

## Improved One-Pot Synthesis of C<sub>3</sub>-Symmetric ClickPhos and Related Ligands: Structures of Unique Triazole–Zinc Complexes

Daniel M. Zink,<sup>[a,b]</sup> Thomas Baumann,<sup>\*[b]</sup> Martin Nieger,<sup>[c]</sup> and Stefan Bräse<sup>\*[a]</sup>

**Keywords:** ClickPhos / Triazole / Click chemistry / Zinc / Helical structures

A number of ClickPhos-type ligands have been prepared by using an improved one-pot procedure. Several [tris(triazolyl)-

phosphane]zinc complexes have been synthesized and characterized by X-ray structure analyses.

### Introduction

The synthesis of novel modular ligand systems has gained considerable attention due to their pivotal role in metal catalysis. Consequently, the need for efficient routes to such compounds is of increasing interest. In the field of cross-coupling reactions mono- and bidentate ligands based on the triazole scaffold **4**<sup>[1]</sup> have been successfully employed as potent catalysts<sup>[2]</sup> in several processes, for example Suzuki reactions or the amination of aryl chlorides.<sup>[3]</sup> In addition, chiral variants have been used for hydrogenation reactions, allylic substitution reactions or reductive aldol reactions.<sup>[4]</sup>

Most of such ligands can be synthesized according to Sharpless by a two-step procedure.<sup>[5]</sup> Even though Zhang et al. reported a one-pot synthesis to furnish various members of the ClickPhos family, they preferred the two-step procedure by Sharpless, because of an easier purification of the products.<sup>[2]</sup> Nevertheless, we used and improved the above described one-pot synthesis by Zhang et al. to provide an easy access not only to members of the ClickPhos family, but also to bis- and tris(triazolyl)phosphanes. These kinds of bi- and tridentate ligands have only been described in the literature by Lammertsma et al.,<sup>[6]</sup> but for their synthesis, which makes use of “classic” click conditions, they state that the phosphorus center has to be protected in order to prevent a Staudinger reduction to occur. This protection not only requires a final deprotection procedure to furnish

the ClickPhos ligand, but also extends the reaction sequence to a total of 4 steps, while in our case the one-pot synthesis allows for a simple preparation and modulation of the corresponding ClickPhos ligands. In addition, by use of our protocol, we can also introduce an additional substituent in position 5 of the triazole ring, which is not accessible by means of classic click chemistry.

Crystal structures of metal complexes with mono-, bis- or tris(triazolyl)phosphanes are very rare in the literature. Except for the work by Lammertsma et al. in which phosphor and nitrogen coordination was combined to give access to a dimetallic Mo/W complex, there are, to the best of our knowledge, no other complexes with tris(triazolyl)phosphanes as ligands. Although, some very few complexes with triazolylphosphanyl- or triazolylphosphanothiyl as bidentate ligands coordinating through the nitrogen atom and the oxygen or rather the sulfur atom instead of the phosphorus atom, e.g. with Co, Rh, Ni,<sup>[7]</sup> and Pd,<sup>[8]</sup> are known, metal complexes with mono- or bis(triazolyl)phosphanes with a bidentate phosphorus/nitrogen complexation behavior have not yet been reported.

### Results and Discussion

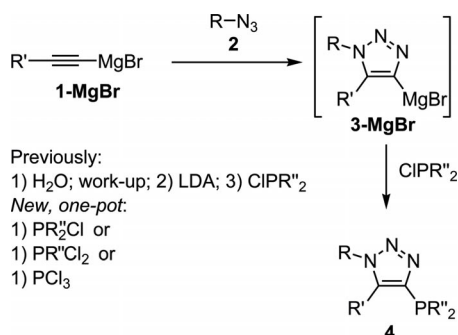
As described in the original paper,<sup>[5]</sup> by starting from an azide, the reaction with an alkynylmagnesium salt leads to a metallated triazole intermediate **3-MgBr**. Aqueous workup, metallation with LDA and treatment with chlorophosphanes gives rise to the ClickPhos family.<sup>[2]</sup> Herein we report a simplified and optimized procedure,<sup>[9]</sup> which allows for the synthesis of a number of new members of this family. For the first step, we used the procedure as described by Sharpless et al. employing the Grignard reagents to form the corresponding magnesium salt **1** starting with an alkyne at low temperature. Subsequent addition of aryl or alkyl azides **2** (1.10 equiv.)<sup>[10]</sup> at slightly elevated temperature forms the triazolylmagnesium salt **3-MgBr** (Scheme 1).

