ORGANOMETALLICS
Communication
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A Novel Trisamidophosphine Ligand and Its Group(IV) Metal Complexes

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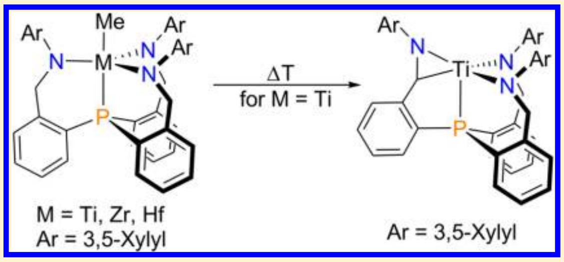
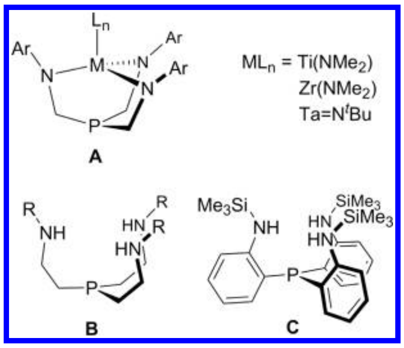
Supporting Information

ABSTRACT: A novel trisamidophosphine ligand scaffold has been synthesized and employed to coordinate all of the group(IV) metals. The resulting complexes feature closed half-cage geometries with the phosphorus donor and all three amides binding to the metal. Out of nine complexes of the type [PN$_3$]MX (M = Ti, Zr, Hf; X = NMe$_2$, OTf, CH$_3$), the zirconium derivatives have been studied by X-ray diffraction and shown to exhibit metal−phosphorus distances that are well in range of a coordinative bond. In contrast to its heavier homologues, the titanium methyl species [PN$_3$]TiMe is prone to thermally induced ligand CH activation with concomitant loss of methane.



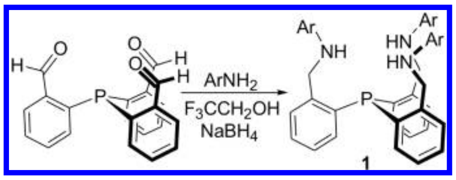
Ligands combining hard and soft donor functionalities (so-called hybrid ligands) are frequently used in cases that require a high degree of electronic flexibility at the coordinated metal ion. Amidophosphines are certainly among the most prominent hybrid ligand systems and have been widely applied, inter alia, to support metal-catalyzed hydrosilylations, (de)-hydrogenations, and polymerizations as well as numerous noncatalytic transformations.[1] The amidophosphine ligand family is commonly categorized by the ligands' number of N- and P-donor sites, and the resulting subclasses are then abbreviated as [NP],[2] [NPN],[3] [PNP],[4] and [P$_2$N$_2$].[5] While all of the former NP combinations have been well explored, [PN$_3$]-based systems are fairly underdeveloped, with coordination compounds of only one tris-anionic trisamidophosphine ligand scaffold reported so far (complexes **A**; see Scheme 1).[6] A closer look, however, reveals that the central metal of the latter methylene-linked system **A** is coordinated by three amides only with the phosphine lone pair pointing away from the metal (*exo*-P configuration). Thus, polynuclear species are formed easily, while the interaction between the phosphine and the amido-coordinated metal ion is limited substantially.[6]

Scheme 1. Known Methylene-Linked Trisamidophosphine Complexes A and the C$_2$-Linked Trisaminophosphine Ligands B and C



