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Double [3+2]-dimerisation cascade synthesis of bis(triazolyl)bisphosphanes, a new scaffold for bidentate bisphosphanes

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Coralie Laborde[a], Muh-Mei Wei,[b] Arie van der Lee,[c] Eric Deydier,[b] Jean-Claude Daran, [b] Jean-Noël Volle[a], Rinaldo Poli,[b,d] Jean-Luc Pirat,[a] Eric Manoury,[b,*] and David Virieux[a,*]

A highly convergent synthesis of bis(triazolylphosphane oxides) was developed by a tandem copper-mediated Huisgen reaction - oxidative coupling. The phosphane oxides were reduced by trichlorosilane and the coordination of the resulting bisphosphanes was studied with various transition metals.

Introduction

The development of innovative, efficient, cost-effective and environmental-friendly processes is essential for the manufacture of new chemical entities.[1] For this purpose, the processes involving the use of catalysis have clear advantages over those requiring stoichiometric amounts of reagents.[2] That is why catalysis has become one of the most practical methodologies to build organic molecules, including in enantioselective ways. Most impressive developments have led over the past two decades to numerous products of interest by connecting various building blocks using catalysed hydrogenation or coupling reactions (Heck, Kumada, Negishi, Sonogashira, Stille, Suzuki or Buchwald-Hartwig, etc). In this context, phosphane-based catalysts play an outstanding role because significant achievements have been made in achiral and chiral transition metal catalysed reactions or more recently in phosphane nucleophilic organocatalysed organic transformations.[3]

The design of phosphane ligands has played a key role in the evolution of catalysis.[4] Fine tuning of the catalytic activity by modification of the electronic/steric properties of the ligand systems is far from trivial mainly because of the difficulty and cumbersome procedures for structural modification of the ligand scaffolds. Therefore, in spite of the large number of developed catalytic processes, much remains to be done in this field in order to develop applicable and highly productive catalysts. Bidentate phosphanes are currently used for their intrinsic chelation properties. Numerous bidentate bisphosphanes are C2-symmetric and DIOP[5] or BINAP[6] are probably the most known archetypical ligands of this category (fig. 1). Phosphanes for which the phosphino group is directly connected to a heterocyclic ring can take advantage of both electronic and steric modulations induced by the presence of an extra heteroelement.[7] The dihedral angle in biaryl bisphosphanes has been shown to affect the catalytic properties.[8] The presence of heteroelements in this biaryl backbone, such as for instance oxygen atoms in SEGPHOS or SYNPHOS, induces stereoelectronic repulsions and consequently narrower dihedral angles.[9] In this context, still very few phosphanes involves a five-membered ring as structural subunit. Then axially chiral bisphosphanes derived from 1,1'-naphthyl-benzimidazole core (BIMINAP **1** and BIMIONAP **2**) were used as ligands.[10] Another relevant example, the 2,2'-bis(diphenylphosphanyl)-1,1'-bibenzimid-azole (BIMIP **3**) ligand is an electron-poor ligand derived from five-membered bis-heteroaromatic diphosphanes which possess a hindered rotation on the N–N linkage.[11] By contrast, bis(thyenyl)bisphosphanes (BITIOP **4**) is considered as electron rich bisphosphane.[12]

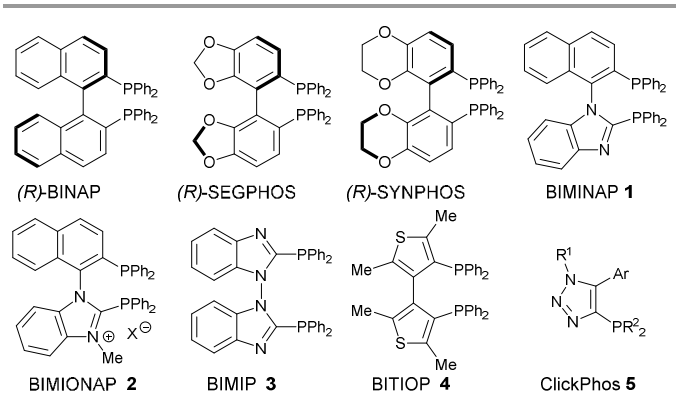

Fig. 1 Representative biaryl bisphosphanes **1**-**4** and ClickPhos **5**.

Zhang and coworkers introduced ClickPhos **5** (i.e. triazolylphosphanes) as potent heterocyclic phosphane ligands.[13] ClickPhos **5** were synthesized from a two-step procedure using phenyl azide and various aryl acetylenes. They revealed interesting ligand properties, particularly in Suzuki-Miyaura coupling reactions

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or in amination reactions of aryl halides.[14] In parallel, extensions of their synthesis and luminescence properties were studied by Bräse and coworkers.[15]

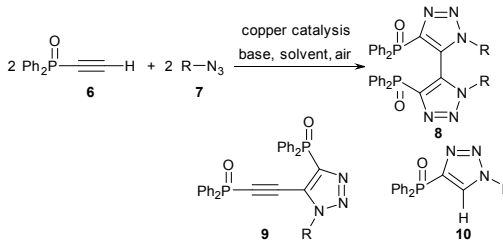
Results and discussion

By contrast, the bis(triazole) backbone is an unprecedented scaffold for the development of new bisphosphane based ligands. We would like to report herein a new class of heterobisphosphanes. Their synthesis is straightforward by a tuneable and convergent methodology which involves the creation of 5 bonds in one chemical step from simple precursors available in large scale using a literature methodology developed with simple substrates.[16] This reaction was first observed by Sharpless in his early work on click chemistry and was considered at that time as an unwanted side process.[17]