[a] Institute for Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany  
Fax: +49-721-608-8581  
E-mail: braese@kit.edu

[b] Cynora GmbH, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[c] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P. O. Box 55 (A.I. Virtasen aukio 1), 00014 University of Helsinki, Finland

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Scheme 1. Conventional and improved synthesis of ClickPhos members.<sup>[9]</sup>

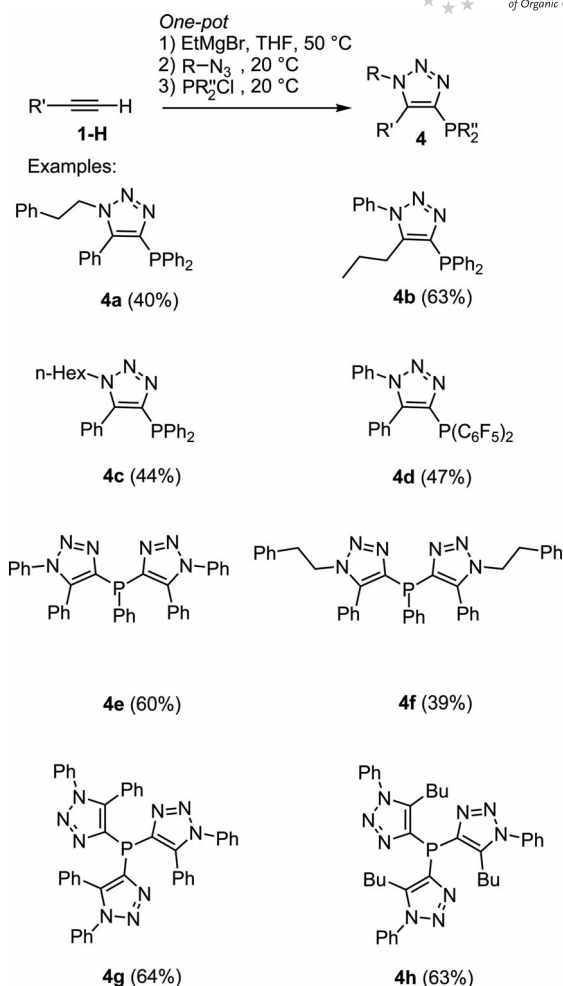
Direct treatment of these salts with various diarylchlorophosphanes (1.20 equiv.) furnished the triazoles **4a–d** in moderate to good yields. This method can be carried out on a gram scale, while the yields are comparable with the two-step procedure described by Zhang et al.<sup>[2]</sup> The only by-products are the protonated triazoles **3-H** (7–27%), which can be removed easily by flash chromatography.

This new method was extended to dichloro(phenyl)phosphanes, which results in the formation of novel bis(triazolyl)phosphanes **4e,f**. In addition, the use of phosphorus trichloride<sup>[11]</sup> allowed for the synthesis of new tris(triazolyl)phosphanes **4g,h** in good yields. The latter ligands are related to the well-known scorpionate ligands (Scheme 2).<sup>[12]</sup>

In order to proof their complex formation ability, we synthesized several zinc complexes by reaction of the triazolyl ligands with the corresponding zinc halide in dichloromethane, with the complexation being completed after a few hours. The purification of the complexes was achieved by precipitation of the filtered reaction mixture in cyclohexane. The synthesized complexes are summarized in Table 1, and the three-dimensional structure of the tris(triazolyl)phosphane ligand **4g** and two corresponding zinc complexes of **4h** (**6**) and **4g** (**7**) were determined by X-ray structure analysis.