Trisaminophosphines with ethylene or phenylene NP linkers are known as well (**B** with R = H, SiMe$_3$ and **C**; see Scheme 1),[7] but no coordination compounds of these ligands have been reported so far.[8] In case of **B** (R = SiMe$_3$), it is documented that attempts to prepare molybdenum complexes led to the formation of insoluble materials instead of well-defined complexes.[7a] A possible explanation for this finding is that the hypothetical coordination of all four donor atoms might generate highly strained cages, which in turn favors the formation of *exo*-P-configured and polynuclear systems. This hypothesis is supported by a computational study on sila-[PN$_3$] cages, which predicts the *exo*-P configuration to be lower in energy in the case of ligand **B** (R = H). The latter study finally arrived at the conclusion that the cage configuration (*exo*-P vs *endo*-P) is mainly dependent on the linkage between the phosphine and the amido donor atoms.[9] As these sila-[PN$_3$] cages are predicted to favor the desired *endo* configuration in case of C$_3$ linkages (propylene or benzylene spacers), we turned our attention to the benzylene-linked trisaminophosphine **1** (see Scheme 2), bearing in mind that related neutral trisamino [PN$_3$] derivatives have been studied earlier.[10] The targeted protio ligand H$_3$[PN$_3$] (**1**) was synthesized starting from the corresponding trisaldehyde[11]

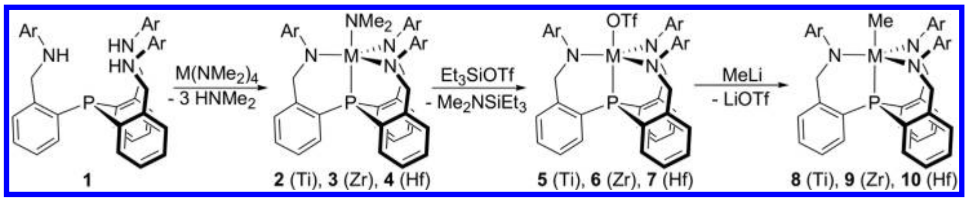
Scheme 2. Synthesis of H$_3$[PN$_3$] (1; Ar = 3,5-Xylyl)



Received: October 18, 2013
Published: January 24, 2014

dx.doi.org/10.1021/om401018f | *Organometallics* 2014, 33, 612−615

Scheme 3. Syntheses of Complexes 2−10 (M = Ti, Zr, Hf, Ar = 3,5-Xylyl)



via reductive amination. A method described by Tajbakhsh and co-workers[12] employing sodium borohydride in 2,2,2-trifluoroethanol was utilized for this purpose, and the protio ligand **1** was obtained in acceptable yield (51%) and high purity after recrystallization from ethanol (see Scheme 2).

Complexes of titanium, zirconium, and hafnium were obtained by the reaction of **1** with the corresponding tetrakis(dimethylamido) precursors of the group(IV) metals. These conversions proceeded cleanly to afford the corresponding dimethylamido complexes [PN$_3$]M(NMe$_2$) (M = Ti (**2**), Zr (**3**), Hf (**4**)) in good yields (70−85%) (Scheme 3). Interestingly, **3** and **4** are formed within 2 h at 75 °C, while the respective titanium complex (**2**) requires higher temperatures (120 °C in toluene) and prolonged reaction times (3 days) to reach full conversion. In each case, the reaction can be monitored by ^{31}P NMR spectroscopy, as the formation of the dimethylamido complexes is indicated by the emergence of new signals at −46.0 (**2**), −46.5 (**3**), and −51.0 ppm (**4**) and a decreasing intensity of the signal of **1** (−36.5 ppm). The ^{1}H and ^{13}C NMR spectra of **2**−**4** are indicative of C_3-symmetric complexes, with only one resonance each observed for the equivalent sets of atoms of the individual side arms. The resonance for the six methylene protons is broadened, possibly due to the dimethylamido group, which disrupts the global symmetry to some extent. The observed upfield shift of the ^{31}P NMR signals upon complex formation is rather counterintuitive,[6d] as the coordination of the phosphorus lone pair to a metal center is usually accompanied by a deshielding of the phosphorus nucleus. To elucidate this phenomenon, the molecular structure of **4** was determined in the solid state by means of single-crystal X-ray diffraction. Suitable crystals for this purpose were grown by slow diffusion of pentane into a solution of the complex in toluene at −40 °C (see Figure 1). In accordance with the NMR data, X-ray analysis overall confirms the expected approximate C_3-symmetric half-cage structure, with the three amido moieties holding the central metal in place. The configuration at the phosphorus atom is revealed to be *endo* with a Zr−P distance of 2.824(1) Å, which is in the range of those of comparable amidophosphine complexes.[13] The trigonal-bipyramidal coordination sphere is completed by the remaining apical dimethylamido ligand, which is positioned *trans* with respect to the phosphine (N4−Zr−P 173.13(5)°). To confirm that the observed *endo* configuration is maintained in solution, variable-temperature NMR spectroscopic studies were performed, but no differences between the ^{31}P and ^{1}H spectra were recognized upon comparison of the room-temperature spectra to those taken at −80 °C. Thus, we propose that the structures in the solid state and solution are fairly equivalent. DFT studies of complexes **2**−**4** (including NBO calculations and second-order perturbation analyses in NBO basis) indicate the presence of donor−acceptor interactions between filled phosphorus-centered and virtual metal-centered orbitals. Wiberg bond indices of approximately 0.5 were determined for the metal−phosphine interaction in **2** - **4** (see the Supporting Information).

