, 1.09 mmol, 47%). Elemental analysis calcd for $C_{26}H_{35}ZrI_2N_2PSi_2$: C 38.66, H 4.37, N 3.47, found: C 38.73, H 4.32, N 3.70. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.44–7.39 (m, 2 H, *o*-PPh), 7.36 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, 6-ArH), 7.24 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, 6-ArH), 7.09–7.02 (m, 4 H, *m*-PPh/*p*-PPh /5-ArH), 7.00–6.95 (m, 1 H, 5-ArH), 6.92–6.87 (m, 2 H, 4-ArH/3-

ArH), 6.85 (t, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, 4-ArH), 6.73–6.70 (m, 1 H, 3-ArH), 2.96 (dd, $^{3}J_{H,P}$ = 4.5 Hz, $^{2}J_{H,H}$ = 13.7 Hz, 1 H, PCH_2), 2.78 (dd, $^{3}J_{H,P}$ = 4.1 Hz, $^{2}J_{H,H}$ = 12.7 Hz, 1 H, PCH_2), 2.62 (t, $^{2}J_{H,H}$ = 13.7 Hz, 1 H, PCH_2), 2.62 (t, $^{2}J_{H,H}$ = 12.7 Hz, 1 H, PCH_2), 0.43 (s, 9 H, $SiMe_3$), −0.01 (s, 9 H, $SiMe_3$); $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 146.1 (d, $^{3}J_{C,P}$ = 3.7 Hz, 1-ArC), 139.0 (d, $^{3}J_{C,P}$ = 9.9 Hz, 1-ArC), 135.3 (s, 2-ArC), 134.4 (d, $^{4}J_{C,P}$ = 3.3 Hz, 6-ArC), 132.4 (d, $^{2}J_{C,P}$ = 9.0 Hz, *o*-PPh), 131.4 (d, $^{3}J_{C,P}$ = 5.0 Hz, 3-ArC), 130.8 (d, $^{5}J_{C,P}$ = 1.9 Hz, 5-ArCH), 130.6 (d, $^{3}J_{C,P}$ = 5.5 Hz, 3-ArC), 129.4 (d, $^{4}J_{C,P}$ = 2.2 Hz, 6-ArC), 129.1 (d, $^{5}J_{C,P}$ = 3.3 Hz, 5-ArC), 129.0 (d, $^{2}J_{C,P}$ = 2.0 Hz, 2-ArC), 128.7 (d, $^{3}J_{C,P}$ = 8.1 Hz, *m*-PPh), 128.5 (s, *ipso*-PPh), 126.7 (d, $^{4}J_{C,P}$ = 2.2 Hz, 4-ArC), 125.0 (s, 4-ArC), 32.3 (d, $^{1}J_{C,P}$ = 7.6 Hz, PCH_2), 28.9 (d, $^{1}J_{C,P}$ = 9.8 Hz, PCH_2), 2.0 (s, $SiMe_3$), 1.9 (s, $SiMe_3$); $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 8.5 (s).

