

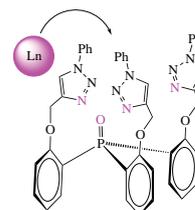
# Tripodal 1,2,3-triazole click ligand based on the triphenylphosphine oxide platform: atrane-type lanthanide complexes in solutions

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**Tris[2-(1-phenyl-1,2,3-triazol-4-ylmethoxy)phenyl]phosphine oxide, a novel tripodal polytopic ligand produces stable complexes with  $\text{La}(\text{NO}_3)_3$  and  $\text{Lu}(\text{NO}_3)_3$ . According to IR, multinuclear NMR and DFT data, the complexes have atrane-type structure with tetradentate O,N,N,N-coordination of ligand in MeCN solutions.**



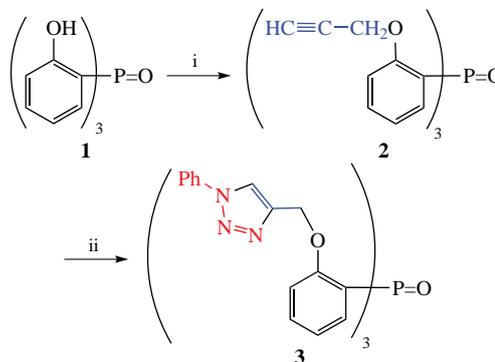
**Keywords:** tripodal 1,2,3-triazole ligands, tris[2-(1-phenyl-1,2,3-triazol-4-ylmethoxy)phenyl]phosphine oxide, X-ray diffraction analysis, lanthanide complexes, vibrational spectroscopy, NMR spectroscopy, solution structure.

In recent time, tripodal ligands with various scaffolds containing 1,2,3-triazole rings in side arms (TLTRs) become more widespread due to the use of  $\text{Cu}^I$ -catalyzed azide–alkyne cycloaddition (the first example of so-called ‘click’ reaction).<sup>1–5</sup> Moreover, TLTRs produce complexes with cations of *d*- and *f*-block elements. Such TLTRs complexes with  $\text{Fe}^{II}$  display spin-crossover properties,<sup>1,2</sup> while complexes with lanthanides and transition metals are promising as contrast agents for magnetic resonance tomography,<sup>1,2</sup> catalysis,<sup>5</sup> and designing photo- and electroluminescent materials.<sup>4</sup> Compounds with triazole rings are also of interest for biomedical purposes,<sup>3</sup> as molecular containers and transport molecules for transfer of cations and anions, as sensors and artificial receptors.<sup>6–10</sup> Therefore, the search and development of new approaches to the synthesis of new TLTRs is urgent. In this work, we propose a simple and convenient two-step synthesis of new TLTR based on  $\text{Ph}_3\text{P}(\text{O})$  platform (Scheme 1).<sup>†</sup>

Compounds **2** and **3** were characterized by the data of elemental analysis, IR, Raman, and multinuclear NMR spectroscopy. The structure of ligand **3** was established by X-ray diffraction.<sup>‡</sup> The compound crystallizes as hydrate **3**· $\text{H}_2\text{O}$  whose

molecules in crystal form dimers due to hydrogen bonding via water molecules (Figure 1).

The dimerization leads to stabilization of conformation where two side arms are directed to the same side as the  $\text{P}=\text{O}$  bond.



**Scheme 1** Reagents and conditions: i,  $\text{BrCH}_2\text{C}\equiv\text{CH}$ ,  $\text{K}_2\text{CO}_3$ , DMF,  $\Delta$ ; ii,  $\text{PhN}_3$ ,  $\text{CuBr}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\Delta$ .

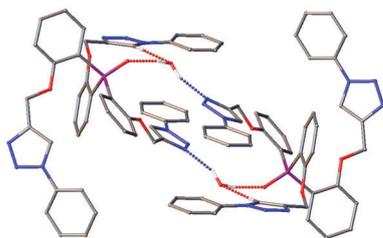
<sup>†</sup> *Propargyl ether 2*. A mixture of oxide **1** (0.65 g, 2.0 mmol),  $\text{K}_2\text{CO}_3$  (2.76 g, 20 mmol), propargyl bromide (2.38 g, 20 mmol), and DMF (20 ml) was stirred at 80 °C for 2 h. The solvent was removed under reduced pressure, water (20 ml) was added to the residue. The resultant precipitate was washed with water ( $2 \times 10$  ml) and acetone (3 ml). The precipitate was refluxed with acetone (20 ml), filtered off, and dried at 70 °C in a vacuum (2 Torr) to give 0.66 g (75%) of product **2**, mp 204–206 °C.

