

Supplementary Material

The synthetic routes to the ligands BDP and BTMP, as presented in Schemes 1 and 2 in the text, are given below.

2,2'-bis(hydroxymethyl)biphenyl(II).

Diphenic acid (I, 20.0g, 0.08257 mol) was dissolved in dry THF (300ml) and cooled to 0°C. A solution of Boron-dimethyl sulfide (23.5 ml, 0.2354 mol) in 15ml of dry THF was added dropwise (35min.) with stirring, under an argon atmosphere, to the cold diphenic acid solution. The reaction mixture was heated at reflux for 12h and cooled to room temperature. NaOH (1M, 2ml) was added dropwise to the mixture and stirred for 1 h. The reaction mixture was then concentrated to 1/3 of its initial volume to obtain a two phase system. The system was let stand until crystallization of a solid was complete, collected by filtration and dried. This solid was extracted with boiling ethyl acetate twice (50ml + 20ml). The extracts were combined and evaporated to dryness to yield 14.61 g of the crude diol. Crystallization from ethyl acetate yielded 11.62g (65%) of 2,2'-bis(hydroxymethyl)biphenyl, II. MP 110-112°C (literature value 112.4-113.5°C,¹). The NMR spectrum was identical to that reported by Casarini, et al.²

2,2'-bis(bromomethyl)biphenyl(III).

The diol (II)(2.882g, 0.01333mol) was added to a solution of 33% HBr in glacial acetic acid (6.9ml, 0.03998 mol). The solution was heated to obtain two liquid phases and left for ca 12h during which crystallization was initiated. The crude dibromide was filtered, washed with hexane and dried in air: yield 4.1180g (91%). Recrystallization was effected from 96% ethanol (20ml). Yield, 3.2988 g (73%), MP 85-88° (literature value¹³ 82-83°C).

Tetraisopropyl biphenyldiyl-2,2'-Bis(methylphosphonate)(IV).

2,2'-Bis(bromomethyl)biphenyl(III)(2.9833g, 0.00878 mol) was added to triisopropyl phosphite (4.5ml, 0.01962 mol) and was slowly heated. The first evidence of isopropyl bromide formation was observed at ~126°C. The mixture was kept at 145-150° for 0.5h. Then all volatile components were removed under reduced pressure and the residue was subject to column chromatography (flash silica gel, ethyl acetate) to yield IV, 2.731g (61%) as a colorless oil which solidified upon standing. $R_f = 0.20$ (silica gel on PET plates with fluorescent indicator 254 nm; eluent ethylacetate, visualization with UV lamp). IR (neat): ν_{\max} 2979, 1381, 1245, 1107, 1001, 986, 762 cm^{-1} . ¹H NMR (300 MHz, CDCl₃): δ 7.66-7.61 (m, 2H, C-6H and C-6'H), 7.33-7.24 (m, 6H, C-3H, C-3'H, C-5H, C-5'H, C-4H, and C-4'H), 4.56 (dheptet, ³J_{HP} = 14.4 Hz, ³J_{HH} = 6.0 Hz, 4H, CHOP), 2.92 (dd, ²J_{HP} = 14.7 Hz, ²J_{HH} = 15.1 Hz, 2H, CH_AP), 2.83 (dd, ²J_{HP} = 13.8 Hz, ²J_{HH} = 15.3 Hz, 2H, CH_BP), 1.23 (d, ³J_{HH} = 2.1 Hz, 6H, POCCH₃), 1.21 (d, ³J_{HH} = 2.1 Hz, 6H,

POCCH₃), 1.17 (d, ³J_{HH} = 6.2 Hz, 6H, POCCH₃), 1.04 ((d, ³J_{HH} = 6.2 Hz, 6H, POCCH₃), .
³¹P {¹H} NMR(121 MHz, CDCl₃): δ 26.90 (s). ¹³C NMR (75 MHz, CDCl₃): δ 140.91 (d, ³J_{PC} = 9.1 Hz, C-1 and C-1'), 130.79 (s, C-5 and C-5'), 130.48 (d, ²J_{PC} = 7.8 Hz, C-2 and C-2'), 129.93 (d, ³J_{PC} = 4.8 Hz, C-3 and C-3'), 127.53 (d, ⁴J_{PC} = 3.0 Hz, C-4 and C-4'), 126.30 (d, ⁴J_{PC} = 2.9 Hz, C-6 and C-6'), 70.56 (d, ²J_{PC} = 6.9 Hz, C_AOP), 70.24 (d, ²J_{PC} = 6.9 Hz, C_BOP), 31.46 (d, ¹J_{PC} = 140.7 Hz, CP), 24.06 (d, ³J_{PC} = 4.0 Hz, CH_{3A}), 23.94 (d, ³J_{PC} = 4.3 Hz, CH_{3B}), 23.90 (d, ³J_{PC} = 5.3 Hz, CH_{3C}), and 23.63(d, ³J_{PC} = 4.7 Hz, CH_{3D}).

Biphenyldiyl-2,2'-bis(methylphosphonic)acid(V).