^{bn}[NPN]HfI$_2$ (5-Hf). Following the procedure provided for the zirconium derivative, the title compound was prepared starting from **4-Hf** (2.25 g, 3.10 mmol, 1.00 eq.) and trimethylsilyl iodide (967 μl, 1.36 g, 6.8 mmol, 2.20 eq.). The product was obtained as a colourless crystalline powder (1.63 g, 1.81 mmol, 59%). Elemental analysis calcd for $C_{26}H_{35}HfI_2N_2PSi_2$: C 34.89, H 3.94, N 3.13, found: C 35.06, H 4.10, N 3.31. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.37–7.34 (m, 2 H, *o*-PPh), 7.32 (d, $^{3}J_{H,H}$ = 7.9 Hz, 1 H, 6-ArH), 7.27 (dd, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 0.7 Hz, 1 H, 6-ArH), 7.12–7.08 (m, 1 H, 5-ArH), 7.08–7.05 (m, 2 H, *m*-PPh), 7.04–7.01 (m, 1 H, *p*-PPh), 6.99–6.94 (m, 1 H, 5-ArH), 6.92 (d, $^{3}J_{HH}$ = 7.3 Hz, 1 H, 3-ArH), 6.90–6.84 (m, 2 H, 4-ArH), 6.76–6.73 (m, 1 H, 3-ArH), 3.12 (dd, $^{3}J_{H,P}$ = 5.2 Hz, $^{2}J_{H,H}$ = 13.8 Hz, 1 H, PCH_2), 2.87 (dd, $^{3}J_{H,P}$ = 4.8 Hz, $^{2}J_{H,H}$ = 12.9 Hz, 1 H, PCH_2), 2.72 (t, $^{2}J_{H,H}$ = 13.8 Hz, 1 H, PCH_2), 2.42 (t, $^{2}J_{H,H}$ = 12.9 Hz, 1 H, PCH_2), 0.44 (s, 9 H, $SiMe_3$), 0.00 (s, 9 H, $SiMe_3$); $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 146.3 (d, $^{3}J_{C,P}$ = 3.8 Hz, 1-ArC), 138.9 (d, $^{3}J_{C,P}$ = 9.6 Hz, 1-ArC), 135.0 (d, $^{4}J_{C,P}$ = 0.9 Hz, 6-ArC), 134.7 (d, $^{2}J_{C,P}$ = 3.2 Hz, 2-ArC), 132.5 (d, $^{2}J_{C,P}$ = 8.5 Hz, *o*-PPh), 131.2 (d, $^{3}J_{C,P}$ = 5.2 Hz, 3-ArC), 130.8 (d, $^{4}J_{C,P}$ = 2.0 Hz, *p*-PPh), 130.6 (d, $^{3}J_{C,P}$ = 5.5 Hz, 3-ArC), 130.5 (s, *ipso*-PPh), 129.8 (d, $^{4}J_{C,P}$ = 2.1 Hz, 6-ArC), 129.5 (d, $^{2}J_{C,P}$ = 2.5 Hz, 2-ArC), 129.1 (d, $^{5}J_{C,P}$ = 3.3 Hz, 5-ArC), 128.9 (d, $^{5}J_{C,P}$ = 2.1 Hz, 5-ArC), 128.6 (d, $^{3}J_{C,P}$ = 8.2 Hz, *m*-PPh), 126.2 (d, $^{4}J_{C,P}$ = 2.2 Hz, 4-ArC), 124.8 (s, 4-ArC), 32.3 (d, $^{1}J_{C,P}$ = 10.3 Hz, PCH_2), 28.8 (d, $^{1}J_{C,P}$ = 12.3 Hz, PCH_2), 2.3 (s, $SiMe_3$), 2.0 (s, $SiMe_3$); $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 13.4 (s).

[PN$_2$]H$_2$. Neat diphenyl phosphine (5.0 mL, 5.40 g, 29.0 mmol) was added to *N*,*N*′-bis-(*tert*-butyl)-2-(aminomethyl)-allylamine (100 mL) and the resulting mixture heated to 60 °C. Over the period of 7 d, AIBN (total amount: 250 mg, 1.59 mmol, 5 mol%) was added in equal portions in intervals of one day. The conversion was monitored by ^{31}P NMR spectroscopy and the reaction halted at conversions of approximately 90%. The solvent was removed *via* distillation (130 °C, 10^{-1} mbar) and reused for further preparations of the title compound. The residue was dissolved in pentane and filtered through a pad of Celite. The solvent was removed in vacuum and the remaining yellow solid was washed with $(Me_3Si)_2O$ (10 mL) to remove minor amounts of Ph_4P_2. The remaining solid was dried in vacuum to afford the title compound as a colourless powder (5.5 g, 14.3 mmol, 49%). ^{1}H NMR (600 MHz, THF-d_8): δ [ppm] = 7.44 (t, $^{3}J_{H,H}$ = 7.5 Hz, 4 H, *o*-Ph), 7.28 (m, 4 H, *m*-Ph), 7.26 (m, 2 H, *p*-Ph), 2.66 (dm, $^{3}J_{H,H}$ = 17.9 Hz, 4 H, NCH_2), 2.16 (d, $^{2}J_{H,P}$ = 6.9 Hz, 2 H, PCH_2), 1.48 (m, 1 H, CH) 1.02 (s, 18 H, CMe_3); $^{13}C\{^{1}H\}$ NMR (151 MHz, THF-d_8): δ [ppm] = 140.8 (d, $^{1}J_{C,P}$ = 14.6 Hz, *ipso*-Ph), 134.9 (d, $^{2}J_{C,P}$ = 13.2 Hz, *m*-Ph), 133.5 (d, $^{2}J_{C,P}$ = 18.9 Hz, *p*-Ph), 128.8 (d, $^{2}J_{H,P}$ = 6.6 Hz, *o*-Ph), 50.3 (s, NCH_2), 46.6 (d, $^{3}J_{C,P}$ = 9.4 Hz, CMe_3), 39.3 (d, $^{1}J_{H,P}$ = 13.4 Hz, PCH_2) 30.9 (d, $^{2}J_{C,P}$ = 12.8 Hz, CH), 29.3 (s, CMe_3); $^{31}P\{^{1}H\}$ NMR (243 MHz, THF-d_8): δ [ppm] = −20.28 (s). HR-MS (FAB$^+$): found *m*/*z* = 385.2766, calcd *m*/*z* for $C_{24}H_{38}N_2P$ [MH$^+$] = 385.2767 (Δ = −1.8 ppm).

