ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 691 (2006) 5585–5591

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, crystal structure and DFT calculations on 2,6-diisopropylphenylcopper; its use in the preparation of dichloro-2,6-diisopropylphenylphosphine

René T. Boeré *, Jason D. Masuda [1], Peter Tran

Department of Chemistry and Biochemistry, The University of Lethbridge, Lethbridge, AB, Canada T1K 3M4

Received 10 July 2006; received in revised form 5 September 2006; accepted 5 September 2006
Available online 19 September 2006

Abstract

The homoleptic aryl copper reagent $[Cu_4Dipp_4]$ (Dipp = 2,6-diisopropylphenyl) has been prepared and structurally characterized by a single-crystal X-ray diffraction study. Its tetrameric structure differs in significant details from that of the previously reported $[Cu_4Tripp_4]$ (Tripp = 2,4,6-triisopropylphenyl). The electronic structure of the cluster has been probed through B3LYP/6311G(2d,p)//B3LYP/6-31G calculations on $[Cu_4Ph_4]$ constrained to D_{2d} symmetry. The utility of the new copper reagent is demonstrated by the preparation of pure $DippPCl_2$, for which the crystal structure is also reported.

Keywords: Organocopper; Dichlorophosphine; X-ray Crystallography; NMR

1. Introduction

Organocopper(I) reagents find extensive use in organic synthesis, where they generally impart greater selectivity than conventional Grignard and organolithium reagents [1]. The most popular copper(I) synthetic reagents are ternary lithium diorganocuprates $[R_2Cu]Li$ [2] and "higher order" cuprates [3], especially those containing the cyanide ligand, and in general these are utilized only in coordinating solvents such as THF or CH_3SCH_3. Homoleptic organocopper reagents are used less often and correspondingly less is known about them. However, they are of great utility in main group organometallic chemistry [4], and more recently have found application in supramolecular cluster synthesis [5,6]. Like organolithium reagents, they can be used in non-coordinating solvents. There are still relatively few structural characterizations of the homoleptic, Lewis base-free, reagents. Structures have been reported for $[Cu_5Mes_5]$ [7], $[Cu_4Tripp_4]$ [8], $[Cu_4(CH_2SiMe_3)_4]$ [9], $[Cu_4(C_6F_5)_4]$ [10], $[Cu_4(C_6Me_5)_4]$ [11], $[Cu_4(C_6H_4\{CH{=}CH_2\}\text{-}2)_4]$ [12], $[Cu_3(C_6H_3Ph_2\text{-}2,6)_3]$ [13] and $[Cu_2(C_6H_3Mes_2\text{-}2,6)_2]$ [13], suggesting in general a decreasing cluster nuclearity with increasing steric bulk of the organic group. The monomeric structure of the terphenyl derivative $[CuC_6H_2Ph_3\text{-}2,4,6]$ [14] has been questioned [15]. However, the structure determination of $[Cu_4Mes_4]$ [16] and solution studies [7] suggest that the nuclearity of aryl copper(I) reagents is variable depending on the medium, leading many researchers to describe them by the generic formula $(RCu)_x$. Herein we report the synthesis and X-ray crystal structure of a new aryl copper reagent based on the 2,6-diisopropylphenyl (Dipp) substituent, which we have been exploiting as a new bulky group in phosphorus chemistry [17], $[Cu_4Dipp_4]$, and its use in the preparation of $DippPCl_2$.

---

* Corresponding author. Tel.: +1 403 329 2045; fax: +1 403 329 2057.
E-mail address: boere@uleth.ca (R.T. Boeré).

[1] Present address: Department of Chemistry, University of California, Riverside, CA, USA.