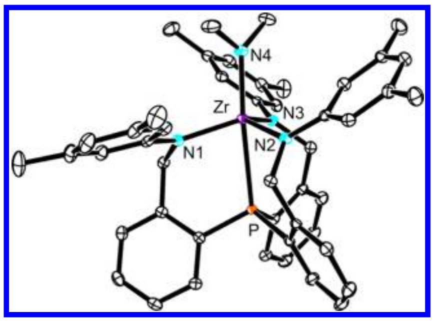


Figure 1. ORTEP diagram of **3** (solvent molecules and protons omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths (Å) and angles (deg): Zr−N4 2.050(2), Zr−N1 2.088(2), Zr−N2 2.099(2), Zr−N3 2.129(2), Zr−P 2.824(1); N4−Zr−N1 105.67(6), N4−Zr−N2 102.96(6), N1−Zr−N2 108.93(6), N4−Zr−N3 96.35(6), N1−Zr−N3 124.14(6), N2−Zr−N3 115.10(7), N4−Zr−P 173.13(5), N1−Zr−P 79.65(5), N2−Zr−P 78.97(5), N3−Zr−P 76.93(5).

In order to convert the dimethylamido complexes **2**−**4** to the corresponding halides [PN$_3$]M(Hal), reactions with trimethylsilyl halides were studied. Upon treatment of **4** with trimethylsilyl chloride (Me$_3$SiCl) in toluene, incomplete conversion with concomitant formation of several unidentified side products was observed. Employing a slight excess of Me$_3$SiCl or heating the former mixture resulted in extensive decomposition. In some cases, purification of the reaction mixture via crystallization was pursued (see the Supporting Information for the X-ray structure of [PN$_3$]ZrCl); however, the exchange of the dimethylamido groups for halides seemed to be unreliable and hardly reproducible in general. This is not the case when triethylsilyl trifluoromethanesulfonate is used instead. Thus, the dimethylamido complexes **2**−**4** were cleanly converted into the corresponding triflates [PN$_3$]MOTf (M = Ti (**5**), Zr (**6**), Hf (**7**)) in good yields (60−80%) and under mild conditions. Similar to the case for **2**−**4**, the ^{1}H NMR spectra of **5**−**7** reveal a 3-fold symmetry, indicating either free rotation of the coordinated triflates or the presence of noncoordinating triflato anions in solution. The ^{31}P NMR shifts (−31.8 ppm (**5**), −43.1 ppm (**6**), −34.9 ppm (**7**)) suggest these complexes to have a stronger P−M interaction than the dimethylamido compounds, which is consistent with weakly coordinating or noncoordinating triflates. To further elucidate the nature of the M−OTf interaction, single crystals of **6** were grown by slowly cooling a saturated solution of the complex in toluene to −40 °C. In **6**, the ligand coordinates in the expected fashion, forming a half-cage complex (see Figure 2). The coordinated ancillary triflato anion completes the trigonal-bipyramidal coordination geometry, which resembles the binding situation found in **3**.[14] In comparison to **3**, the metal−N (approximately 2.06 Å) and metal−P (2.720(7) Å) bond lengths are slightly shorter in **6**, suggesting a stronger zirconium−ligand interaction. The stronger metal−phosphine interactions in **5**−**7** have also been confirmed by DFT studies. NBO analysis indicates the presence