In order to avoid a possible Staudinger reaction, we decided to focus on the combination of diphenylethynylphosphane oxide **6** rather than the free phosphane with alkyl- or arylazides in a tandem copper-mediated Huisgen reaction - oxidative coupling, forming bis(triazolylphosphane) oxides **8** (table 1). Diphenylethynyl-phosphane oxide **6** was synthesized in two steps from the reaction of chlorodiphenylphosphane and ethynylmagnesium bromide followed by oxidation of the resulting phosphane with hydrogen peroxide in 78% overall yield.[18]

The conditions of the tandem [3+2] cyclisation/dimerization were optimized with diphenylethynylphosphane oxide **6** and benzylazide **7.1** (table 1, R = Bn). Representative assays of this optimization are listed in Table 1. The solvent appeared to have a deep effect on the formation of the desired product. When using a mixture of DMF and water (entries 1-3), only the 1,4-triazole **10** was formed whatever the carbonate base. THF/water (entries 4-6) gave better results, but the best solvent mixture was acetonitrile/water (entries 7-9). We also explored the effect of the copper catalyst nature. CuBr alone worked as well as the $Cu^0/CuSO_4$ mixture, even in submolar quantities (entry 8). However, the best results were obtained with 1 equivalent of CuBr (entry 9).

Table 1 Synthesis of bis(triazolylphosphane) dioxides **8**.



Entry	Base[1]	Eq. R-N_3[2]	Cosolvent[3]	Copper catalysts[4]	Product distribution 8/9/10 [%]
1	Na_2CO_3	1	DMF	$Cu/CuSO_4$	0/0/100
2	K_2CO_3	1	DMF	$Cu/CuSO_4$	0/0/100
3	Cs_2CO_3	1	DMF	$Cu/CuSO_4$	0/0/100
4	Cs_2CO_3	1	THF	$Cu/CuSO_4$	16/74/10
5	Cs_2CO_3	1	THF	$Cu/CuSO_4$	10/71/19
6	Cs_2CO_3	5	THF	CuBr (1 eq)	61/35/4
7	Na_2CO_3	1	ACN	$Cu/CuSO_4$	65/8/30
8	Cs_2CO_3	5	ACN	CuBr (0.3 eq)	47/44/8
9	Cs_2CO_3	5	ACN	CuBr (1 eq)	80/11/9

1) 2 eq of base were used 2) R = benzyl. 3) 50/50 mixture of the indicated solvent with water. 4) 1eq / 0.3 eq for the $Cu/CuSO_4$ mixtures.

Having these optimized conditions in hand, we then changed the nature of the R group linked to the azide reagents (Table 2). The best yields were obtained for the benzyl and *n*-butyl derivatives **8.1** and **8.2** with respectively 49% and 42%. The reaction tolerated the presence of functional groups such as esters or methylether functions but failed when the reactions were carried out with ketoazides (products **8.8** and **8.9**) giving mainly the monotriazole **10** along with some degradation. Compounds **8.1** and **8.3** were crystallized in a form suitable for single-crystal X-ray diffraction experiments, which confirmed the nature and the positions of the R group on the triazole ring (Fig. 2).

Table 2 Synthesis of bis(triazolylphosphane) dioxides **8.1**-**8.7**

	R	Yield[1]		R	Yield[1]
8.1	Bn	49	**8.6**	CH_2CO_2Me	20
8.2	*n*-Bu	42	**8.7**	CH_2OBn	12
8.3	*i*-Bu	23	**8.8**	$CH_2C(O)Me$	-
8.4	*c*-Hex	6	**8.9**	$CH_2C(O)Ph$	-
8.5	CH_2CO_2Bn	29			

1) Isolated yield

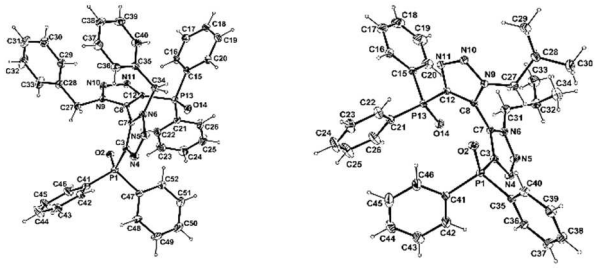
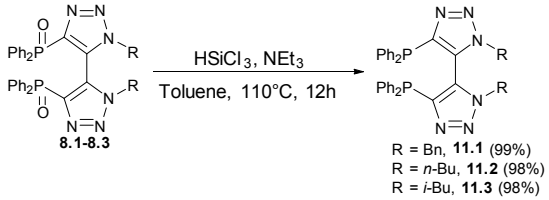


Fig. 2 Views of the molecular geometries of compounds **8.1** and **8.3**. The thermal ellipsoids are scaled to a 50% probability level.