*Ligand 3*. A mixture of ether **2** (0.35 g, 0.80 mmol), phenyl azide (0.60 g, 5.0 mmol), and  $\text{CuBr}$  (9 mg, 0.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 ml) was refluxed for 4 h. The mixture was concentrated, and the product was isolated by column chromatography on  $\text{SiO}_2$  using  $\text{CHCl}_3$ – $\text{MeOH}$  mixture (20:1) as an eluent. The solvent was removed to leave light solid foam. It was triturated with acetone, filtered off and dried at 70 °C in a vacuum (2 Torr) to give 0.45 g (71%) of ligand **3**, mp 208–210 °C.

<sup>‡</sup> *Crystal data for 3*· $\text{H}_2\text{O}$ .  $\text{C}_{45}\text{H}_{38}\text{N}_9\text{O}_5\text{P}$ ,  $M = 815.81$ , triclinic, space group  $P\bar{1}$ ; at 295 K:  $a = 8.3829(4)$ ,  $b = 14.1947(6)$  and  $c = 18.5412(9)$  Å,  $\alpha = 109.649(2)^\circ$ ,  $\beta = 100.530(2)^\circ$ ,  $\gamma = 97.874(2)^\circ$ ,  $V = 1995.33(16)$  Å<sup>3</sup>,

$Z = 2$ ,  $d_{\text{calc}} = 1.358$  g  $\text{cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.129$  mm<sup>-1</sup>,  $F(000) = 852$ . The intensities of reflections were measured with a Bruker D8 Quest diffractometer (MoK $\alpha$ -radiation,  $\lambda = 0.71073$  Å). The structures were solved by the SHELXT method<sup>11</sup> and refined by full-matrix least squares method against  $F^2$  of all data using SHELXL-2014<sup>12</sup> and OLEX2<sup>13</sup> software. Non-hydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters against a disordered phenyl ring. One phenyl ring is equally disordered over two sites; carbon atoms of this ring were refined isotropically. The positions of hydrogen atoms were calculated and included in refinement in isotropic approximation by the riding model with the  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$  and  $1.2 U_{\text{eq}}(\text{C})$ , where  $U_{\text{eq}}(\text{X})$  are equivalent thermal parameters of parent atoms. Refinement converged to  $R_1 = 0.074$  (for 5396 observed reflections),  $wR_2 = 0.194$  and GOF = 1.01 (for 10309 independent reflections,  $R_{\text{int}} = 0.091$ ).

CCDC 2154424 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.



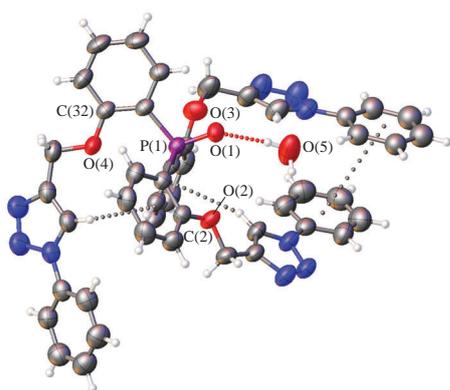
**Figure 1** H-bonded dimer of **3**·H<sub>2</sub>O. Only hydrogen atoms involved in H-bonding with water molecules are depicted.

However, this conformation in solution can be readily transformed. Molecular structure of hydrate **3** is given in Figure 2.