Tetraisopropyl biphenyldiyl-2,2'-bis(methylphosphonate), IV, 2.080g (0.004073mol) was added to 20ml of a 1:1 conc. HCl-water mixture and refluxed with stirring for 12 h. The acid, V, was filtered off, washed with ddi H₂O and dried in air. Yield: 1.3329g (82%). IR (KBr): ν_{max} 3383, 3323, 2712, 2281, 1666, 1138, 988, 937, 768, 480 cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ 7.58 (ddd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.5 Hz, ⁵J_{PH} = 1.5 Hz, 2H, C-6H and C-6'H), 7.30 (ddd, ³J_{PH} = 7.8 Hz, ³J_{HH} = 7.5 Hz, ⁵J_{HP} = 1.4 Hz, 2H, C-4H and C-4'H), 7.22 (dddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.5 Hz, ⁶J_{HP} = 1.5 Hz, ⁶J_{PH} = 1.5 Hz, 2H, C-5H and C-5'H), 7.13 (ddd, ³J_{HH} = 7.5 Hz, ⁴J_{HH} ≅ ⁴J_{PH} ≅ 1 Hz, 2H, C-3H and C-3'H), 2.83 (dd, ²J_{HAHB} = 22.1 Hz, ²J_{PH} = 15.0 Hz, , 2H, CH_AP), 2.75 (dd, ²J_{HAHB} = 22.4 Hz, ²J_{PH} = 15.0 Hz, , 2H, CH_BP),. ³¹P {¹H} NMR(121 MHz, DMSO-d₆): δ 23.06 (s). ¹³C NMR (75 MHz, DMSO-d₆): δ 141.20 (d, ³J_{PC} = 8.5 Hz, C-1 and C-1'), 132.51 (d, ²J_{PC} = 7.5 Hz, C-2 and C-2'), 130.79 (s, C-5 and C5'), 130.61 (d, ³J_{PC} = 4.5 Hz, C-3 and C-3'), 127.54 (d, ⁵J_{PC} = 1.7 Hz, C-6 and C-6'), 126.20 (d, ⁴J_{PC} = 1.9 Hz, C-4 and C-4') and 32.37 (d, ¹J_{PC} = 132.8 Hz, CH₂P).

Trimethyl-1,3,5-benzenetricarboxylate(VII) was obtained from trimesic acid (IV) and methanol in the presence of conc. H₂SO₄ as previously reported.⁴

1,3,5-Tri(hydroxymethyl)benzene(VIII).

Trimethyl-1,3,5-benzenetricarboxylate(VII) (4.570g, 0.01820mol) was reduced with lithium aluminum hydride (1.73g, 0.0455mol) in 75ml of dry THF according to a literature procedure.⁵ Following the basic work-up as described in ref. 5 a crude 1,3,5-trihydroxymethylbenzene crystallized, yield 1.982 g (55%) M.P. 64-74 (literature value⁵ 78-79°C).

1,3,5-Tri(bromomethyl)benzene(IX).

1.8727g of VIII (0.01114 mol) was warmed with 33% HBr in glacial acetic acid (11.7 ml, 0.068 mol) to obtain a deep brown solution which then was left at room temperature for 12 hr. The crystalline crude product was filtered off, washed with glacial acetic acid twice with 1ml and finally with 5ml of hexane and dried in air. The crude product (2.5712g) was crystallized from hexane (50ml) to yield the pure bromide, light yellow needles: 1.8989g (55%) M.P. 101-103°C (literature value 101-102°C).⁵

Hexaisopropyl benzenetriyl-1,3,5-tris(methylphosphonate),X.

1.6683g (0.005382 mol) of IX and 4.1ml (0.01776mol) of triisopropyl phosphite were heated together on a Wood's metal bath. Bubbles were observed to form at 120°C indicative that the Arbuzov reaction commenced. The mixture was then heated to 145-150° and kept at this temperature for 30 min. Then all the volatile components were removed under reduced pressure and the residue was subject to column chromatography (flash silica gel, ethyl acetate-ethanol 100:5 V/V) to give hexaisopropyl benzenetriyl-1,3,5-tri(methylphosphonate),X : 1.3517g (41%) as an oil, $R_f = 0.038$ (silica gel on PET plates with fluorescent indicator 254 nm; eluent ethyl acetate, visualization with UV lamp. IR (neat): ν_{\max} 2979, 2935, 1385, 1245, 1107, and 986 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.7.15-7.11 (m, 3H, C-2H and C-2'H), 4.61 (dheptet, $^3J_{\text{HP}} = 7.5$ Hz, $^3J_{\text{HH}} = 6.3$ Hz, 6H, CHOP), 3.05 (d, $^2J_{\text{PH}} = 22.2$ Hz, CH_2P), 1.27 (dd, $^3J_{\text{HP}} = 6.2$ Hz, 18H, CH_3), 1.18 (dd, $^3J_{\text{HP}} = 6.2$ Hz, 18H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR(121 MHz, CDCl_3): δ 25.90 (s). ^{13}C NMR (75 MHz, CDCl_3): δ a multiplet centered at 132.23 (C-1, C-3 and C-5), a multiplet centered at 129.91 (C-2, C-4 and C-6), a multiplet centered at 70.53 (COP), 34.62 (d, $^2J_{\text{CP}} = 139.8$ Hz, CP), a multiplet centered at 24.06 ($\text{CH}_{3\text{A}}$) a multiplet centered at 23.91 ($\text{CH}_{3\text{B}}$).