[PN$_2$]TiCl$_2$ (6-Ti). Solid $(Me_2N)_2TiCl_2$ (124 mg, 600 μmol, 1.00 eq.) was added to a solution of $[PN_2]H_2$ (230 mg, 600 μmol, 1.00 eq.) in toluene (4 mL) and the resulting reaction mixture stirred for 2 h at 60 °C. The resulting dark solution was allowed to slowly cool to room temperature. After approximately 2 h dark microcrystals formed and were isolated *via* filtration. The obtained solid was washed with pentane (2 × 1 mL) and dried in vacuum to afford the product as a red-brown crystalline powder (83 mg, 166 μmol, 27%). Elemental analysis calcd for $C_{24}H_{35}Cl_2N_2PTi$: C 57.50, H 7.04, N 5.59, found: C 57.16, H 7.07, N 5.83. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.83 (dd, $^{3}J_{H,H}$ = 8.3 Hz, $^{3}J_{H,P}$ = 7.9 Hz, 4 H, *o*-Ph), 7.39 (m, 4 H, *m*-Ph), 7.38 (m, 2 H, *p*-Ph), 4.25 (d, $^{2}J_{H,H}$ = 13.9 Hz, 2 H, NCH_2), 3.69 (dd, $^{2}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 3.9 Hz, 2 H, NCH_2), 2.22 (dm, $^{3}J_{H,P}$ = 27.0 Hz, 1 H, CH), 2.72 (dd, $^{2}J_{H,P}$ = 7.3 Hz, $^{3}J_{H,H}$ = 4.5 Hz, 2 H, PCH_2), 1.17 (s, 18 H, CMe_3); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 136.4 (d, $^{1}J_{C,P}$ = 14.1 Hz, *ipso*-Ph), 132.4 (d, $^{2}J_{C,P}$ = 12.5 Hz, *m*-Ph), 130.3 (d, $^{2}J_{C,P}$ = 1.9 Hz, *p*-Ph), 129.3 (d, $^{2}J_{C,P}$ = 8.3 Hz, *o*-Ph), 64.5 (s, NCH_2), 61.9 (d, $^{3}J_{C,P}$ = 4.7 Hz, CMe_3), 38.7 (d, $^{2}J_{C,P}$ = 5.9 Hz, CH), 28.2 (s, CMe_3), 26.0 (d, $^{1}J_{C,P}$ = 6.1 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −8.4 (s).

[PN$_2$]ZrCl$_2$ (6-Zr). A solution of $(Me_3SiCH_2)_2ZrCl_2(OEt_2)_2$ (483 mg, 1.00 mmol, 1.00 eq.) in toluene (15 mL) was added to a stirred solution of $[PN_2]H_2$ (405 mg, 1.00 mmol, 1.00 eq.) in toluene (5 mL) over a period of 5 min. The reaction was stirred at 60 °C for 48 h then heated to 110 °C. The lightly beige suspension was filtered hot and the resulting solution allowed to cool to room temperature resulting in the precipitation of a brown solid. To ensure complete precipitation of the product, the suspension was concentrated to a volume of 4 mL and the precipitate then filtered off. The obtained beige powder was washed with pentane (2 × 2 mL) and dried in vacuum to afford the title compound as a pale beige powder (320 mg, 0.59 mmol, 59%). In multiple attempts low carbon values were obtained upon combustional analysis (*e.g.* calcd for $C_{23}H_{35}Cl_2N_2PZr$: C 52.99, H 6.48, N 5.14, found: C 51.82, H 6.42, N 5.31), possibly due to carbide formation during combustion. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.87 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{3}J_{H,P}$ = 8.2 Hz, 4 H, *o*-Ph), 7.40 (m, 4 H, *m*-Ph), 7.38 (m, 2 H, *p*-Ph), 3.89 (d, $^{2}J_{H,H}$ = 12.7 Hz, 2 H, NCH_2), 3.40 (dd, $^{2}J_{H,H}$ = 12.6 Hz, $^{3}J_{H,H}$ = 3.1 Hz, 2 H, NCH_2), 3.07 (dm, $^{3}J_{H,P}$ = 31.2 Hz, 1 H, CH), 2.71 (dd, $^{2}J_{H,P}$ = 9.5 Hz, $^{3}J_{H,H}$ = 2.9 Hz, 2 H, PCH_2), 1.09 (s, 18 H, CMe_3); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2):