The structure of polytopic tripodal ligands on the Ph<sub>3</sub>P(O) platform with different donor groups in the side arms allows the formation of mononuclear complexes with multicharged cations with bulky coordination sphere and large coordination number (CN).<sup>14,15</sup> Coordination properties of ligand **3** were studied by the example of complexation with La<sup>3+</sup> and Lu<sup>3+</sup> nitrates whose cations differ considerably in radii. The reaction of **3** with the corresponding nitrates in MeCN–CHCl<sub>3</sub> solution leads to complexes **4** and **5** of 1 : 1 composition.<sup>§</sup>

IR and Raman spectra of solid complexes **4** and **5** are similar (see also Online Supplementary Materials). Vibration frequencies of P=O bond change as expected and indicate coordination of P=O group to metal cation. In contrast to IR spectra of model triazole compounds,<sup>16</sup> where band of triazole ring distortion is observed at ~1046 cm<sup>-1</sup>, the IR spectra of **2** and **3** show overlapping of bands of triazole rings and platform vibrations at ~1046 cm<sup>-1</sup>. Frequencies assignment and conclusion on coordination of triazole rings in **4** and **5** were drawn based on normal coordinate analysis of model compounds.<sup>16</sup> The bands of NO<sub>3</sub> groups are complicated and, in first approximation, correspond to bidentate coordination. The selected parameters of IR and NMR spectra for the solution of complexes **4**, **5** in comparison with the data for the free ligand **3** are given in Table 1. Subtraction of ligand spectrum from complex spectrum was used for frequencies assignment of triazole ring.

In all NMR spectra of complex **4** in CD<sub>3</sub>CN, the signals are narrow and chemical shifts differ from those for free ligand. The shift of ligand signal on coordination with La ( $\Delta\delta_P = 9.2$  ppm) is



**Figure 2** Asymmetric unit of **3**·H<sub>2</sub>O view as thermal ellipsoids. Selected O–H···O, C–H···π and π···π interactions are depicted as dotted lines.

<sup>§</sup> Complexes **4** and **5**. A solution of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or Lu(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (0.1 mmol) in MeCN (3 ml) was added dropwise with stirring to a solution of ligand (0.1 mmol) in CHCl<sub>3</sub> (3 ml). The mixture was stirred at 60–65 °C for 3 h and allowed to stand overnight. The solvent was removed under reduced pressure, diethyl ether was added, and the precipitate was separated and dried at 80 °C in a vacuum (0.1 Torr). Yield of complex La(L)(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O **4** was 92%, mp (decomp.) > 170 °C. Yield of complex Lu(L)(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O **5** was 88%, mp (decomp.) > 140 °C.

**Table 1** Diagnostic IR ( $\nu$ , cm<sup>-1</sup>), <sup>13</sup>C and <sup>13</sup>P NMR ( $\delta$ , ppm) spectroscopic data for the ligand **3** and complexes **4**, **5** in CD<sub>3</sub>CN and CDCl<sub>3</sub>.

Compound	Solvent	$\nu(\text{P}=\text{O})$	Ring vibration	$\nu(\text{NO}_3)$	$\delta_{\text{C}}(\text{C}^4)$	$\delta_{\text{P}}(\text{W}_{1/2})^a$
<b>3</b>	CD <sub>3</sub> CN	1186 m	– <sup>b</sup>	–	144.21 s	22.0 s (0.16)
	CDCl <sub>3</sub>	1174 sh	1046 s <sup>c</sup>	–	144.39 s	26.0 s (0.3)
<b>4</b>	CD <sub>3</sub> CN	1119 m	1046 m, <sup>c</sup> 1066 m	~1470 sh, 1303 s	143.24 s	31.4 s (0.2)
	CDCl <sub>3</sub>	1119 m	1046 m, <sup>c</sup> 1066 m	~1470 sh, 1311 m, 1300 sh	143.53 s	30.9 s (1.3)
<b>5</b> <sup>d</sup>	CD <sub>3</sub> CN	1128 m	1045 sh, <sup>c</sup> 1070 br	~1520 sh, ~1314 sh, 1304 s	143.18 s	34.1 s (0.18)

<sup>a</sup>The band width at half-height (in ppm). <sup>b</sup>Poor solubility ( $c < 0.05$  M).

<sup>c</sup>Bands of triazole rings distortion are overlapping with platform vibrations.

