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3,4,5-Triphenyl-1,2-diphosphacyclopentadienyl copper(I) complexes: synthesis and molecular structure

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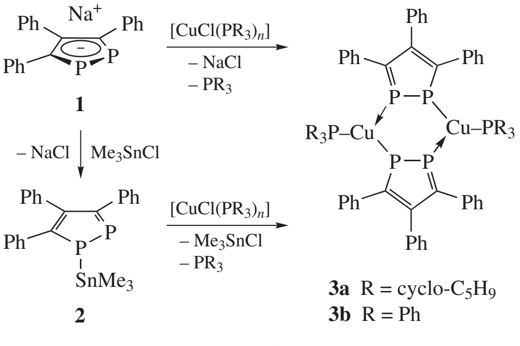
Sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide or 1-trimethylstannyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene reacts with [Cu(Cl)L] [L = PPh_3, P(cyclo-C_5H_9)$_3$] to form dimeric complexes with three-coordinate copper atoms.

Phosphacyclopentadienide anions are isolobal analogues[1] of the cyclopentadienide anion Cp^-. However, the presence of a lone pair of electrons at phosphorus causes an essential diversity in coordination modes with metals that made the phosphacyclopentadienyl ligands very attractive building blocks for the construction of polynuclear complexes and clusters.[2–4] Copper(I) halides show a variety of different bonding modes of phosphacyclopentadienyl ligands depending on the nature and number of phosphine ligands. For example, the well-studied 1,2,4-triphosphacyclopentadienide anion forms two types of compounds with phosphine copper(I) halides – a dinuclear complex, containing two $Cu(PMe_3)_2$ fragments connected by the 1,2,4-triphosphacyclopentadienyl ligand,[5] or monomeric half-sandwich complexes containing $Cu(PPh_3)$ which demonstrate fluxional behaviour in solution and react with $[W(CO)_5(thf)]$ to form binuclear or trinuclear complexes with different bonding modes of the 1,2,4-triphosphacyclopentadienyl ligand to copper.[6] Therefore, it was of interest to study the complexation properties of the 3,4,5-triphenyl-1,2-diphosphacyclopentadienide anion[7,8] which is an isolobal analogue of both the Cp^- anion and the pyrazolate anion and may form monomeric as well as dimeric (or polymeric as pyrazolate[9,10]) copper(I) complexes.



Scheme 1

We have found that the reaction of sodium 3,4,5-triphenyl-1,2-diphosphacylopentadienide **1** or 1-trimethylstannyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene with copper(I) chloride phosphine complexes, $[CuCl(PR_3)]$ (R = cyclopentyl or phenyl),[11,12] yields only the dimeric complexes **3a**,**b** (Scheme 1) which were characterised by NMR spectroscopy.[†] The structure of **3a** was ultimately established by X-ray diffraction analysis (Figure 1).[‡]

In the crystal of compound **3a**, the molecule is located on a crystallographic inversion centre which is located in the centre of the Cu_2P_4 ring which is formed by two 1,2-diphosphacyclopentadienyl rings connected by two copper atoms. Two THF molecules are also present in the unit cell. Both 1,2-diphosphacyclopentadienyl ligands are planar and parallel in contrast to the dimeric 1,2,4-triphosphacyclopentadienyl copper(I) complex[5] which exhibits an orthogonal orientation of both 1,2,4-triphosphacyclopentadienyl rings. Each copper atom has an almost planar environment – the sum of bond angles around copper is 355.3°. No significant electron delocalisation has been observed in **3a**,

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[†] A solution of 0.62 g (1 mmol) sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide[8] **1** or 0.49 g (1 mmol) 1-trimethylstannyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene[14] **2** in 20 ml THF was added to a solution of 0.62 g (1 mmol) {CuCl[P(cyclo-C_5H_9)$_3$]$_2$}[13] in 50 ml THF at –78 °C. The mixture was stirred for 2 h at room temperature, the solvent was evaporated and the residue washed with hexane (3×20 ml) and dried in a vacuum. The resulting powder was extracted with 50 ml toluene, the suspension was filtered and the filtrate was evaporated to dryness. Recrystallisation from THF at –30 °C afforded 0.45 g (70%) of orange crystals of bis(3,4,5-triphenyl-1,2-diphosphacyclopentadienyl)bis(tricyclopentylphosphine)dicopper(I) **3a**, mp 128 °C (decomp.). Complex **3b** was obtained in a similar manner.

For **3a**: ^{1}H NMR (400 MHz, THF-d_8) δ: 1.7–3.5 (m, 27H, cyclo-C_5H_9), 6.7–7.9 (m, 15H, Ph). ^{31}P NMR (161.98 MHz, THF-d_8) δ: 128.2, 15.4.