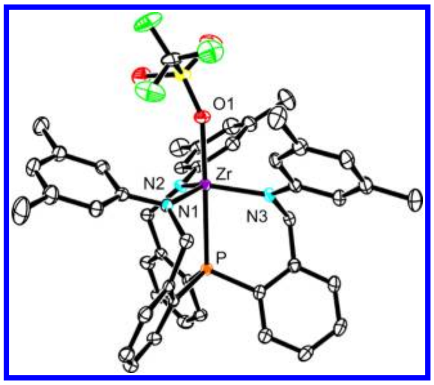


Figure 2. ORTEP diagram of **6** (solvent molecules and protons omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths (Å) and angles (deg): Zr−P 2.7199(7), Zr−O1 2.148(2), Zr−N1 2.062(2), Zr−N2 2.065(2), Zr−N3 2.066(2); O1−Zr−P 178.14(5), N1−Zr−P 81.05(6), N1−Zr−O1 99.22(8), N1−Zr−N2 119.05(8), N1−Zr−N3 113.96(8), N2−Zr−P 80.47(6), N2−Zr−O1 97.82(8), N2−Zr−N3 119.79(8), N3−Zr−P 81.55(6), N3−Zr−O1 99.99(8).

of polarized metal−phosphorus bonds (approximately 80% P centered and 20% metal centered) with Wiberg bond indices of approximately 0.6 (see the Supporting Information).

Treatment of the triflato complexes **5**−**7** with a solution of methyllithium at −78 °C in toluene afforded the corresponding methyl complexes $[PN_3]MCH_3$ (M = Ti (**8**), Zr (**9**), Hf (**10**)) in acceptable yields (50−60%). The ^1H NMR spectra again indicate the presence of C_3-symmetric species in solution, with only one set of side arm signals present. The protons of the methyl groups resonate at 1.93 ppm (**8**), 0.40 ppm (**9**), and 0.22 ppm (**10**), respectively, and the ^{31}P NMR spectra exhibit singlets in all cases (−58.0 ppm (**8**), −58.5 ppm (**9**), and −54.7 ppm (**10**)). The observed upfield shift of the ^{31}P NMR resonances once more supports that the phosphine is actually coordinated in solution. NBO calculations including second-order perturbation analyses on **8**−**10** suggest the presence of donor−acceptor interactions between the individual lone pairs at phosphorus and metal-centered virtual orbitals. In case of **8**, electron delocalization involves an antibonding Ti−Me orbital (see the Supporting Information). Wiberg bond indices for the metal−phosphine interactions in **8**−**10** (approximately 0.5) are roughly equivalent to the respective indices determined for **2**−**4** (see the Supporting Information, Table S4). Single crystals of the zirconium methyl complex **9** were generated by cooling a freshly prepared solution of **9** in dichloromethane to −40 °C (see Figure 3). X-ray diffraction analysis of these crystals revealed that the molecular structure of **9** compares well to the structures of **3** and **6**, as all species exhibit trigonal-bipyramidal coordination spheres with local C_3 symmetry at the central metals. With respect to the $[PN_3]Zr$ fragment, the metric parameters of the dimethylamido (**3**) and methyl (**9**) species are fairly similar, with the Zr−P bond length being slightly shorter (2.807(8) Å) in the case of **9**. In comparison to other zirconium methyl complexes, the Zr−C bond length (2.286(3) Å) in **9** is found within the usual boundaries.[13]