The reduction of the phosphane oxides **8.1**-**8.3** was accomplished by the reaction with trichlorosilane in the presence of triethylamine (Scheme 1).[19] Under such conditions the resulting bisphosphanes **11** were isolated in almost quantitative yields.



Scheme 1. Reduction of the bis(triazolylphosphane) oxides **8.1**-**8.3** to bisphosphanes **11.1**-**11.3**.

The ability of the new triazolylphosphanes to form complexes with different transition metals was also studied (scheme 2). In all cases, ligands **11** bind in the κ^2-*P,P'* mode without any involvement of the triazole nitrogen atoms. The copper complex **15** was prepared upon reaction of stoichiometric amounts of **11.1** and 1,10-phenanthroline with $[Cu(CH_3CN)_4]BF_4$ in dichloromethane. Similarly, the Pd^{II} complexes **12.1**-**12.3** and **13** were obtained by coordination of ligands **11.1**-**11.3** to palladium dichloride or bis(acetonitrile) dichloropalladium(II). Platinum complex **14** was also synthesized from **11.1** and bis(acetonitrile)dichloroplatinum(II) and its structure was confirmed by X-ray diffraction (see Supporting Information). Finally, the addition of **11.1** to $[IrCl(COD)]_2$ afforded either complex [IrCl(COD)(**11.1**)] **16** or the $[Ir(COD)(\mathbf{11.1})]^+$ $[IrCl_2(COD)]^-$ salt **17**

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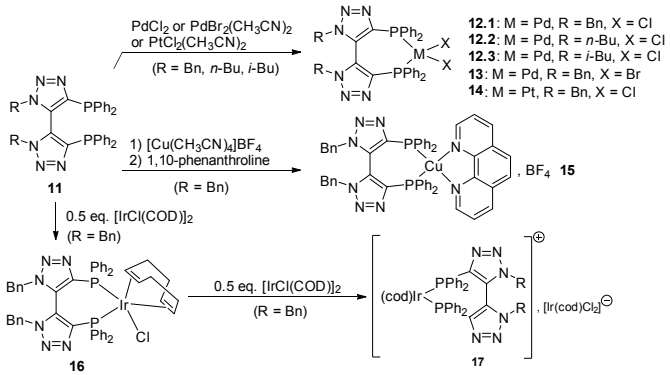
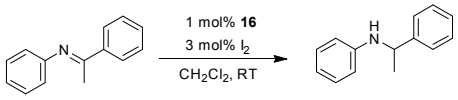
when using either a 1:1 or a 2:1 Ir/ligand ratio. The 5-coordinate geometry of **16** was confirmed by an X-ray diffraction study (Fig. 3); it is similar to that of other $[IrCl(COD)L_2]$ complexes.[20] As expected the Pd^{II}-complex **12.1** showed a narrower dihedral angle of 48.4° compared to the BINAP-$PdCl_2$ complex (71.5°)[21], Synphos (73.6°) or difluorphos (73.0°)[9] and was a direct consequence of the 5-membered ring backbone rather than the 6-one.



Scheme 2. Synthesis of bis(triazolylphosphane) complexes **12-17**.

The iridium complex **16** was tested as a precatalyst in the hydrogenation of N-(1-phenylethylidene)-aniline **11** into secondary amine **18** (see table 3).[22] Full conversion was achieved at room temperature under 30 bars of hydrogen after 2 h with only 1% of complex **16**. The *in situ* made precatalyst (**11** /$[Ir(COD)Cl]_2$ = 1) was also effective, although slightly less than the complex **16** (table 3, entries 2-5).

Table 3 Hydrogenation of N-(1-phenylethylidene)-aniline with iridium complex **16**.



Entry[a]	Catalyst	Time (h)	Yield of amine
1	**16**	0.5	57%
2	**16**	2	100%
3	**16**	4	100%
4	**11**/$[Ir(COD)Cl]_2$ (ligand/iridium ratio =1)	2	80%
5	**11**/$[Ir(COD)Cl]_2$ (1/1) (ligand/iridium ratio =1)	4	100%

a: 1% **16** , 3% I_2, at RT in CH_2Cl_2.

Conclusions

In summary, the copper mediated [3+2]-cycloaddition/dimerization of diphenylethynylphosphane oxide with various alkyl azides readily allowed the highly convergent formation of bis(triazolylphosphane) oxides in a one-pot useful process. Reduction into bisphosphanes is very efficient, and coordination of the latter to various transition metals was demonstrated, introducing a new family of C_2-symmetric bisphosphanes with a quite rare triazolyl backbone. Preliminary catalytic studies in imine hydrogenation have shown good catalytic activities with an iridium complex. The determination of configurational stability and the unusual heteroatom backbone could offer numerous perspectives for catalytic applications.

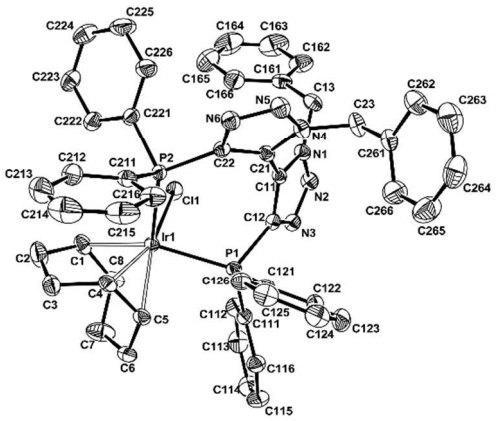


Fig. 3. ORTEP view of the molecular geometry of **16**. The thermal ellipsoids are scaled to a 50% probability level and the hydrogen atoms are omitted for clarity.