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.09.004

2. Experimental

2.1. General methods

DippBr was prepared as previously reported [18]. Anhydrous CuCl, 1,2-dibromoethane and PCl_3 (Aldrich) were used as received. THF was distilled from sodium benzophenone immediately before use. Hexanes and heptane were distilled from $LiAlH_4$; toluene and 1,4-dioxane from sodium under N_2. All reactions were performed in an atmosphere of dry N_2 in oven-dried glassware (>4 h at >160 °C) unless otherwise noted. NMR spectra (250 or 300 MHz) were referenced to the solvent (^1H and ^{13}C) or to external H_3PO_4 (^{31}P).

3. Synthesis of $(DippCu)_x$

1.76 g (72.5 mmol) of activated Mg turnings were suspended in 60 mL THF, 0.15 mL (0.33 g, 1.8 mmol) 1,2-dibromoethane was added, and refluxed for 30 m. 15.0 g (62.2 mmol) DippBr in 195 mL THF was added dropwise at RT, and the mixture was then refluxed overnight. 6.16 g (62.2 mmol) of CuCl was added at RT and the mixture then refluxed for 30 m. Next 37.5 mL of 1,4-dioxane was added at RT, the mixture filtered and the solvent removed. An off-white residue was redissolved in 150 mL warm toluene, filtered and evaporated to yield 11.3 g (50.3 mmol, 81% based on DippBr) of moisture- and light-sensitive off-white $(DipCu)_x$. Single crystals obtained by slow cooling of heptane solutions under N_2, mp 150 °C (dec) were pure by NMR (C_6D_6): ^1H δ 7.25 (t, 8 Hz, 1H, *p*-C*H*), 7.05 (d, 8 Hz, 2H, *m*-C*H*), 3.86 (sept, 7 Hz, 2H, C*H*(CH_3)$_2$), 1.26 (d, 7 Hz, 12H, CH(C*H*$_3$)$_2$); ^{13}C δ 167.3 (*o*-C), 139.2 (*i*-C), 132.5 (*p*-C), 123.0 (*m*-C), 42.2 (*C*H(CH_3)$_2$), 27.7 (CH(*C*H$_3$)$_2$). MS(70 eV): *m*/*z* (calculated on ^{63}Cu) 896 ($Dipp_4Cu_4^+$, 2%), 735 ($Dipp_3Cu_4^+$, 100%, exact mass: 735.115, calc. 735.117), 162 ($DippPH^+$, 17%), 147 ($[DippH–CH_3]^+$, 50%), 119 ($[DippH–CH(CH_3)_2]^+$, 20%).

3.1. Synthesis of pure $DippPCl_2$

$(DippCu)_x$ (7.8 g. 35 mmol) was suspended in 100 mL of THF, and PCl_3 (4.8 g, 35 mmol) in 10 mL THF was added dropwise at 0 °C. After stirring at room temperature for 14 h, filtering off the precipitate, extracting in hexanes, filtering again, the solvent was removed in vacuo. Distillation of the residue (bp 91 °C at 0.1 Torr) yielded 4.5 g (50%) of a colourless liquid which was pure by NMR in $CDCl_3$: ^1H δ 7.45 (t, 8 Hz, 1H, *p*-C*H*), 7.25 (d of d, 8 and 3 Hz, 2H, *m*-C*H*), 4.12 (sept. of d., 7 and 5 Hz, 2H, C*H*(CH_3)$_2$), 1.31 (d, 7 Hz, 12H, CH(C*H*$_3$)$_2$); ^{13}C δ 154.6 (d, 23 Hz, *o*-C), 134.7 (d, 69 Hz, *i*-C), 133.4 (*p*-C), 125.0 (*m*-C), 30.9 (d, 31 Hz, *C*H(CH_3)$_2$), 24.9 (CH(*C*H$_3$)$_2$); ^{31}P δ +165.3. MS(70 eV) (calculated on ^{35}Cl): *m*/*z* 262.0436 (within 4 ppm calc. $DippPCl_2^+$, 37%), 227.0751 (within 2 ppm calc. $DippPCl^+$, 100%), 191.0988 (within 1 ppm calc. $C_{12}H_{16}P^+$, 59%), 175.0674 (within 0.5 ppm calc. $C_{11}H_{12}P^+$, 25%), 161.1324 (within 4 ppm calc. $C_{12}H_{17}^+$, 19%), 149.0521 (within 0.5 ppm of $C_9H_{10}P^+$, 25%). Previously prepared only as a mixture of $DippPCl_2$ along with DippPBrCl and $DippPBr_2$ [19].