Both the zirconium and hafnium methyl species (**9** and **10**) are temperature-sensitive and decompose in an nonspecific manner upon heating, while no signs of hydrides were evident upon addition of gaseous H_2 (10 bar). The titanium system (**8**), however, is cleanly converted upon heating (75 °C for 2 h) to afford the CH-activated product **11** shown in Scheme 4 along with methane (detected by ^1H NMR). The difference in reactivity between **8** and both heavier homologues might very well be explained by the aforementioned electron delocalization, which involves a $\sigma^*_{\mathrm{Ti-Me}}$ orbital in the case of **8**. As single crystals of **11** suitable for X-ray diffraction could not be obtained, careful analysis by ^{31}P, ^1H, and ^{13}C and various two-dimensional NMR techniques (see the Supporting Information) was employed to establish the proposed structure of **11**. What is evident from the ^1H NMR spectrum of **11** is that the overall C_3 symmetry is lost and that only five protons for the ligand's benzylic positions are observed. One of these benzylic signals (singlet at 4.17 ppm) is coupled to no other proton (according to ^1H,^1H−COSY) but is found in coupling range to the ^{31}P nucleus (^1H,^{31}P-HMBC cross peak) and therefore assigned to the CH-activated methyne position. A matching ^{13}C resonance was found at 83.9 ppm, and the assignment was ascertained by HSQC spectroscopy. APT and DEPT spectra confirmed that this ^{13}C signal indeed corresponds to a methyne group.

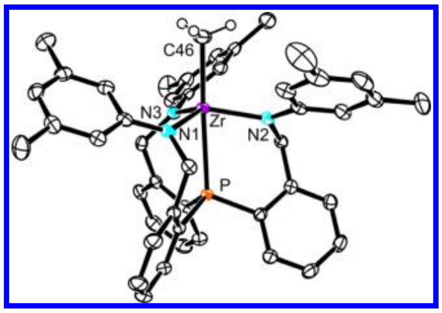
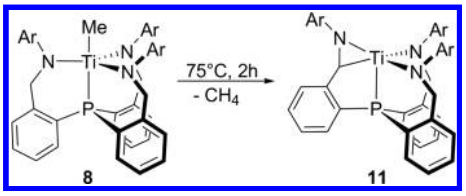


Figure 3. ORTEP diagram of **9** (solvent molecules and protons omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths (Å) and angles (deg): Zr−N2 2.085(3), Zr−N1 2.092(3), Zr−N3 2.095(3), Zr−C46 2.286(3), Zr−P 2.807(8); N2−Zr−N1 118.0(1), N2−Zr−N3 114.7(1), N1−Zr−N3 115.9(1), N2−Zr−C46 100.0(1), N1−Zr−C46 99.5(1), N3−Zr−C46 104.6(1), N2−Zr−P 77.88(7), N1−Zr−P 78.64(7), N3−Zr−P 79.40(7), C46−Zr−P 176.0(1).

Scheme 4. Synthesis of 11 Starting from 8 (Ar = 3,5-Xylyl)



Particularly interesting is the observed ^{31}P resonance of **11** at +46.1 ppm (singlet), as it experienced a downfield shift of over 100 ppm in comparison to the signal for **8** (−58.0 ppm). This observation is in accordance with DFT calculations on **11**, which suggest a rather strong coordination of the central phosphine (Ti−P_{calcd} 2.425 Å) with a Wiberg bond index of approximately 0.74 (bonding interaction indicated by NBO analysis; see the Supporting Information). Thus, the experimentally and computationally obtained results are both in agreement with the proposed structure of **11**.

In conclusion, we synthesized a tripodal trisamidophosphine ligand and explored its coordination chemistry with the group(IV) metals. Nine complexes of the type $[PN_3]MX$ (M = Ti, Zr, Hf, X = NMe_2, OTf, CH_3; **2**−**10**) and the CH-activated species **11** have been prepared and the molecular structures of the zirconium derivatives elucidated by X-ray diffraction. To the best of our knowledge, **1** is the first example of a tris-anionic trisamidophosphine ligand that coordinates in a tetradentate fashion. Studies directed toward the application of **11**, for example in dehydrocoupling reactions,[15] are currently under way in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures and characterization data for the preparation of **1**−**11**, including ^{1}H and ^{31}P NMR spectra, X-ray characterization data for **2**, **6**, **9**, and [PN$_3$]ZrCl, and computational results and Cartesian coordinates for **1**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the *Fond der Chemischen Industrie* (Liebig-Stipenium for J.B. and FCI-Doktorandenstipendium for M.S.) The authors thank Prof. L. H. Gade for generous support and helpful discussions and S. Batke as well as C. Blasius for experimental assistance. We are grateful to an unknown reviewer who brought ref 7a to our attention.

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