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Experimental

General

All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques otherwise stated. Solvents were carefully dried by conventional or were purified with an MBRAUN Solvent Purification System. ^1H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker Avance 500 FT-NMR or a bruker Avance 400 spectrometer. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. For all characterized compounds, the peak assignments in the ^1H and ^{13}C NMR spectra were based on COSY, HSQC and HMBC 2D experiments. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray method or with a LC-TOF spectrometer (Micromass).

Synthesis of bistriazolyl phosphane oxides 8.1-8.7

General procedure

In a round bottom flask, ethynyldiphenylphosphane oxide (250 mg, 1.1 mmol) was dissolved in acetonitrile (3 mL). Then the corresponding azide (3.3 mmol) and aqueous cesium carbonate solution at 2 $mol.L^{-1}$ (1.65 mL) were added followed by copper bromide (158 mg, 1 mmol). The resulting mixture was stirred at room temperature in an open vessel for 12 hours. After complete reaction as monitored by TLC, the solvent was

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removed under reduced pressure and the residue was dissolved in dichloromethane, washed with aqueous ammonia solution (10%, 3 x 10mL), brine, then dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The product was isolated as specified below.

4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole dioxide (8.1). The compound was isolated as a white solid after recrystallization from ethanol; Yield: 49%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ 8.13 - 7.97 (m, 4H), 7.65 - 7.41 (m, 10H), 7.39 - 7.08 (m, 12H), 6.91 - 6.77 (m, 4H), 5.51 (d, *J* = -14.7 Hz, 2H), 4.70 (d, *J* = -14.7 Hz, 2H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 141.18 (d, *J* = 130.4 Hz), 132.88 (s), 132.36 (d, *J* = 2.8 Hz), 132.04 (d, *J* = 2.8 Hz), 131.65 (d, *J* = 10.0 Hz), 131.39 (dd, J = 55.3 Hz, *J* = 109.07 Hz), 131.23 (d, *J* = 10.9 Hz), 130.85 (d, *J* = 241.7 Hz), 128.92(s), 128.83 (s), 128.62 (d, *J* = 12.6 Hz), 128.54 (d, *J* = 12.8 Hz), 128.15 (s), 53.13 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 16.80 (s); HRMS (EI): *m/z* Calcd. for $C_{42}H_{34}N_6O_2P_2$ $[M+H]^+$:717.22; Found: 717.2306; mp: 224.5-227.4°C.

4,4'-bis(diphenylphosphinoxy)-1,1-dibutyl-5,5'-bis-1,2,3-triazole dioxide (8.2). The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield: 42%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ7. 96 (dd, *J* = 7.6 Hz, *J* = 12.1 Hz, 4H), 7.61 - 7.35(m, 10H), 7.33 - 7.21 (m, 2H), 7.20 - 7.08 (m, 4H), 4.23 - 4.40 (m, 2H), 4.13 - 4.01 (m, 2H), 1.92-1.78(m, 2H), 1.77 - 1.64 (m, 2H), 1.22 - 1.08 (m, 4H), 0.78 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ140.82 (d, *J* = 130,0 Hz), 133.27 (d, *J* = 2.7 Hz), 131.98 (d, *J* = 2.7 Hz), 131.66 (d, *J* = 10,0 Hz), 131.57 (dd, *J* = 29 Hz, *J* = 110.3 Hz), 131.27 (d, *J* = 10.9 Hz), 130.42 (d, *J* = 21.9 Hz), 129,57 (d, *J* = 12.7 Hz), 129.47 (d, *J* = 13,0 Hz), 49.40 (s), 31.07 (s), 19.84 (s), 13.31 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ16,52 (s); HRMS (EI): *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:649.25; Found: 649.2607; mp: 172.2-172.7 °C.

4,4'-bis(diphenylphosphinoxy)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole dioxide (8.3). The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield: 23%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ 8.05 - 7.92 (m, 4H), 7.61 - 7.44 (m, 10H), 7.38 - 7.27 (m, 2H), 7.23 - 7.14 (m, 4H), 4.20 (dd, *J* = 7.5 Hz, *J* = -13.9 Hz, 2H), 3.88 (dd, *J* = 7.4 Hz, *J* = -13.9 Hz, 2H), 2.10 (ht, *J* = 6.87 Hz, *J* = 6.87 Hz, 2H), 0.81 (d, *J* = 6.7 Hz, 6H), 0.73 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 140.87 (d, *J* = 131.2 Hz), 133.26 (d, *J* = 41.9 Hz), 132.27 (d, *J* = 2.7 Hz), 132.00 (d, *J* = 2.8 Hz), 131.71 (d, *J* = 10.0 Hz), 131.22 (d, *J* = 10.8 Hz), 130.67 (d, *J* = 22 Hz), 128.58 (d, *J* = 12.6 Hz), 128.08 (d, *J* = 13.0 Hz), 56.97 (s), 28.02 (s), 20.16 (s), 20.03 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 16.5 (s); HRMS (EI): *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:649.25; Found: 649.2618; mp: 237.1-238.0 °C.