δ [ppm] = 136.0 (d, $^{1}J_{C,P}$ = 20.3 Hz, *ipso*-Ph), 132.3 (d, $^{3}J_{C,P}$ = 13.0 Hz, *m*-Ph), 130.5 (d, $^{4}J_{C,P}$ = 2.2 Hz, *p*-Ph), 129.4 (d, $^{2}J_{C,P}$ = 8.8 Hz, *o*-Ph), 58.0 (s, NCH_2), 56.6 (d, $^{3}J_{C,P}$ = 2.1 Hz, CMe_3), 37.3 (d, $^{2}J_{C,P}$ = 4.7 Hz, CH), 27.90 (CH_3, CMe_3), 25.77 (d, $^{1}J_{C,P}$ = 9.9 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −9.5 (s).

[PN_2]HfCl$_2$ (6-Hf). A solution of $Bn_2HfCl_2(OEt_2)$ (143 mg, 250 μmol, 1.00 eq.) in toluene (5 mL) was added to a stirred solution of [PN_2]H_2 (100 mg, 250 μmol, 1.00 eq.) in toluene (5 mL) and the reaction mixture heated to 60 °C for 24 h. The resulting brown suspension was condensed to dryness and the residue taken up in dichloromethane (5 mL) and filtered through a pad of Celite. The volume of the filtrate was reduced to 1 mL and pentane (6 mL) was added to precipitate a brownish yellow powder. These solids were collected on a sinter glass frit, washed with diethylether (2 mL) and dried in vacuum to afford the product as a pale yellow powder (87.0 mg, 138 μmol, 55%). Elemental analysis calcd for $C_{23}H_{35}Cl_2N_2PHf$: C 45.62, H 5.58, N 4.43, found: C 44.91, H 5.58, N 4.44. ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.87 (dd, $^{3}J_{H,H}$ = 8.7 Hz, $^{3}J_{H,P}$ = 8.7 Hz, 4 H, *o*-Ph), 7.41 (m, 4 H, *m*-Ph), 7.40 (m, 2 H, *p*-Ph), 3.96 (dd, $^{2}J_{H,H}$ = 12.3 Hz, $^{3}J_{H,H}$ = 2.1 Hz, 2 H, NCH_2), 3.64 (dd, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 3.9 Hz, 2 H, NCH_2), 2.94 (dm, $^{3}J_{H,P}$ = 31.7 Hz, 1 H, CH), 2.74 (dd, $^{2}J_{H,P}$ = 9.8 Hz, $^{3}J_{H,H}$ = 4.0 Hz, 2 H, PCH_2), 1.07 (s, 18 H, CMe_3); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 135.6 (d, $^{1}J_{C,P}$ = 22.6 Hz, *ipso*-Ph), 132.0 (d, $^{3}J_{C,P}$ = 12.4 Hz, *m*-Ph), 130.2 (d, $^{4}J_{C,P}$ = 2.0 Hz, *p*-Ph), 129.0 (d, $^{2}J_{C,P}$ = 8.9 Hz, CH, *o*-Ph), 56.3 (s, NCH_2), 56.2 (d, $^{3}J_{C,P}$ = 1.7 Hz, CMe_3), 36.5 (d, $^{2}J_{C,P}$ = 3.5 Hz, CH), 27.7 (s, CMe_3), 25.9 (d, $^{1}J_{C,P}$ = 11.6 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = −1.8 (s).