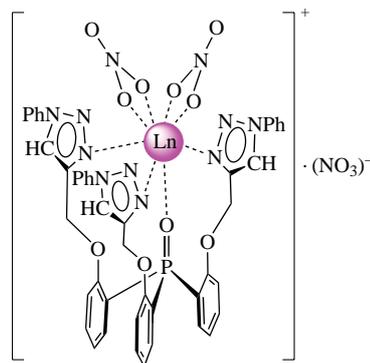
<sup>d</sup>Complex **5** is insoluble in CDCl<sub>3</sub>.

quite large, which is typical for ionic complexes of phosphoryl compounds with Ln nitrates in CD<sub>3</sub>CN.<sup>17</sup> In the case of neutral complexes, the value of  $\Delta\delta_P$  is always lower.<sup>17</sup> NMR experiment on addition of Bu<sub>4</sub>NNO<sub>3</sub> to solution of **4** to shift equilibrium from ionic to neutral complex leads to the decrease of  $\delta_P$  by 2 ppm. This effect was also described earlier.<sup>17</sup>

DFT calculations (see Online Supplementary Materials) at the PBE0/Def2-TZVP level, SMD solvation model (MeCN) showed that cationic complex with tetradentate O,N,N,N-coordination of ligand (CN = 8) is more stable than neutral complex with tridentate coordination of ligand in MeCN ( $\Delta G_{298}^0 = 4.9$  kcal mol<sup>-1</sup>).

According to IR spectra for complex **4** in CD<sub>3</sub>CN, one can suppose that the ligand is coordinated in O,N,N,N-tetradentate mode. The bands of NO<sub>3</sub> groups are complicated. These states are determined not only by the type of species (neutral complex, contact ion pair, solvent-separated ion pair, etc.) but also by symmetrical or nonsymmetrical environment of ion within these species. Thus, the body of data allows us to conclude that in CD<sub>3</sub>CN solution complex **4** presents a contact ion pair [La(O,N,N,N-L)(O,O-NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>·(NO<sub>3</sub>)<sup>-</sup> whose cation is a rare case of atrane-type complex (Figure 3). IR spectral data agree well with the suggested structure.

Based on the IR and NMR spectra of solutions of **3** and **4** in CDCl<sub>3</sub> (see Table 1), we can conclude that complex **4** in CDCl<sub>3</sub> is neutral with tetradentate coordination of ligand [La(O,N,N,N-**3**)(O,O-NO<sub>3</sub>)<sub>2</sub>]<sup>0</sup>, (CN = 10). The value of  $\Delta\delta_P$  is 5 ppm which corresponds to a neutral complex. The bands of NO<sub>3</sub> groups in IR spectrum are complicated and not symmetrical. Signal broadening in <sup>1</sup>H and <sup>31</sup>P NMR spectra of **4** in CDCl<sub>3</sub> indicates the presence of minor complex species of another structure in equilibrium.



**Figure 3** Visualization of structure of complexes **4** and **5** in MeCN. Ln = La (**4**), Lu (**5**).

Complex **5** is insoluble in  $\text{CDCl}_3$ . The spectral data of **5** in  $\text{CD}_3\text{CN}$  are somewhat more complicated than those of **4** (see Table 1). The body of data allows us to conclude that in  $\text{CD}_3\text{CN}$  both complexes **4** and **5** present a contact ion pair  $[\text{Ln}(\text{O},\text{N},\text{N},\text{N}-\text{L})(\text{O},\text{O}-\text{NO}_3)_2]^+(\text{NO}_3)^-$  ( $\text{Ln} = \text{La}, \text{Lu}$ ). The value of  $\Delta\delta_{\text{p}}$  for complex **5** is 12.0 ppm. Significant signal broadening in  $^1\text{H}$  NMR spectrum and complication of bands of  $\text{NO}_3$  groups in IR spectrum of **5** as compared with spectra of **4** (see Online Supplementary Materials and Table 1) indicate the presence in equilibrium of larger number of minor complex species. Coordination number 8 is acceptable for both  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$ . However,  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  cations differ considerably in radius; therefore, the large number of minor species in solution of **5** is expectable.

In summary, we developed a convenient method for preparing novel tripodal polytopic triazole ligand. The ligand produces stable complexes with  $\text{La}(\text{NO}_3)_3$  and  $\text{Lu}(\text{NO}_3)_3$ . According to IR, multinuclear NMR, and DFT data, the complexes have atrane-type structure with tetradentate O,N,N,N-coordination of the ligand in solutions. These data may be useful for application in catalysis, electroluminescent materials, biomedicine, and as transport molecules.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.006.

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