4,4'-bis(diphenylphosphinoxy)-1,1'-dicyclohexyl-5,5'-bis-1,2,3-triazole dioxide (8.4). The compound was isolated as a white solid after sublimation; Yield: 6%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ7.95 - 7.89 (qt, 3H), 7.51 - 7.38 (m, 11H), 7.27 - 7.21 (m, 6H), 3.70 (tt, *J* = 11.74 Hz,3.70 Hz, 2H), 2.53 - 2.56 (m, 2H), 2.11 - 2.02 (m, 2H), 1.91 - 1.83 (m, 2H), 1.75 - 1.66 (m, 4H), 1.56 - 1.48 (m, 4H), 1.18 - 1.11 (m, 2H), 0.99 - 0.89 (m, 2H), 0,84 - 0.74 (m, 2H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 140.47 (d, *J* = 132.1 Hz), 133.13 (d, *J* = 40.3 Hz), 132.23 (d, *J* = 2.9 Hz), 131.94 (d, *J* = 2.8 Hz), 131.79 (d, *J* = 10 Hz), 131.56 (d, *J* = 11 Hz), 130.20 (d, *J* = 21.9 Hz), 128.62 (d, *J* = 12.6 Hz), 128.40 (d, *J* = 13,0 Hz), 34.27 (s), 59.71 (s), 32.35 (s), 25.39 (s), 25.22 (s), 24.89 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 17,07 (s); HRMS (EI): *m/z* Calcd. for $C_{40}H_{42}N_6O_2P_2$ $[M+H]^+$:701.28; Found: 701.2908; mp: 282.4-283.0 °C.

4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxyacetyl)-5,5'-bis-1,2,3-triazole dioxide (8.5). The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield: 28%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ 7.97 - 7.89 (m, 4H), 7,59 - 7,52 (m, 2H), 7.51 - 7.39 (m, 8H), 7.34 - 7.28 (m, 8H), 7.25 - 7.19 (m, 4H), 7.17 - 7.09 (m, 4H), 5.40 (d, *J* = -17.8 Hz, 2H), 5.18 (d, *J* = -17.8 Hz, 2H), 5.05 (d, *J* = -12.1 Hz, 2H), 4.99 (d, *J* = -12.1 Hz, 2H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 165.89 (s), 141.10 (d, *J* = 129.7 Hz), 134.58 (s), 132.54 (d, *J* = 2.7 Hz), 132.3 (dd, *J* = 20.8 Hz, *J* = 110.9 Hz), 132.19 (d, *J* = 2.7 Hz), 131.83 (d, *J* = 10.2 Hz), 131.82 (d, *J* = 21.7 Hz), 131.21 (d, *J* = 10.9 Hz), 128,77 (d, *J* = 12.6 Hz), 128.75 (s), 128,72 (s), 128.55 (s), 128.5 (d, *J* = 13.0 Hz), 68.04 (s), 50.11 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 17,36 (s); HRMS (EI): *m/z* Calcd. for $C_{46}H_{38}N_6O_6P_2$ $[M+H]^+$:833.23; Found: 833.2400; mp: 157.4-157.9 °C.

4,4'-bis(diphenylphosphinoxy)-1,1'-bis(methoxyacetyl) -5,5'-bis-1,2,3-triazole dioxide (8.6). The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield: 20%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ 7.92 - 7.84 (m, 4H), 7.50 - 7.32 (m, 10H), 7.24 - 7.18 (m, 2H), 7.09 - 7.03 (m, 4H), 5.29 (d, *J* = -17.8 Hz, 2H), 5.06 (d, *J* = -17.8 Hz, 2H), 3.58 (s, 6H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 166.45 (s), 147.07 (d, *J* = 129.0 Hz), 132.57 (d, *J* = 2.78 Hz), 132.19 (d, *J* = 2.8 Hz), 131.82 (d, *J* = 10.9 Hz), 131.6 (dd, *J* = 23.4 Hz, *J* = 110.81 Hz), 131.17 (d, *J* = 10.9 Hz), 130.93 5 (s), 128,78 (d, *J* = 12.8 Hz), 128.5 (d, *J* = 13,0 Hz), 52.99 (s), 49.89 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 17.22 (s); HRMS (EI): *m/z* Calcd. for $C_{34}H_{30}N_6O_6P_2$ $[M+H]^+$:681.17; Found: 681.1790; mp: 211.7-212.1°C.

4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxymethyl)-5,5'-bis-1,2,3-triazole dioxide (8.7). The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield: 12%; ^{1}H NMR (400,13 MHz, $CDCl_3$) δ 8.04-7.89 (m, 4H), 7.64 - 7.40 (m, 10H), 7.37 - 7.11 (m, 16H), 5.87 (d, *J* = -11.2 Hz, 2H), 5.75 (d, *J* = -11.2 Hz, 2H), 4.42 (s, 4H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 141.51 (d, *J* = 129.5 Hz), 135.72 (s), 132.43 (d, *J* = 2.6 Hz), 132.07 (d, *J* = 2.7 Hz), 131.84 (dd, *J* = 31.1 Hz, *J* = 111 Hz), 131.78 (d, *J* = 10.2 Hz), 131.22 (d, *J* = 10.9 Hz), 130.84 (dd, *J* = 21.3 Hz), 128.64 (d, *J* = 12.8 Hz), 128.50 (s), 128.42 (d, *J* = 12.9 Hz), 128.36 (s), 128.26 (s), 76.79 (s), 71.29 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ 17,34 (s); HRMS (EI): *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:777.24; Found: 777.25183; mp: 154.0-154.8 °C.