3.2. Crystallography

The data were corrected for Lorentz and polarization effects and for absorption using Bruker SADABS [20]. The structures were solved by direct methods and expanded using Fourier techniques [21]. Crystal, solution and refinement details for both structures are found in Table 1. Selected interatomic distances and angles for $Dipp_4Cu_4$ are presented in Table 2, and for $DippPCl_2$ in Table 3. The structure of $Dipp_4Cu_4$ is overwhelmingly successful, but the huge model with 969 refined parameters resulted in less than ideal anisotropic thermal parameters for C43 (and hence for the attached H atom). A careful analysis of the structure shows that all the *para* and *meta* phenyl ring carbon atoms show similar, though less severe, flattening as in C43. This effect can be attributed to a rocking motion of whole Dipp groups perpendicular to the Cu_4 planes, which is an entirely plausible molecular vibration in the crystal lattice.

3.3. Computational study

Hybrid HF/DFT calculations were performed on key model systems at the B3LYP/6-311G(2d,p)//B3LYP/6-31G level of theory using GAUSSIAN-98 [22]. The Dipp groups are modeled by Ph groups, and symmetry was imposed at the D_{2d} level.

4. Results and discussion

4.1. Synthesis of $(DippCu)_x$ and $DippPCl_2$

In a typical procedure, the Grignard reagent is prepared from DippBr using activated magnesium chips in THF. To the solution of this reagent is added anhydrous copper(I) chloride. Filtration of the resulting suspension and removal of the solvent affords an off-white powder of DippCu that is synthetically useful.

Jäkle and Manners have shown the utility of, specifically, $(MesCu)_x$ for the synthesis of a variety of main group mesityl derivatives [4]. Thus with $(MesCu)_x$ and excess PCl_3, $MesPCl_2$ can be produced in 95% yield based on the organocopper reagent (NMR evidence). According to Xie and Neilson, $MesPCl_2$ can also be produced on a large scale by the reaction of MesMgBr with PCl_3, but no details of the procedure are given [23]. In our experience, the reaction of DippMgBr with PCl_3 in many trials leads exclusively to a mixture of all three halides, $DippPBr_2$, DippPBrCl and $DippPCl_2$ in distributions that imply that *all* the bromide originally introduced from the Grignard

Table 1
Crystal data and structure refinement for the compounds

Compound	DippCu	$DippPCl_2$
Crystal colour and habit	Colourless prism	Colourless parallelepiped
Crystal size (mm)	$0.28 \times 0.52 \times 0.62$	$0.26 \times 0.23 \times 0.22$
Chemical formula	$C_{48}H_{68}Cu_4$	$C_{12}H_{17}Cl_2P$
a (Å)	12.5923(8)	7.843(3)
b (Å)	16.2213(10)	9.838(3)
c (Å)	21.9435(14)	17.429(6)
α (°)	90.7850(10)	
β (°)	98.6040(10)	
γ (°)	91.3950(10)	
Wavelength (Å)	0.71073	0.71073
Temperature (K)	193(2)	173(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
Z	4	4
Diffractometer	Bruker Smart	Bruker APEX II
Data collection	ω and φ scans	ω and φ scans
Reflections collected	21279	15886
Independent reflections (R_{int})	17776 (0.0234)	3312 (0.0202)
Completeness to θ	26.40°, 97.8%	27.95°, 99.6%
Absorption coefficient (mm^{-1})	1.925	0.569
Absorption correction	SADABS	SADABS
Maximum and minimum transmission	0.518 and 0.409	0.885 and 0.866
Data/restraints/parameters	17776/0/969	3312/0/140
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0292$, $wR_2 = 0.0745$	$R_1 = 0.0258$, $wR_2 = 0.0650$
R indices (all data)	$R_1 = 0.0415$, $wR_2 = 0.0783$	$R_1 = 0.0310$, $wR_2 = 0.0677$
Goodness-of-fit on F^2	0.966	1.049
Hydrogen atoms	Riding model	Riding model
Largest difference in peak and hole (e/Å^{-3})	0.494 and −0.433	0.306 and −0.131