As seen in Figure 1, the tris(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)phosphane (**4g**) has a helical structure and C<sub>3</sub> symmetry. The phosphorus atom is coordinated by three carbon atoms, which form, together with the free electron pair of the central phosphorus atom the corners of a tetrahedron. This geometry can therefore undergo several different coordination modes such as a tripodal complexation involving three nitrogen atoms, one from each triazol ring, thereby behaving like the related tris(pyrazolyl)phosphane oxide that complexes to Cu<sup>I</sup>,<sup>[13a]</sup> ZnCl<sub>2</sub>,<sup>[13a]</sup> Ti<sup>I</sup>,<sup>[13b]</sup> and Mo(CO)<sub>3</sub>.<sup>[13c]</sup> (Figure 1). Another possibility to coordinate to a metal atom is provided by the lone electron pair of the phosphorus atom. In addition, both coordination modes can occur within the same complex. All of these different coordination modes have been shown by Lammertsma et al.<sup>[6]</sup> in several carbonyl[tris(triazolyl)phosphane]rhodium, -tungsten, or -molybdenum complexes.

The crystal structure analysis of compound **6** revealed the a charged complex, with the cationic part consisting of



Scheme 2. Synthesis of new ClickPhos members. For details, see the Exp. Sect.

Table 1. Synthesized zinc complexes.

Compound	Ligand	Metal salt	Stoichiometry <sup>[a]</sup>	Yield [%]
<b>5</b>	<b>4g</b>	ZnBr <sub>2</sub>	[L <sub>2</sub> Zn][Zn <sub>2</sub> Br <sub>6</sub> ]	11
<b>6</b>	<b>4h</b>	ZnBr <sub>2</sub>	[L <sub>2</sub> Zn][Zn <sub>2</sub> Br <sub>6</sub> ]	30
<b>7</b>	<b>4g</b>	ZnI <sub>2</sub>	LZnI <sub>2</sub>	85

[a] Based on mass spectrometry and X-ray crystallography.

two tris(triazolyl)phosphane ligands together with a zinc ion, and the anionic part being composed of two zinc and four bromide ions. In the twofold positively charged cationic part, the zinc ion is octahedrally coordinated by six nitrogen atoms of two tris(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)phosphane ligands. The coordination to the metal core occurs solely by the nitrogen atom in 3-position of the triazole ring, which results in very similar zinc–nitrogen bond lengths in the range of 2.103–2.196 Å. This cationic part of the complex exhibits an inversion centre on the zinc ion and a twofold screw axis. The counter anion of the complex, which is formed by two zinc and six bromide ions, has the

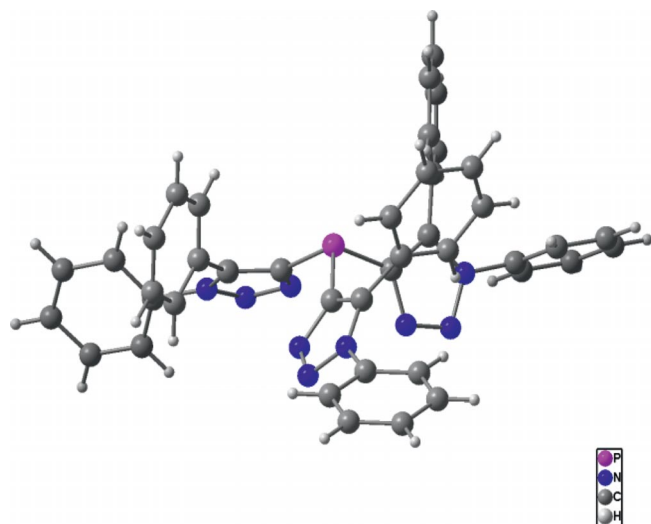


Figure 1. X-ray structure of tris(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)phosphane (**4g**).