[PN_2]ZrBn$_2$ (7-Zr). Solid $Bn_2MgBn_2(THF)_2$ (65.0 mg, 184 μmol, 1.00 eq.) was added in small portions to a vigorously stirred suspension of **6-Zr** (100 mg, 184 μmol, 1.00 eq.) in toluene (5 mL) maintained at −78 °C. The resulting reaction mixture was allowed to warm to room temperature over the course of 1 h and the brown suspension filtered subsequently. The filtrate was evaporated and the residue taken up in approximately 1 mL dichloromethane and filtered once again. The clear beige filtrate was layered with pentane (8 mL) and the stored at −30 °C overnight resulting in the formation of beige needle-shaped crystals. These were separated from the clear brownish supernatant by decantation and dried in vacuum to afford the title compound in form of beige needles (84.0 mg, 128 μmol, 70%). In multiple attempts low carbon values were obtained upon combustional analysis (*e.g.* calcd for $C_{38}H_{49}N_2PZr$: C 69.57, H 7.53, N 4.27, found: C 68.88, H 7.32, N 4.57), possibly due to carbide formation during combustion. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.41 (dd, $^{3}J_{H,H}$ = 8.0 Hz, $^{3}J_{H,P}$ = 8.0 Hz, 4 H, *o*-Ph), 7.22 (t, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, axial *m*-Bn), 7.18 (m, 2 H, equatorial *m*-Bn) 7.10 (dd, $^{3}J_{H,H}$ = 7.7 Hz, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, axial *o*-Bn), 7.04 (m, 4 H, *m*-PPh), 7.04 (m, 2 H, *p*-PPh), 7.02 (m, 2 H, equatorial *o*-Bn), 6.92 (t, $^{3}J_{H,H}$ = 8.1 Hz, 1 H, axial *p*-Bn), 6.88 (d,$^{3}J_{H,H}$ = 8.1 Hz, 1 H, equatorial *p*-Bn), 3.33 (d, $^{2}J_{H,H}$ = 12.9 Hz, 2 H, NCH_2), 3.04 (dd, $^{2}J_{H,H}$ = 13.2 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 2 H, NCH_2), 2.53 (d, 2 H, $^{3}J_{H,P}$ = 0.4 Hz, axial CH_2Ph), 2.35 (d, $^{3}J_{H,P}$ = 2.0 Hz, 2 H, equatorial CH_2Ph), 1.98 (m, 1 H, CH), 1.96 (s, 2 H, PCH_2), 1.08 (d, $^{5}J_{H,P}$ = 2.9 Hz, 18 H, CMe_3); $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 139.2 (d, $^{1}J_{C,P}$ = 6.3 Hz, *ipso*-PPh), 132.9 (d, $^{2}J_{C,P}$ = 17.3 Hz, *o*-Ph), 129.2 (s, *p*-Ph), 129.1 (s, axial *m*-Bn), 128.9 (d, $^{1}J_{C,P}$ = 5.2 Hz, *m*-Ph), 128.8 (s, equatorial *m*-Bn), 126.7 (s, axial *o*-Bn), 126.6 (s, equatorial *o*-Bn), 121.3 (s, axial *p*-Bn), 120.9 (s, equatorial *o*-Bn), 64.2 (d, $^{2}J_{C,P}$ = 18.8 Hz, axial CH_2Ph), 61.5 (d, $^{2}J_{C,P}$ = 10.5 Hz, equatorial CH_2Ph), 57.2 (s, CMe_3), 55.6 (d, $^{3}J_{C,P}$ = 5.8 Hz, CH_2, NCH_2), 40.5 (s, CH), 30.3 (s, PCH_2), 28.8 (s, CMe_3); $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −17.7 (s).

Conclusions

In summary, the phosphine-tethered diamidophosphines ^{pr}[NPN]H_2 and ^{bn}[NPN]H_2 were prepared and the structures of their group 4 complexes analysed in solution and in the solid state. In contrast to the known [NPN] ligands with five-membered chelates, these systems incorporate six-membered chelates and form complexes that adopt C_1-symmetric solid state structures. In solution, an averaged C_S-symmetry was found for the ^{pr}[NPN]-coordinated species (**1-M**, **2-M**, **3-Zr**), but not for the ^{bn}[NPN]-coordinated derivatives (**4-M**, **5-M**). Based on these findings, the ligand backbones in ^{pr}[NPN]H_2 and ^{bn}[NPN]H_2 were modified and the new facially coordinating diamidophosphine [PN_2]H_2 was designed. This trimethylene-methane-tethered tripod was then prepared and its coordination chemistry examined employing group 4 metals. In the case of **6-M** and **7-Zr**, C_S-symmetric structures were detected not only in solution, but also in the solid state. The dibenzyl derivative **7-Zr** was found to be well-soluble in (commonly) inert solvents (*e.g.* in C_6H_6) and was therefore identified as the most promising candidate for future reactivity studies. In a wider context, the three new diamidophosphines reported herein certainly contribute to diminish the "development gap" between [PNP] and [NPN] ligands, although late transition metal complexes of the new ligands have not yet been explored. Nevertheless, the arrangement of the three donor atoms within the new [PN_2] system allowed for an adaption to different metal radii (Ti *vs.* Zr), which provides a basis for further studies directed towards the complexation of other metals. These efforts are currently ongoing in our laboratory in addition to an extensive screening for applications of the new group 4 complexes in catalysis.

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