reagent ends up on phosphorus, a remarkable testimony to the greater nucleophilicity of bromide relative to chloride (^{31}P NMR and mass spectroscopic evidence) [19]. Similar halide-scrambling reactions have been reported by others, e.g. in the synthesis of $Mes_2P(Br,Cl)$ [24]. While there are undoubtedly many situations in which the preparation of such mixed halides is of no consequence, a reliable and convenient way to prepare the pure chloride is worth having, and the copper reagents provide one such route. Thus the reaction of one equivalent of $(DippCu)_x$ with PCl_3 leads to the production of pure $DippPCl_2$.

Table 2
Selected interatomic distances (Å) and angles (°) for $[Cu_4Dipp_4]$

Molecule 1			
Cu(1)–Cu(2)	2.4161(3)	Cu(2)–Cu(1)–Cu(4)	97.326(13)
Cu(1)–Cu(4)	2.4175(3)	Cu(3)–Cu(2)–Cu(1)	82.361(12)
Cu(2)–Cu(3)	2.4071(3)	Cu(4)–Cu(3)–Cu(2)	97.924(12)
Cu(3)–Cu(4)	2.4045(4)	Cu(3)–Cu(4)–Cu(1)	82.388(12)
Cu(1)–C(1)	2.027(2)	C(1)–Cu(2)–Cu(3)	132.02(6)
Cu(1)–C(37)	2.028(2)	C(1)–Cu(1)–Cu(4)	145.24(6)
Cu(2)–C(1)	2.0183(19)	C(13)–Cu(2)–Cu(1)	132.16(6)
Cu(2)–C(13)	2.024(2)	C(13)–Cu(3)–Cu(4)	145.99(6)
Cu(3)–C(25)	2.030(2)	C(25)–Cu(3)–Cu(2)	145.82(6)
Cu(3)–C(13)	2.033(2)	C(25)–Cu(4)–Cu(1)	132.12(6)
Cu(4)–C(25)	2.024(2)	C(37)–Cu(1)–Cu(2)	145.13(6)
Cu(4)–C(37)	2.026(2)	C(37)–Cu(4)–Cu(3)	131.66(6)
Molecule 2			
Cu(5)–Cu(6)	2.4150(4)	Cu(8)–Vu(5)–Cu(5)	98.206(13)
Cu(5)–Cu(8)	2.4140(4)	Cu(5)–Cu(6)–Cu(7)	81.581(12)
Cu(6)–Cu(7)	2.4217(4)	Cu(8)–Cu(7)–Cu(6)	98.261(13)
Cu(7)–Cu(8)	2.4053(4)	Cu(7)–Cu(8)–Cu(5)	81.937(12)
Cu(5)–C(49)	2.040(2)	C(49)–Cu(5)–Cu(8)	144.73(6)
Cu(5)–C(85)	2.028(2)	C(85)–Cu(5)–Cu(6)	147.03(6)
Cu(6)–C(49)	2.025(2)	C(61)–Cu(6)–Cu(5)	130.38(7)
Cu(6)–C(61)	2.021(2)	C(49)–Cu(6)–Cu(7)	130.90(6)
Cu(7)–C(61)	2.026(2)	C(61)–Cu(7)–Cu(8)	145.58(6)
Cu(7)–C(73)	2.033(2)	C(73)–Cu(7)–Cu(6)	146.04(6)
Cu(8)–C(73)	2.028(2)	C(85)–Cu(8)–Cu(7)	131.63(6)
Cu(8)–C(85)	2.034(2)	C(73)–Cu(8)–Cu(5)	131.93(6)