structure of two edge-sharing tetrahedrons (Figure 2). It possesses therefore three mirror planes, an inversion centre and three twofold screw axes.<sup>[14]</sup>

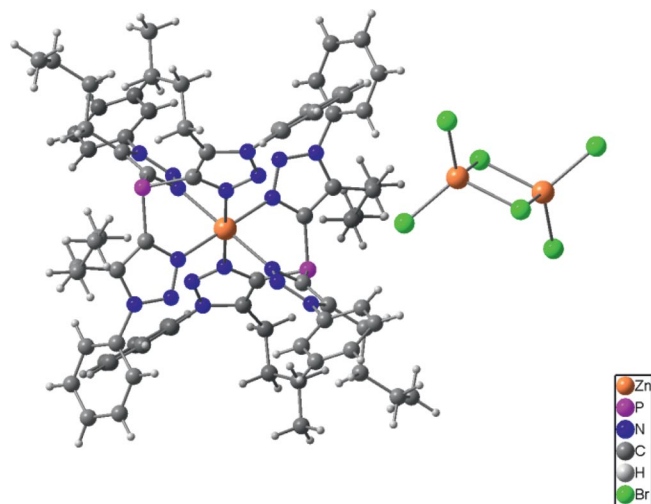


Figure 2. X-ray structure of complex **6**.

Although several characterization techniques such as mass spectrometry suggest an identical coordination mode and geometry to that of complex **6**, we have not been able to obtain any suitable crystals of complex **5** for X-ray analysis yet.

In contrast, complex **7** adopts an “open” structure by coordination of only two nitrogen atoms of one tris(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)phosphane (**4g**), and two iodide ions in a distorted tetrahedral coordination. The third triazole ring is rotated away from any complexation ability and therefore prevents a third nitrogen coordination of the zinc ion (Figure 3).

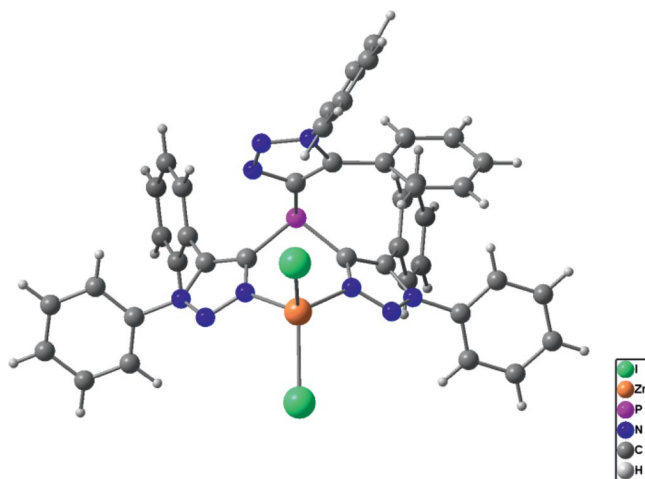


Figure 3. X-ray structure of complex **7**.

Since both complexes **6** and **7** feature an almost identical ligand system, a rational explanation for the different geometrical structures might account for the different zinc halides. On the one hand, the structure of tetrahedrally coordinated zinc complexes is well known in the literature, and therefore, it appears that complex **7** represents the expected structural motif for this kind of complexes. On the other hand, zinc complexes with an octahedrally coordinated zinc ion are also widely established in the literature. In the case of complex **6**, the formation of the unusual counterion  $[\text{Zn}_2\text{Br}_6]^{2-}$  to compensate for the positive charge could facilitate the octahedral coordination of the central zinc ion by two triazole ligands. Even though an equivalent structural motif for  $[\text{Zn}_2\text{I}_6]^{2-}$  exists in the literature (although in contrast to  $[\text{Zn}_2\text{Cl}_6]^{2-}$ , a structurally well-characterized species), only a few examples of  $[\text{Zn}_2\text{Br}_6]^{2-}$  and  $[\text{Zn}_2\text{I}_6]^{2-}$  are known.<sup>[15]</sup> Therefore, there is no obvious reason, why in the case of complex **6** dismutation into a fully nitrogen-coordinated cation and a fully halide-coordinated anion has occurred. The formation of the tetrahedral complex **7** might result from the lower donor strength of the triazole nitrogen atom, which cannot compete against the two iodide ligands for coordination to the zinc atom. Eventually, the size of the halide atoms is also important for the formation of either complex **6** or complex **7**.

