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Homoleptic tris(diacetoneglucose)phosphite as a novel entry into chiral phosphorus derivatives in organometallic chemistry

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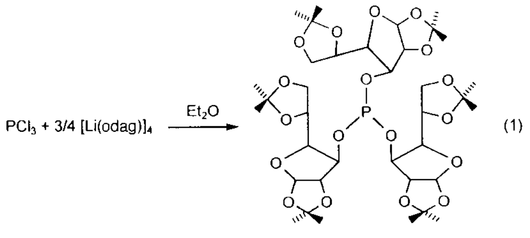
A novel chiral C_3 phosphite P(odag)$_3$ (odag = 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranoside) has been synthesized on a large scale; when treated with Cu(CO)Cl it gave the cubane [{CuCl[P(odag)$_3$]}$_4$], which is in equilibrium with a dimeric form in solution.

Phosphines and phosphites are ubiquitous ligands in organometallic chemistry and catalysis. Three major modifications of phosphorus centred ligands have been pursued: (*i*) change of the basicity; (*ii*) steric hindrance control *via* the so-called cone-angle;[1] (*iii*) the introduction of a variety of chiral substituents.[2] The latter point has been rarely approached using carbohydrates as substituents at phosphorus. This is surprising considering that they perfectly fit the 'chiron approach',[3] and also have a chiral backbone which can be easily modified. The sugar-type substituent[4] has been limited to two significant examples: (*i*) the replacement of a phenyl group in PPh$_3$;[5] (*ii*) to function as a support for two PPh$_2$ fragments. The latter strategy was particularly successful in providing a ligand for a metal-assisted enantioselective hydrocyanation.[6]

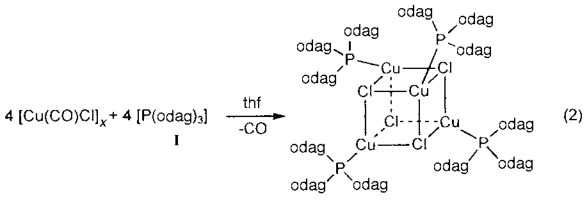
The steric hindrance and the chirality are the characteristics of the first example of a homoleptic tris-sugar phosphite, in the form of tris(1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranosido)phosphite [P(odag)$_3$], that we report here.† The binding ability of such a ligand has been preliminarily investigated for copper(I) halides.

The phosphite was synthesized by reacting PCl$_3$ with the appropriate amount of the lithium salt[7] of the sugar [equation (1)]. The compound is conveniently prepared on a large scale (up to 100 mmol) and easily purified. It is a white crystalline solid which is very moisture sensitive due to nucleophilic displacement reactions at the phosphorus atom.[8] The phosphite is extremely soluble in hydrocarbons and other non-polar and polar solvents. The single peak in the ^{31}P-{^{1}H} NMR spectrum at δ +145 is in the expected range for phosphites.[9] The ligand P(odag)$_3$ has C_3 symmetry which is uncommon for chiral ligands. There are only a few examples known[10] which do not belong to the ubiquitious class of C_2 symmetric chiral ligands. Due to the steric constraint exerted by the three sugar molecules, the 'Tolman angle' of this phosphite is close to 180° (see below).



P(odag)$_3$ **I**

The phosphite I has been treated with [Cu(CO)Cl]$_x$[11,12] according to equation (2).‡ The ^{31}P-{^{1}H} NMR spectrum of the white, crystalline compound **1** shows a single peak at δ +121.9 (293 K). The optical rotatory power is $[\alpha]_D^{20}$ = −283.63° cm^3 dm^{-1} g^{-1} [c = 0.1 g dm^{-3}, l = 1 cm, tetrahydrofuran (thf)]. Crystals suitable for X-ray analysis were obtained from toluene–decane.§