Benzenetriyl-1,3,5-tri(methylphosphonic) acid (XI).

Hexaisopropyl benzenetriyl-1,3,5-tris(methylphosphonate) (X, 0.9745 g, 0.001591 mol), concentrated HCl (7 cm^3) and distilled water (7 cm^3) were refluxed for 10 h. The crystallized during hydrolysis product was filtered off and dried in air. Benzenetriyl-1,3,5-tri(methylphosphonic) acid (XI) was obtained as a white solid: 0.3977 g (70%), **Anal. Found: P, ?**. Calcd for $\text{C}_9\text{H}_{12}\text{O}_9\text{P}_3$ (357.11): P, 8.67%. IR (KBr): ν_{\max} 2913, 2805, 2471, 1725, 1662, 1586, 1465, 1243, 1137, 1010, 920, and 815 cm^{-1} . ^1H NMR (300 MHz, D_2O): δ 7.09-7.06 (m, 3H, C-2H, C-4H, and C-6H), and 3.12 (d, $^2J_{\text{PH}} = 21.8$ Hz, 6H, CH_2P). ^1H NMR (300 MHz, DMSO-d_6): δ 7.00-6.98 (m, 3H, C-2H, C-4H, and C-6H), and 2.85 (d, $^2J_{\text{PH}} = 21.7$ Hz, 6H, CH_2P). $^{31}\text{P}\{^1\text{H}\}$ NMR(121 MHz, D_2O): δ 26.74 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR(121 MHz, DMSO-d_6): δ 23.11 (s). ^{13}C NMR

(75 MHz, D₂O): δ a multiplet centered at 133.29 (C-1, C-3, and C-5), a multiplet centered at 129.29 (C-2, C-4, C-6), 34.09 (d, $^2J_{PC} = 130.8$ Hz, CH₂P). ¹³C NMR (75 MHz, DMSO-d₆): δ a multiplet centered at 133.82 (C-1, C-3, and C-5), a multiplet centered at 129.46 (C-2, C-4, C-6), and 35.48 (d, $^2J_{PC} = 132.9$ Hz, CH₂P).

References

1. A. G. J. Ligtenbarg, E.K. van den Beuker, A. Meetsma, N. Veldman, W. J. J. Smeets, A. L. Spek, B. L. Feringa, Dalton Trans. 273 (1998).
2. D. Casarini, L. Lunazzi, M. Mancinelli, A. Mazzanti, C. Rosini, J. Org. Chem. 72, 7667 (2007).
3. W. Wenner, J. Org. Chem. 17, 523 (1951).
4. M. P. Cataldi, S.E. Gibson, M. Rudd, A. J. P. White Chem. Eur. J. 12, 138 (2001).
5. Y. Yamagiwa, Y. Koreishi, S. Kiyoyumi, M. Kobayashi, T. Kamikawa, M. Tsukino, H. Goi, M. Yamamoto, M. Munakata Bull. Chem. Soc. Jpn. 69, 3317 (1996).

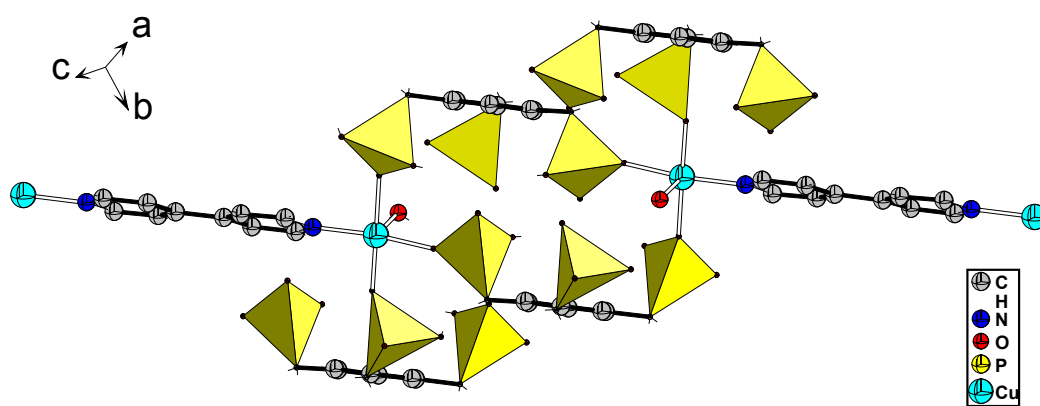


Figure S1: A view of a portion of the Cu BTMP structure taken at a right angle relative to figure 10 showing that all the phosphonic acid groups are on the same side of the phenyl rings to which they are bonded.