Another explanation might consider the formation of a second coordination sphere out of two complexes as some kind of loose dimer with distorted trigonal-bipyramidal geometry, in which the two nitrogen atoms and I2 adopt the equatorial positions and I1 and I2(#1) the axial positions. In each moiety, one of the iodine atoms acts as a bridging ligand to the zinc ion of the other moiety, whereas the other iodide ion is a terminal ligand (Figure 4). Such pentacoordinate zinc complexes represent a well-known structural motif,<sup>[16]</sup> but so far only a few examples with a pentacoordinate zinc ion including two iodide ions and no example for a pentacoordinate complex including three iodide ions have been reported. The Zn(1)–I(1) distance with 2.54 Å is in the range of comparable complexes with covalent Zn–I bonds;<sup>[16c]</sup> however, the Zn(1)–I(2)#1 distance with 4.28 Å

lies in the range of literature-known ionic interactions between Zn and I.<sup>[17]</sup> According to these values, a second coordination sphere in the crystal structure of complex **7**, which is formed through ionic interactions between two zinc and two iodide ions, might be taken into account (Table 2).

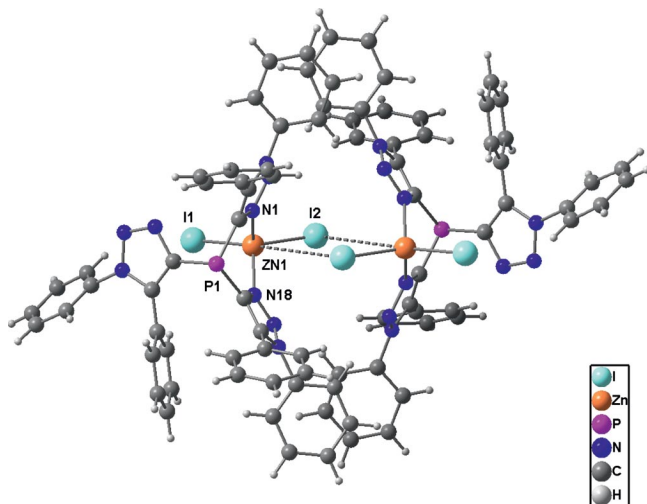


Figure 4. Second coordination sphere of complex **7**.

Table 2. Selected bond lengths [Å] and angles [°] for **7**.<sup>[a]</sup>

I(1)–Zn(1)	2.5434(6)
I(2)–Zn(1)	2.5436(6)
I(2)–Zn(1)#1	4.2836(7)
I(2)–I(2)#1	4.3055(6)
Zn(1)–N(1)	2.075(3)
Zn(1)–N(18)	2.086(3)
Zn(1)–I(2)#1	4.2836(7)
Zn(1)–I(2)–Zn(1)#1	106.754(15)
Zn(1)–I(2)–I(2)#1	72.302(15)
Zn(1)#1–I(2)–I(2)#1	34.451(9)
N(1)–Zn(1)–N(18)	91.18(11)
N(1)–Zn(1)–I(1)	113.39(8)
N(18)–Zn(1)–I(1)	112.41(8)
N(1)–Zn(1)–I(2)	109.65(8)
N(18)–Zn(1)–I(2)	112.05(8)
I(1)–Zn(1)–I(2)	115.649(18)
N(1)–Zn(1)–I(2)#1	61.33(8)
N(18)–Zn(1)–I(2)#1	62.03(8)
I(1)–Zn(1)–I(2)#1	171.105(15)
I(2)–Zn(1)–I(2)#1	73.246(15)

[a] Symmetry transformations used to generate equivalent atoms: #1:  $-x + 1, -y + 1, -z$ .