[{CuCl[P(odag)$_3$]}$_4$] **1**

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† A solution of PCl$_3$ (3.66 g, 26.62 mmol) in diethyl ether (20 cm^3) was added slowly at room temperature to a stirred solution of [Li(odag)]$_4$ (21.26 g, 79.86 mmol) in diethyl ether (200 cm^3). The beginning of the reaction was marked by immediate precipitation of LiCl. After complete addition stirring was maintained overnight. Lithium chloride was removed by filtration over a bed of Celite. Evaporation to dryness yielded a white syrupy product which was analytically and spectroscopically pure (90.2%) (Found: C, 53.25; H, 7.05. $C_{36}H_{60}O_{18}P$ requires C, 53.45; H, 7.10%). δ_H(CD$_2$Cl$_2$, 298 K), 5.88 (6 H, d, J = 4), 4.71 (3 H, dd, J = 4), 4.64 (3 H, d, J = 4 Hz), 4.12 (18 H, m), 1.47 (9 H, s), 1.40 (9 H, s), 1.32 (9 H, s), 1.28 (9 H, s). δ_P(CD$_2$Cl$_2$, 298 K), +145. $[\alpha]_D^{20}$ (c = 0.1 g dm^{-3}, l = 1 cm, thf) = −260° cm^3 dm^{-1} g^{-1}.

‡ A suspension of CuCl (0.155 g, 1.56 mmol) was stirred in thf (150 cm^3) under an atmosphere of carbon monoxide until the CuCl was completely dissolved while forming a white solution of [Cu(CO)Cl]$_x$. A solution of P(odag)$_3$ (1.28 g, 1.57 mmol) in thf (10 cm^3) was added which resulted in the vigorous evolution of carbon monoxide. The solution was heated at 50 °C for 2 h, reduced to half of its volume and filtered. Evaporation of the solvent yielded a white syrupy product which was washed with *n*-hexane (2 × 10 cm^3) and dried. The product was dissolved in a minimum amount of CH$_2$Cl$_2$, to remove the last traces of unreacted CuCl, filtered and then evaporated. Crystals of **1** suitable for X-ray analysis were obtained from toluene–decane (yield 76.9%) (Found: C, 47.65; H, 6.5. $C_{36}H_{57}ClCuO_{18}P$ requires C, 47.65; H, 6.35%). δ_H(CD$_2$Cl$_2$, 298 K), 5.90 (3 H, d, J = 4), 5.02 (3 H, dd, J_1 2, J_2 12), 4.76 (3 H, d, J 4 Hz), 4.10 (15 H, m), 1.48 (9 H, s), 1.48 (9 H, s), 1.38 (9 H, s), 1.33 (9 H, s). δ_P(CD$_2$Cl$_2$, 298 K), +121.9. $[\alpha]_D^{20}$ (c = 0.1 g dm^{-3}, l = 1 cm, thf) = −283.63° cm^3 dm^{-1} g^{-1}.

§ Crystal data for compound **1**. $C_{144}H_{228}Cl_4Cu_4O_{72}P_4$, M = 3631.1, orthorhombic, space group $I222$, a = 27.051(8), b = 19.324(5), c = 18.033(4) Å, U = 9426(4) Å^3, Z = 2, D_c = 1.279 g cm^{-3}, $F(000)$ = 3824, Cu-Kα radiation (λ = 1.541 78 Å, μ = 20.7 cm^{-1}), T = 298 K, crystal dimensions 0.18 × 0.31 × 0.48 mm. The analysis was performed on a colourless prismatic crystal using a Siemens AED diffractometer. Refinement of the structure converged to R = 0.064, R' = 0.086, with $w = 1/[\sigma^2(F) + 0.005F^2]$ and goodness of fit = 0.0983 for 2538 reflections with $F_o > 4\sigma(F_o)$. An absorption correction was applied using ABSORB.[13a] The estimated standard deviations of bond distances range from 0.003 Å for the heaviest atoms to 0.03 Å for C and O, while