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Reduction of bistriazolylphosphane oxides 8 into bisphosphanes 11

GENERAL PROCEDURE

To a mixture of bistriazole (1eq) and triethylamine (12 eq) in anhydrous toluene (0.15 $mol.ml^{-1}$) was added dropwise trichlorosilane (10 eq) at room temperature under a nitrogen atmosphere. The mixture was stirred at reflux for 12 h. After complete reduction, observed by ^{31}P RMN, the reaction mixture was quenched with 2M NaOH aq and diluted with dichloromethane and water. The organic layer was separated, washed with water and dried over Na_2SO_4. After concentration under vacuum, the diphosphane was obtained.

4,4'-bis(diphenylphosphino)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole (11.1). The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield: 99%; ^1H NMR (400,13 MHz, $CDCl_3$) δ 7.68 - 7.65 (m, 4H), 7.40 - 7.16 (m, 22H), 6.84 - 6.82 (m, 4H), 4.98 (d, *J* = -14.9 Hz, 2H), 4.55 (d, *J* = -14.9 Hz, 2H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 145.74 - 145.72 (m (ABX)), 145.57 - 145.56 (m (ABX)), 13.49 - 135.44 (m (ABX)), 134.92 - 134.87 (m (ABX)), 134.48 (d, *J* = 21.7 Hz), 133.38 (s), 133.30 (d, *J* = 20.7 Hz), 130.56 (d, *J* = 44.4 Hz), 129.14 (d, *J* = 65 Hz), 128.93 (s), 128.67 (s), 128.67 - 128.59(m (ABX)), 128.41-128.32 (m (ABX)), 128.22 (s), 52.49 - 52.45 (m (ABX)); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ - 37.97 (s); HRMS (EI): *m/z* Calcd. for $C_{42}H_{34}N_6P_2$ $[M+H]^+$:685.23; Found: 685.2398; mp: 205.4-206.5 °C.

4,4'bis(diphenylphosphino)-1,1'-dibutyl-5,5'-bis-1,2,3-triazole (11.2). The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield: 98%; ^1H NMR (400,13 MHz, $CDCl_3$) δ 7.48 - 7.58 (m, 4H), 7.30 - 7.22 (m, 6H), 7.21 - 7.06 (m, 10H), 3.96 - 3.78 (m, 4H), 1.63 - 1.50 (m, 4H), 1.08 - 0.89 (m, 4H), 0.63 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 144.02 - 145.96 (m (ABX)), 144.88 - 144.82 m (ABX)), 135.51 - 135.46 (m (ABX)), 135.08 - 135.04 (m (ABX)), 134,37 - 134.14 (m (ABX)), 133.48 - 133.24 (m (ABX)), 130.64 (d, *J* = 44.9 Hz), 129.11 (d, *J* = 53.3 Hz), 128.71 - 128.59 (m (ABX)), 128.44 - 128.32 (m (ABX)), 49.07 (m (ABX)), 31.72 (m (ABX)), 19.81 (s), 13.30 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ - 37.75 (s); HRMS (EI): *m/z* Calcd. for $C_{36}H_{38}N_6P_2$ $[M+H]^+$: 617.26; Found: 617.2715; mp: 154.1-155.0 °C.

4,4'bis(diphenylphosphino)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole (11.3). The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield: 98%; ^1H NMR (400,13 MHz, $CDCl_3$) δ 7.99 - 7.49 (m, 4H), 7.28 - 7.23 (m, 6H), 7.22 - 7.16 (m, 4H), 7.16 - 7.07 (m, 6H), 3.79 (dd, *J* = 7.6 Hz, *J* = 13.6 Hz, 2H), 3.67 (dd, *J* = 7.6 Hz, *J* = 13.6 Hz, 2H), 1.99 - 1.75 (m, 2H), 0.61 (d, *J* = 6.7 Hz, 6H), 0.58 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100,61 MHz, $CDCl_3$) δ 145.15 - 145.06 (m (ABX)), 144.96 - 144.91 (m (ABX)), 135.71 - 135.67 (m (ABX)), 135.05 - 135.00 (m (ABX)), 133.56 - 133.29 (m (ABX)), 133.13 - 133.14 (m (ABX)), 131.20 (d, *J* = 1.20 Hz), 130.74 (d, *J* = 1.37 Hz), 129.06 (d, *J* = 66.8 Hz), 128.68 - 128.50 (m (ABX)), 128.42 - 128.24 (m (ABX)), 56.45 - 56.6 (m (ABX)), 45.85 (s), 28.68 (s), 19.88 (s); ^{31}P NMR (161.97 MHz, $CDCl_3$) δ - 38.08 (s) ; HRMS (EI): *m/z* Calcd. for $C_{36}H_{38}N_6P_2$ $[M+H]^+$: 617.26 ; Found: 617.2714; mp: 154.2-154.8 °C.