However, at this point, and based on the few examples, no clear explanations can be given so far. Further structural and theoretical investigations will help to better understand the parameters that effect the different coordination geometries.

## Conclusions

In order to simply access this kind of mono(triazolyl)-phosphane ligands, we improved the one-pot syntheses of

Zhang et al. for ClickPhos ligands. By modifying this synthetic route, we developed a possibility to synthesize bis- and tris(triazolyl)phosphane ligands. Several novel [tris(triazolyl)phosphane]zinc complexes have been prepared for the first time, and X-ray structure analyses revealed two different kinds of structures. We will explore these new ligands and complexes for their properties in catalysis, for example copper- and/or palladium-catalyzed cross coupling methodologies, such as Suzuki, Negishi or Sonogashira reactions.

## Experimental Section

**General:** All reactions were performed in oven-dried glassware under argon. Solvents and chemicals used were purchased from commercial suppliers. Solvents were dried by standard conditions. All materials were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel plates (Kiesel-gel 60, F254, Merck) with detection by UV spectroscopy. Purification was performed by preparative chromatography on normal-phase silica gel (Silica gel 60, 230–400 mesh, Merck). <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded with a Bruker AM 400 or a Bruker DRX 250 spectrometer. Chemical shifts are reported as  $\delta$  values (ppm). The signal abbreviations include: Ar-H = aromatic proton. The signals of the <sup>13</sup>C NMR spectra were allocated by the DEPT (Distortionless Enhancement by Polarisation Transfer) technology. The signal abbreviations include: C-Ar = aromatic carbon atom, + = primary or tertiary carbon atom, – = secondary carbon atom, C<sub>quat</sub> = quaternary carbon atom.

### 4,4'-(Phenylphosphanediy)bis(1,5-diphenyl-1H-1,2,3-triazole) (**4e**):

Ethylmagnesium chloride (2.0 M in tetrahydrofuran, 5.00 mL, 10.0 mmol, 2.00 equiv.) was diluted with dry tetrahydrofuran (10 mL). Phenylethyne (1.02 g, 10.0 mmol, 2.00 equiv.) was added slowly through cannula. After 15 min at 50 °C, the mixture was cooled to room temperature, and phenyl azide (1.31 g, 11.0 mmol, 2.20 equiv.) was added through cannula. The mixture was stirred at room temperature for 40 min and at 50 °C for 1 h, after which it was cooled to room temperature. Dichloro(phenyl)phosphane (0.89 g, 5.00 mmol, 1.00 equiv.) in dry tetrahydrofuran (10 mL) was added, and the mixture was stirred at room temperature for 4.5 h. The reaction was quenched with water (50 mL), the phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with brine (60 mL) and dried with magnesium sulfate. Purification by flash chromatography (4.5 cm, cyclohexane/ethyl acetate, 5:1 → 1:1) yielded 1.62 g (3.00 mmol, 60%) of an orange solid. M.p. 185–195 °C.  $R_f$  = 0.64 (cyclohexane/ethyl acetate, 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.95–6.97 (m, 2 H, Ar-H), 7.10–7.17 (m, 9 H, Ar-H), 7.20–7.27 (m, 10 H, Ar-H), 7.77–7.82 (m, 2 H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 124.9 (+, C-Ar), 126.8 (C<sub>quat</sub>), 128.2 (+, C-Ar), 128.3 (+, C-Ar), 128.8 (+, C-Ar), 129.0 (+, C-Ar), 129.0 (+, C-Ar), 129.4 (+, C-Ar), 130.0 (+, C-Ar), 130.1 (+, C-Ar), 133.0 (C<sub>quat</sub>), 134.7 (+, C-Ar), 134.9 (+, C-Ar), 136.4 (C<sub>quat</sub>), 140.5 (d, <sup>1</sup>J<sub>CP</sub> = 6.5 Hz, C<sub>quat</sub>), 142.0 (d, <sup>1</sup>J<sub>CP</sub> = 33.1 Hz, C<sub>quat</sub>, C-4, C-4') ppm. <sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = –57.5 ppm. IR (drift):  $\tilde{\nu}$  = 3065 (m), 2928 (m), 2853 (w), 2337 (w), 1967 (w), 1885 (w), 1815 (w), 1739 (m), 1595 (m), 1497 (m), 1448 (m), 1411 (m), 1271 (m), 1064 (m), 998 (m), 918 (m), 771 (m), 697 (m), 597 (m), 514 (m) cm<sup>–1</sup>. MS (70 eV, EI):  $m/z$  (%) = 548 (6)