4.2. Structure of $(DippCu)_x$

The crystal structure of $(DippCu)_x$ (Tables 1 and 2, Fig. 1) consists of two highly similar independent molecules in the asymmetric unit of the triclinic unit cell, which are,

Table 3
Selected interatomic distances (Å) and angles (°) for $DippPCl_2$

P(1)–C(1)	1.8262(14)	C(1)–P(1)–Cl(1)	102.73(6)
P(1)–Cl(1)	2.0681(8)	C(1)–P(1)–Cl(2)	102.55(5)
P(1)–Cl(2)	2.0707(8)	Cl(1)–P(1)–Cl(2)	101.07(3)
C(1)–C(6)	1.4165(19)	C(6)–C(1)–C(2)	120.27(12)
C(1)–C(2)	1.4258(18)	C(6)–C(1)–P(1)	114.00(10)
C(2)–C(3)	1.3890(19)	C(2)–C(1)–P(1)	125.73(10)
C(2)–C(7)	1.5265(18)	C(3)–C(2)–C(1)	118.04(12)
C(3)–C(4)	1.384(2)	C(3)–C(2)–C(7)	117.32(12)
C(4)–C(5)	1.377(2)	C(4)–C(3)–C(2)	121.71(13)
C(5)–C(6)	1.3948(19)	C(5)–C(4)–C(3)	120.14(13)
C(6)–C(10)	1.529(2)	C(4)–C(5)–C(6)	121.11(14)
		C(5)–C(6)–C(1)	118.74(13)

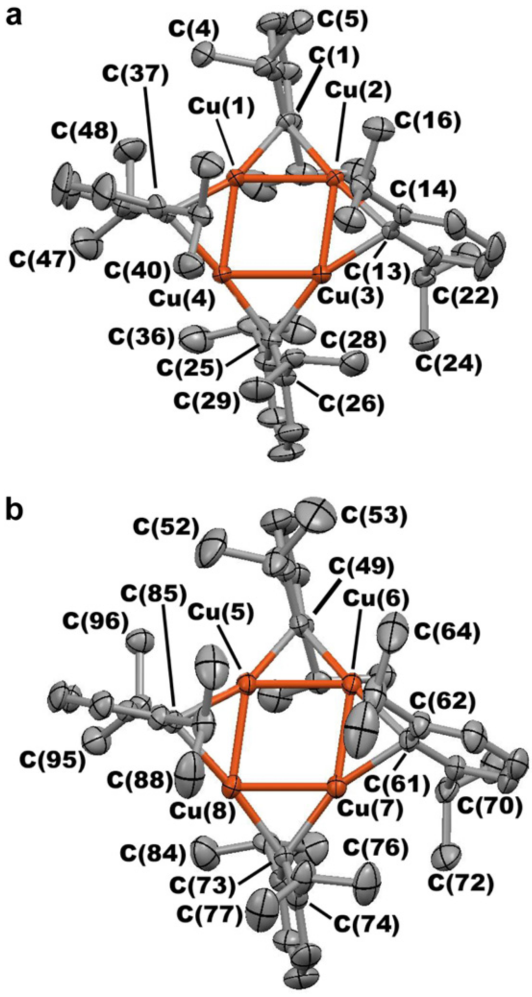
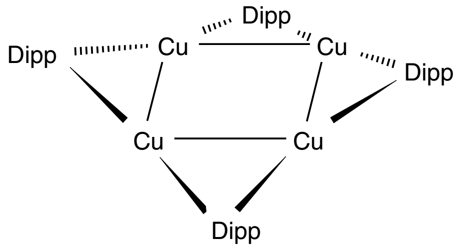


Fig. 1. Structures of DippCu in the crystal at −80 °C (two independent molecules in unit cell) viewed perpendicular to the Cu_4 plane: (a) molecule 1; (b) molecule 2. Thermal ellipsoids are drawn at the 50% probability level.

however, statistically distinct (e.s.d. of refinement). Each molecule consists of a trapezoidal plane of copper atoms bridged along each Cu–Cu contact by an approximately perpendicular aryl group. The *ispo* carbon atoms are not coplanar with the copper atoms (though such coplanarity has been observed previously [11,16]), and are displaced to different sides of the copper plane in an opposed manner to give a "gull wing" structure that has also been observed before [8].