Synthesis of complexes 12-17

SYNTHESIS OF THE PALLADIUM COMPLEX **(13).** In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and bis(acetonitrile)dibromopalladium (10.1mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at room temperature for 2 hours. The solvent was evaporated and the resulting orange solid was washed by dry pentane. After evaporation of the solvent, 22.1 mg of 12.1 were obtained (80% yield). $^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.98 (4H, m, PPh_2), 7.63 (4H, m, PPh_2), 7.52 (2H, m, PPh_2), 7.49 (2H, m, PPh_2), 7.46 (4H, m, PPh_2), 7.36 (4H, m, PPh_2), 7.32 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.69 (2H, d, J = 15.7 Hz, NCH_2), 4.49 (2H, d, J = 15.7 Hz, NCH_2). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 141.7 (J_{CP} = 61.1 Hz, quat, PCN), 135.8 (J_{CP} = 6.5 Hz, PPh_2), 133.9 (J_{CP} =5.0 Hz, PPh_2), 132.9 (PPh_2), 132.1 (quat, Ph/Bn), 131.2 (PPh_2), 129.2 (J_{CP} = 6.3 Hz, PPh_2), 129.2 (Ph/Bn), 129.0 (Ph/Bn), 128.2 (quat, J_{CP} = 19.9 Hz, PPh_2), 127.7 (J_{CP} = 6.0 Hz, PPh_2), 127.6 (quat, PCCN)127.1 (Ph/Bn), 125.8 (quat, J_{CP} = 40.8 Hz, PPh_2), 52.5 (NCPh). $^{31}P\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 8.4. HR/MS (ES+) m/e: 871.0541 (M-Br, 100%) (calc. M: 871.0311).

SYNTHESIS OF THE PLATINUM COMPLEX **(14).** In a Schlenk tube, under argon, a mixture of ligand **11.1** (20 mg, 0.029 mmol) and bis(benzonitrile)dichloroplatinum (13.7 mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at reflux for 2 hours. The solvent was evaporated and the resulting white solid was washed by dry pentane. After evaporation of the solvent, 19.3 mg of 14.1 were obtained (70% yield). A single crystal of 14 suitable for X-ray diffraction analysis was obtained by slow diffusion of pentane in a dichloromethane solution. $^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.93 (4H, m, PPh_2), 7.63 (4H, m, , PPh_2), 7.50 (2H, m, , PPh_2), 7.48 (2H, m, , PPh_2), 7.45 (4H, m, , PPh_2), 7.34 (4H, m,), 7.33 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.74 (2H, d, J = 15.3 Hz, NCH_2), 4.60 (2H, d, J = 15.3 Hz, NCH_2). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 140.4 (J_{CP} = 82 Hz, quat, PCN), 135.4 (J_{CP} = 6.5 Hz, PPh_2), 134.2 (J_{CP} = 4.9 Hz,PPh_2), 132.8 (PPh_2), 132.2 (quat, Ph/Bn), 131.4 (PPh_2), 129.2 (Ph/Bn), 129.0 (PPh_2), 129.0 (Ph/Bn), 127.7 (J_{CP} = 6.0 Hz, PPh_2), 127.6 (J_{CP} = 6.4 Hz, quat, PCCN), 127.0 (Ph/Bn), 125.5 (quat, J_{CP} = 29.8 Hz, PPh_2), 125.1 (quat, J_{CP} = 41.2 Hz PPh_2), 52.6 (NCPh). $^{31}P\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): -5.1. HR/MS (ES+) m/e: 915.1645 (M-Cl, 100%) (calc. M: 915.2381).

SYNTHESIS OF THE IRIDIUM COMPLEX **(16).** In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and $[Ir(cod)Cl]_2$ (9.8 mg, 0.015 mmol) was dissolved in dry dichloromethane (2 ml). The reaction was carried out at room temperature for 45 minutes. The solvent was evaporated and the resulting yellow solid was washed by dry pentane. After

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evaporation of the solvent, 29.3 mg of 16 were obtained (99% yield). A single crystal of 16 suitable for X-ray diffraction analysis has been obtained by slow diffusion of pentane in a dichloromethane solution. $^{1}H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.75 (4H, m, PPh_2), 7.57 (4H, m, PPh_2), 7.44 (6H, m, PPh_2), 7.33 (2H, m, PPh_2), 7.25 (4H, m, PPh_2), 7.17 (2H, m, Ph/Bn), 7.07 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.65 (2H, d, J = 15.3 Hz, NCH_2), 4.58 (2H, d, J = 15.3 Hz, NCH_2), 3.67 (2H, m, COD), 3.13 (2H, m, COD), 2.00 (2H, m, COD), 1.74 (2H, m, COD), 1.69 (2H, m, COD), 1.53 (2H, m, COD). $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 144.9 (quat, J_{CP} = 49.1 Hz, PCN), 135.3 (J_{CP} = 11.7 Hz, PPh_2), 133.1 (J_{CP} = 9.4 Hz, PPh_2), 132.8 (quat, Ph/Bn), 132.6 (quat, PPh_2), 132.0 (quat, PPh_2), 130.3 (PPh_2), 129.4 (PPh_2), 128.8 (Ph/Bn), 128.4 (Ph/Bn), 128.3 (quat, J_{CP} = 26 Hz, PC<u>C</u>N)128.0 (PPh_2), 127.6 (PPh_2), 127.4 (Ph/Bn), 68.7 (J_{CP} = 7.9 Hz, COD), 67.0 (J_{CP} = 6.8 Hz, COD), 52.5 (NCPh), 32.9 (COD), 32.1 (COD). $^{31}P\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): -17.8. HR/MS (ES+) m/e: 985.2919 (M-Cl, 80%) (calc. M: 985.2888).