[M<sup>+</sup>], 491 (6) [M<sup>+</sup> – 2 N<sub>2</sub>], 333 (13), 300 (15), 221 (30), 193 (100), 165 (48). HR-EIMS: calcd. for C<sub>34</sub>H<sub>25</sub>N<sub>6</sub>P 548.1878; found 548.1877.

[{Tris(5-butyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphane}<sub>2</sub>zinc]-[Zn<sub>2</sub>Br<sub>6</sub>] (**6**): Zinc bromide (104 mg, 0.47 mmol, 1.00 equiv.) and tris(5-butyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphane (**4h**) (300 mg, 0.47 mmol, 1.00 equiv.) were dissolved under nitrogen in dry dichloromethane (8 mL). The solution was stirred at room temperature for 12 h. The complex was precipitated in cyclohexane, filtered and dried in vacuo and obtained as a white solid (270 mg, 0.14 mmol, 30%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): δ = 0.63 (t, *J* = 7.3 Hz, 9 H, CH<sub>3</sub>), 1.02–1.14 (m, 24 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.87–2.96 (m, 12 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 7.51–7.71 (m, 30 H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO): δ = 13.2 (+, CH<sub>3</sub>), 21.5 (–, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.3 (–, CH<sub>3</sub>CH<sub>2</sub>), 30.0 (–, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 125.1 (+, C-Ar), 125.4 (+, C-Ar), 129.6 (+, C-Ar), 129.6 (+, C-Ar), 130.1 (+, C-Ar), 135.3 (C<sub>quat</sub>), 136.5 (d, <sup>2</sup>*J*<sub>CP</sub> = 4.9 Hz, C<sub>quat</sub>), 145.5 (d, <sup>1</sup>*J*<sub>CP</sub> = 27.8 Hz, C<sub>quat</sub>) ppm. IR (drift): ν̄ = 2957 (vw), 2929 (vw), 2870 (vw), 1595 (w), 1497 (w), 1458 (w), 1012 (w), 768 (w), 692 (w), 577 (w), 515 (w) cm<sup>–1</sup>. MS (FAB): *m/z* (%) = 1160 (<1) [LZn<sub>2</sub>Br<sub>3</sub>], 1189 (<1) [LZn<sub>2</sub>Br<sub>4</sub>], 848 (11) [LZn<sub>2</sub>Br], 776 (67) [LZnBr], 160 (100); L = **4h**. C<sub>72</sub>H<sub>84</sub>Br<sub>6</sub>N<sub>18</sub>P<sub>2</sub>Zn<sub>3</sub> (1939.09): calcd. C 44.60, H 4.37, N 13.00; found C 44.40, H 4.47, N 12.61.