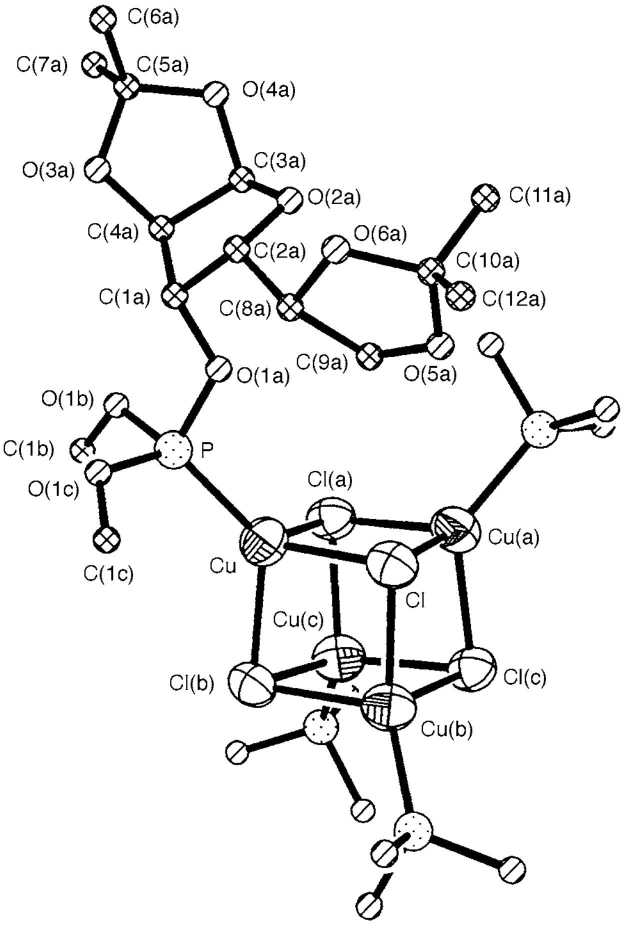

Fig. 1 An ORTEP[13b] plot of the tetramer $[\{CuCl[P(odag)_3]\}_4]$ showing a single odag moiety of the asymmetric unit $CuCl[P(odag)_3]$. Thermal ellipsoids (50% of probability) are drawn only for Cu and Cl. Selected bond distances (Å) and angles (°): Cu–Cl 2.465(4), Cu–Cl(a) 2.460(3), Cu–Cl(b) 2.382(4), Cu–P 2.156(4); Cl–Cu–Cl(a) 98.1(1), Cl–Cu–Cl(b) 92.4(1), Cl(a)–Cu–Cl(b) 91.4(1), Cu–Cl–Cu(a) 81.8(1), Cu–Cl–Cu(b) 87.1(1), Cu(a)–Cl–Cu(b) 87.8(1), P–Cu–Cl 117.4(2), P–Cu–Cl(a) 118.1(1), P–Cu–Cl(b) 131.8(2). Significant non-bonding distances (Å): Cu···Cu(a) 3.225(3), Cu···Cu(b) 3.342(3), Cu···Cu(c) 3.359(3), Cl···Cl(a) 3.719(3), Cl···Cl(b) 3.498(3), Cl···Cl(c), 3.467(3)

Complex **1** has a cubane-like structure[12] which show distorsions of the 'Cu_4Cl_4' core. Fig. 1 reports the most relevant structural parameters. The dpp (d = distal, p = proximal)[14] arrangement of the odag substituents with reference to the Cu–P bond breaks the exact C_3 symmetry of the $P(odag)_3$ ligand. The Cu–P–O(1*n*) angles of the proximal [120.4 and 120.7°] and of the distal substituents [111.1°] follow the same trend as observed for $[Mo_2(odag)_6]$,[14] though they are *ca.* 10° wider because of the shorter M–L distance of the ML_3 calix. The dpp-odag arrangement makes the Tolman cone angle larger than 180°, as shown in Fig. 2.