For **3b**: ^{1}H NMR (400 MHz, THF-d_8) δ: 6.2–8.3 (m, Ph). ^{31}P NMR (161.98 MHz, THF-d_8) δ: 130.2, –1.2.

[‡] *Crystal data for* **3a**: $C_{72}H_{84}Cu_2P_6\cdot 2THF$, $M = 1406.50$, yellow-orange prism, triclinic, space group $P\bar{1}$, $a = 1013.1(2)$, $b = 1144.3(2)$ and $c = 1693.4(3)$ pm, $\alpha = 106.87(1)°$, $\beta = 92.83(2)°$, $\gamma = 107.70(2)°$, $V = 1.7691(6)$ nm^3, $Z = 1$, $d_{calc} = 1.320$ g cm^{-3}, λ(MoKα) = 71.073 pm, $\mu = 0.784$ mm^{-1}, $R_1 = 0.0701$ and $wR_2 = 0.0947$ for all 49217 collected and 10809 independent reflections, 416 parameters, maximal residual electron density 1.118 and –0.818 e Å^{-3}. The data were collected on a Varian Xcalibur-S diffractometer using MoKα radiation and ω-scan rotation. Data reduction was performed with CrysAlis Pro[15] including the program SCALE3 ABSPACK[16] for empirical absorption correction. The structure was solved by direct methods and the refinement of all non-hydrogen atoms was performed with SHELX97.[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms are on calculated positions. Structure figures were generated with ORTEP.[18]

CCDC 763250 contains 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

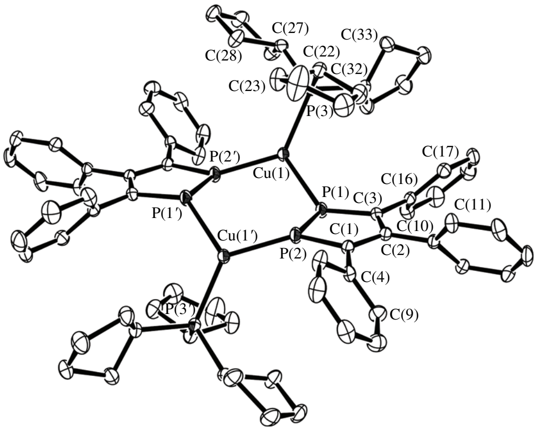

Figure 1 ORTEP view of **3a**. Hydrogen atoms and THF molecules are omitted for clarity. Selected bond lengths (pm) and angles (°): Cu(1)–P(3) 221.84(7), Cu(1)–P(2) 222.26(6), Cu(1)–P(1) 225.45(7), P(1)–C(3) 174.98(18), P(1)–P(2) 208.06(8), P(2)–C(1) 173.62(19); P(3)–Cu(1)–P(2) 129.39(2), P(3)–Cu(1)–P(1) 119.94(2), P(2)–Cu(1)–P(1) 105.94(2), C(3)–P(1)–P(2) 94.44(7), C(3)–P(1)–Cu(1) 131.47(7), P(2)–P(1)–Cu(1) 112.81(3), C(1)–P(2)–P(1) 96.40(7), C(1)–P(2)–Cu(1) 140.52(7), P(1)–P(2)–Cu(1) 119.63(3).

P(1) is in a pyramidal environment with a sum of bond angles of 338.72°, while P(2) has a trigonal planar environment (356.55°). The Cu–P$_{\mathrm{phosphine}}$ bonds [221.84(7) pm] are shorter than those in tricyclopentylphosphine copper(I) complexes, with oligophosphanides $\mathrm{P_4Ph_4}$ [223.9(2)–240.3(2) pm],[10] but are comparable with those of copper complexes of $\mathrm{P_4Bu^t_3}$.[13] The Cu–P$_{\mathrm{ring}}$ distances in **3a** are significantly shorter than those in dimeric 1,2,4-triphosphacyclopentadienide copper(I) complex [225.45(7) *vs.* 236.5(2) pm].[5]

The ^{31}P{^{1}H} NMR spectra of **3** consist of two broad singlets at *ca.* 130 ppm for the 1,2-diphosphacyclopentadienyl ring and at 15 (**3a**) or –1 ppm (**3b**) for the respective phosphine ligand. The ^{31}P{^{1}H} NMR spectra of **3** are temperature independent; heating (up to 320 K) or cooling (up to 180 K) of solutions of **3** in THF does not result in any changes, while dynamic processes were observed for similar phosphine 1,2,4-triphosphacyclopentadienyl copper(I) complexes.[6]

Furthermore, no reaction of **3** with [W(CO)$_5$(THF)] took place at room temperature or at elevated temperature indicating the absence of dynamic processes.

In summary, sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide or 1-trimethylstannyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene reacts with copper(I) phosphine adducts to give stable dinuclear complexes with bridging 1,2-diphosphacyclopentadienyl rings exclusively.

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