**Crystal Structure Determination of 4g, 6 and 7:** The single-crystal X-ray diffraction study was carried out with a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K by using Mo-*K*<sub>α</sub> radiation (λ = 0.71073 Å). Direct methods (SHELXS-97<sup>[18]</sup>) were used for structure solution, and refinement was carried out by using SHELXL-97<sup>[18]</sup> (full-matrix least squares on *F*<sup>2</sup>). Non-hydrogen atoms were refined anisotropically, hydrogen atoms were localized by difference electron density determination and refined by using a riding model. A semiempirical absorption correction was applied for **6** and **7**. In **7** the solvent CH<sub>2</sub>Cl<sub>2</sub> is disordered about a centre of symmetry. **4g**: Colourless crystals, C<sub>42</sub>H<sub>30</sub>N<sub>6</sub>P, *M* = 691.72, crystal size 0.32 × 0.16 × 0.08 mm, monoclinic, space group *P*<sub>2</sub>/c (No. 14), *a* = 16.841(1) Å, *b* = 9.837(1) Å, *c* = 21.057(1) Å, β = 93.80(1)°, *V* = 3480.7(4) Å<sup>3</sup>, *Z* = 4 ρ(calcd.) = 1.320 Mg m<sup>–3</sup>, *F*(000) = 1440, μ = 0.125 mm<sup>–1</sup>, 66160 reflections (2θ<sub>max</sub> = 55°), 7971 unique (*R*<sub>int</sub> = 0.046), 469 parameters, *R*1 [*I* > 2σ(*I*)] = 0.045, *wR*2 (all data) = 0.114, *S* = 1.04, largest diff. peak/hole 0.356/–0.302 e Å<sup>–3</sup>. **6**: Pale yellow crystals, C<sub>72</sub>H<sub>84</sub>N<sub>18</sub>P<sub>2</sub>Zn<sup>2+</sup> – Br<sub>6</sub>Zn<sub>2</sub><sup>2–</sup>, *M* = 1939.08, crystal size 0.24 × 0.09 × 0.03 mm, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 12.1596(9) Å, *b* = 12.5221(9) Å, *c* = 14.8539(18) Å, α = 94.050(9)°, β = 101.684(7)°, γ = 117.543(5)°, *V* = 1928.4(3) Å<sup>3</sup>, *Z* = 1, ρ(calcd.) = 1.670 Mg m<sup>–3</sup>, *F*(000) = 972, μ = 4.130 mm<sup>–1</sup>, 22355 reflections (2θ<sub>max</sub> = 50°), 6761 unique (*R*<sub>int</sub> = 0.082), 457 parameters, *R*1 [*I* > 2σ(*I*)] = 0.063, *wR*2 (all data) = 0.146, *S* = 1.06, largest diff. peak/hole 0.950/–0.593 e Å<sup>–3</sup>. **7**: Yellow crystals, C<sub>42</sub>H<sub>30</sub>I<sub>2</sub>N<sub>6</sub>PZn – 0.5CH<sub>2</sub>Cl<sub>2</sub>, *M* = 1053.35, crystal size 0.24 × 0.12 × 0.08 mm, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 12.073(1) Å, *b* = 12.602(1) Å, *c* = 14.906(2) Å, α = 110.38(1)°, β = 94.94(1)°, γ = 95.19(1)°, *V* = 2100.3(4) Å<sup>3</sup>, *Z* = 2, ρ(calcd.) = 1.666 Mg m<sup>–3</sup>, *F*(000) = 1034, μ = 2.199 mm<sup>–1</sup>, 27829 reflections (2θ<sub>max</sub> = 55°), 9602 unique (*R*<sub>int</sub> = 0.035), 514 parameters, 3 restraints, *R*1 [*I* > 2σ(*I*)] = 0.037, *wR*2 (all data) = 0.079, *S* = 1.03, largest diff. peak/hole 0.987/–1.266 e Å<sup>–3</sup>. CCDC-799089 (**4g**), -799090 (**6**) and -799091 (**7**) 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.

**Supporting Information** (see footnote on the first page of this article): Analytical data for all prepared compounds (**4–7**).

## Acknowledgments

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- [10] **SAFETY:** Whereas ionic azides such as sodium azide are relatively stable, carbon-bound or heavy-metal azides are subject to thermal – sometimes explosive – decomposition. Some organic and other covalent azides are classified as toxic and highly explosive, and appropriate safety measures must be taken at all times: S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188.
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