The average of the 8 Cu–Cu distances is 2.413(6) Å [25], and the angles at copper fall into acute ($Cu_{2,4,6,8}$ average 82.1(4)°) and obtuse ($Cu_{1,3,5,7}$ average 97.9(4)°) groups indicating considerable distortion in the trapezoidal direction. The deviation of the *ipso* carbon atoms from the mean copper planes is also quite uniform at 0.58(2) Å. Unlike the structure of $[Cu_4Tripp_4]$ in which the Cu–C_{ipso} distances are considerably skewed towards one of the two bridged copper atoms, $[Cu_4Dipp_4]$ has very regular bridging distances that average to 2.028(5) Å. In conjunction with the trapezoidal distortion at copper, each Dipp group is tilted from the vertical by a small amount; despite the opposing 'up' and 'down' Cu_2C_{ipso} envelope configurations, all four Dipp groups in a cluster tilt in the *same* direction, imparting a slight helicity to each cluster. The average tilt angles between planes defined by the Cu_4 group and the six carbon atoms of each Dipp group fall into two groups, seven of the rings having fairly uniform tilt angles of 83(1)°, while the eighth ($C_{85,86,90,91,92,93}$) has a tilt of 79.6°; this tilting seems to be dictated by the steric interference between the isopropyl groups on adjacent aryl rings. In general, the structure of $[Cu_4Dipp_4]$ is quite similar to that of the isosteric $[Cu_4Tripp_4]$, but the geometry of its Cu–C–Cu bridges are much more regular. We note that the latter crystallizes in a high symmetry space group with crystallographically imposed fourfold rotation symmetry, whereas our structure has no imposed symmetry and likely reflects a more natural structural arrangement for the molecule. Indeed, these results along with that of the completely regular structure of $[Cu_4(C_6Me_5)_4]$ [11] which has crystallographically imposed square, orthogonal and Cu–C_{ipso} coplanar geometry, suggests that the solid-state geometries of homoleptic aryl copper complexes are extremely susceptible to crystal packing effects. Thus the previously invoked bonding arguments for $[Cu_4Tripp_4]$ on the basis of its distorted structure are most likely over interpreted [8].

4.3. NMR spectroscopic studies

The NMR spectra in solution are extremely similar to those reported for $[Cu_4Tripp_4]$ at RT, but with no evidence of line-broadening in d_6-benzene [8]. There has been considerable discussion in the literature on the possibility of having various stoichiometries in solution for the homoleptic copper aryls [7], and just as reported for $[Cu_5Mes_5]$ dissolved in aromatic solvents, we observed small additional peaks in both d_6-benzene and d_8-toluene solutions made up from pure crystalline $[Cu_4Dipp_4]$. In both solvents, there were two sets of signals quite similar to those of the main peaks (see Section 2); the isopropyl CH_3 doublets are at slightly lower frequency, while the methine CH septets are at slightly higher frequency. Finally, we note that *only* the tetramer is observed in the low-resolution mass spectrum (the observed fragments are $[Cu_4Dipp_4]^+$ and $[Cu_4Dipp_3]^+$). Thus the form of DippCu that crystallizes from petroleum solvents is a tetrameric molecule of considerable thermal stability, which can be ionized intact via electron impact mass spectrometry. However, in solution in aromatic solvents slow equilibration leads to species which are likely to differ in nuclearity from the crystallized tetramer.