It is surprising that a ligand with such an extreme cone angle prefers the cubane structure. Phosphines with comparable steric crowding, *e.g.* tris(2,4,6-trimethoxyphenyl)phosphine[15] and tricyclohexylphosphine[16] give monomers and dimers respectively.

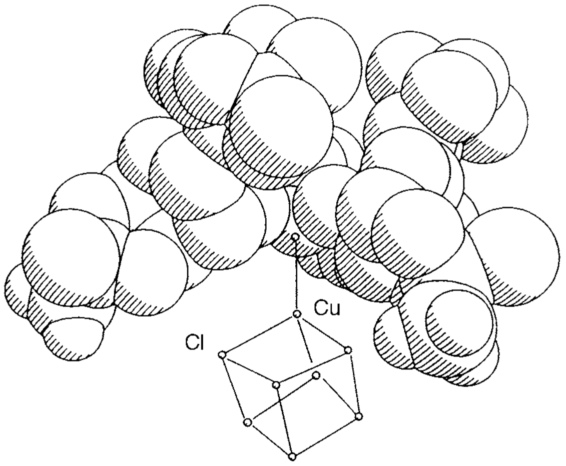

Fig. 2 Space-filling drawing of $P(odag)_3$ with the P atom and the Cu_4Cl_4 cube indicated by small circles. In order to give a clear view of the large value of the Tolman angle, six relevant methyl hydrogens have been included

Those considerations are, however, limited to the solid state. Does **1** remain unchanged in solution?[17] The ^{31}P NMR spectrum is extremely informative in this sense. Lowering the temperature from 313 to 243 K results in a second peak at δ 113.1, in addition to the singlet at δ 121.9, the ratio being 10 : 0.3 at 243 K. The peak at δ 113.1 becomes, however, the main resonance when 1 equivalent of **I** was added to a CD_2Cl_2 solution of **1**. This result shows that a solution of **1** is in equilibrium with the dimer $[\{CuCl[P(odag)_3]_2\}_2]$ **2**. Compound **2** has been isolated and characterized in the solid state by carrying out reaction (1) with a 1 : 2 Cu : P ratio in thf.¶

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those of bond angles range from 0.1 to 2°. The structure analysis at low temperature (120 K) on another crystal sample with a different space group and unit cell [orthorhombic, $P2_12_12_1$, $a = 19.80(1)$, $b = 21.53(1)$, $c = 25.14(2)$ Å, $Z = 4$, $U = 10\,715(7)$ Å^3] was carried out, but the structure showed a partially disordered odag fragment and a not clearly defined solvent molecule; nevertheless the whole complex gave a very good fit with that of the *I*222 sample. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/448.

¶ A suspension of CuCl (0.285 g, 2.87 mmol) in thf (200 cm^3) was vigorously stirred under an atmosphere of carbon monoxide until the CuCl was completely dissolved. Solid $P(odag)_3$ (4.65 g, 5.74 mmol) was added, which caused immediate evolution of CO. Stirring was maintained while heating at 50 °C for 4 h. After evaporation of half of the volume, filtration and evaporation to dryness, a yellow syrupy product (**2**) was obtained (77.8%) (Found: C, 49.75; H, 7.0. $C_{72}H_{114}ClCuO_{36}P_2$ requires C, 50.20; H, 7.0%). $\delta_H(CD_2Cl_2$, 298 K), 5.95 (6 H, d, $J = 4$), 5.11 (6 H, dd, $J_1 = 2$, $J_2 = 12$), 4.81 (6 H, d, $J = 4$ Hz), 4.22 (24 H, m), 1.51 (18 H, s), 1.50 (18 H, s), 1.39 (18 H, s), 1.35 (18 H, s). $\delta_P(CD_2Cl_2$, 298 K), +121.9, 113.1. $[\alpha]_D^{20}$ ($c = 0.1$ g dm^{-3}, $l = 1$ cm, thf) = +1.9° cm^3 dm^{-1} g^{-1}.

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