Synthesis of the iridium complex (17). In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and $[Ir(COD)Cl]_2$ (19.6 mg, 0.029 mmol) was dissolved in dry dichloromethane (4 ml). The mixture was stirred at room temperature for 45 minutes. The solvent was then evaporated and the resulting yellow solid was washed by dry pentane. After evaporation of the solvent, 35.4 mg of 17.1 were obtained (90% yield). $^{1}H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.67 (4H, m, PPh_2), 7.50 (4H, m, PPh_2), 7.50 (2H, m, PPh_2), 7.31 (2H, m, PPh_2), 7.30 (4H, m, PPh_2), 7.24 (4H, m, PPh_2), 6.97 (2H, m, Ph/Bn), 6.91 (4H, m, Ph/Bn), 6.63 (4H, m, Ph/Bn), 5.26 (2H,m, COD), 5.17 (2H, m, COD), 4.92 (2H, d, J = 15.6 Hz, NCH_2), 4.26 (2H, d, J = 15.6 Hz,NCH_2), 2.68 (2H, m, COD), 2.48 (2H, m, COD), 2.37 (2H, m, COD), 2.15 (4H, m, COD), 2.14 (2H, m, COD), 1.98 (2H, m, COD), 1.76 (2H, m, COD), 1.67 (2H, m, COD), 1.45 (2H, m, COD). $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 140.5 (quat, J_{CP} = 70.2 Hz, PCN), 137.4 (J_{CP} = 13.6 Hz, PPh_2), 133.5 (quat, Ph/Bn), 132.6 (J_{CP} = 9.0 Hz, PPh_2), 132.0 (PPh_2), 130.1 (PPh_2), 128.3 (Ph/Bn), 128.2 (J_{CP} = 11.2 Hz, PPh_2), 127.7 (J_{CP} = 10.8 Hz, PPh_2), 127.6 (Ph/Bn), 127.3 (Ph/Bn), 127.1 (quat, J_{CP} = 11.0 Hz, PC<u>C</u>N), 125.3 (quat, J_{CP} = 53.9 Hz, PPh_2), 94.8 (J_{CP} = 13.4 Hz, COD), 94.3 (J_{CP} = 16.1 Hz, COD), 55.4 (COD), 53.2 (COD), 51.7 (NCPh), 34.3 (COD), 32.1 (COD), 29.9 (COD), 29.1 (COD). $^{31}P\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 8.7. HR/MS (ES+) m/e: 985.2916 (M of cation, 100%) (calc. M: 985.2888).

Hydrogenation of N-(1-phenylethylidene)-aniline 17 with complex (16). The catalyst (6.4 μmol: 6.5 mg of complex **16** or 4.4 mg of ligand **11b** and 2.2 mg of $[Ir(COD)Cl]_2$), N-(1-phenylethylidene)-aniline (0.64 mmol, 125 mg) and I_2 (19.2 μmol, 4.9 mg) were placed in a vial which was placed into an autoclave. The autoclave was pressurized with H_2 (30 bar) and the mixture was then stirred at room temperature. After the indicated time, the autoclave was vented and the recovered mixture was filtered through a short silica gel column before being analysed by GC.

Crystallographic studies

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a cryoloop and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR SAPPHIRE-I CCD diffractometer or an Agilent Technologies GEMINI EOS CCD diffractometer. Data were collected using the monochromatic MoKa radiation (l= 0.71073). The structures were solved by direct methods (SIR97)[23] and refined by least-squares procedures on F2 using SHELXL-97.[24] All H atoms attached to carbon were introduced in idealised positions and treated as riding on their parent atoms in the calculations. The drawing of the molecules was realised with ORTEP3.[25] CCDC reference numbers are 1031965-1031970.

Notes and references

[a] Institut Charles Gerhardt / UMR 5253 / AM2N, Ecole Nationale Supérieur de Chimie de Montpellier, 8, Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France.

[b] CNRS, LCC (Laboratoire de Chimie de Coordination) - Université de Toulouse, UPS, INPT - 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France.

[c] Institut Européen des Membranes, CNRS - UMR 5635, Université de Montpellier II - Case Courrier 047 Place E. Bataillon, F-34095 MONTPELLIER Cedex 5, France.

[d] Institut Universitaire de France, 103 bd Saint-Michel, F-75005 Paris, France.

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Graphical Abstract

Double [3+2]-dimerisation cascade synthesis of bis(triazolyl)bisphosphanes, a new scaffold for bidentate bisphosphanes

C. Laborde, M.-M. Wei, A. van der Lee, E. Deydier, J.-C. Daran, J.-N. Volle, R. Poli, J.-L. Pirat, E. Manoury* and D. Virieux*

Highly convergent synthesis of bis(triazolylphosphane oxides) by a tandem copper-mediated Huisgen reaction - oxidative coupling.