4.4. Electronic structure

In order to gain further insights into the electronic structure of homoleptic copper aryl reagents we have performed hybrid DFT calculations on a model compound where phenyl groups replace Dipp. An optimized geometry was obtained for this $[Cu_4Ph_4]$ molecule restrained to D_{2d} symmetry at the B3LYP/6-31G level of theory, and this structure is presented in Fig. 3. The significant frontier Kohn–Sham orbitals and their energies are obtained from a B3LYP/6-311G(2d,p) calculation, namely the LUMO, the HOMO and the doubly degenerate HOMO − 1. Main group organometallic compounds are most often utilized as carbanion sources, and thus we expect to find energetic filled orbitals with considerable electron density – in this instance – on the *ipso* carbon atoms of the aryl ligands. To a certain extent, we do find this, because the degenerate set of orbitals of symmetry e that lie at −5.87 eV have considerable C_{ipso} σ_{LP} character, in conjunction with metal $d_{x^2-y^2}$ acceptor orbitals. However, the HOMO of the cluster at −5.44 eV is an orbital of b_2 symmetry that is effectively non-bonding and is largely composed of copper d_{xy} orbitals, with no contribution from *ipso* carbon orbitals. In this sense, these homoleptic Cu(I) aryl complexes are less “reduced” at carbon than complexes of the more electropositive metals, and it is this character that is responsible for the milder, more selective, reactions that they undergo compared to Grignard or organolithium reagents.

4.5. Structure of $DippPCl_2$

The crystal structure of $DippPCl_2$ (Tables 1 and 3) with atom numbering scheme is shown in Fig. 2. The compound is quite flat, with both the CH atoms of the isopropyl and the P atoms co-planar with the benzene ring. The Cl–P–Cl angle is bisected by the aryl plane almost perfectly (within 1°). In response to steric pressure from the $C_{7–9}$ isopropyl group, the PCl_2 group is distorted from the ideal trigonal angle at C1 by about 6° towards C6 but with the P atom remaining in the aryl ring plane. Since there are no significant intermolecular contacts within the unit cell, the observed structural distortions may be attributed to intramolecular forces.

There are still relatively few published crystal structures for dichlorophosphines, particularly for aryl phosphines [26–39]. The terphenyl compound (2,6-bis(4-*tert*-butylphenyl)phenyl)dichlorophosphine is perhaps the closest valid structure for comparison with that of $DippPCl_2$ [26], as it possesses flanking 2,6-aryl substituents playing much the same role as the isopropyl groups in our structure. While the two Cl atoms are found on opposite sides of the central aryl ring, in contrast to $DippPCl_2$, the group is significantly twisted, an effect that is correlated to the twisting of the 2,6-(4-*tert*-butylphenyl) aryl rings. The PCl_2 unit in this structure is distorted from the trigonal angle by about 8°, but here this is accompanied by being pushed out of the plane of the central benzene ring by 0.42 Å, an effect that is also correlated with the twist of the flanking groups. The C–P distance in the terphenyl at 1.8355 Å is also longer than the 1.826 Å found in $DippPCl_2$. Another aryl PCl_2 compound is 1,8-bis(dichlorophosphino)naphthalene, but its structure is distorted by interactions between the two PCl_2 units on the adjacent side of the naphthalene backbone, making comparisons less valid [27]. Here the C–P bond distances are also longer at 1.8303 Å (average of 4 values). By contrast, when a PCl_2 group is bonded to five-membered rings such as furan [28] or ferrocene [29], the C–P bond distances are noticeably shorter at 1.776, 1.788 or 1.789 Å. None of these structures has any steric congestion from flanking groups, but the values are considerably shorter than the average C–P distances in triarylphosphines at 1.836 ± 0.010 Å determined from 102 examples in the CCDC database [40]. The P–Cl distances in *all* of these examples range from 2.046 to 2.072 Å, rather longer than the average value of 2.008 ± 0.035 Å from the database [40]. Within this range, $DippPCl_2$ is normal.

4.6. NMR spectra of $DippPCl_2$

The ^{31}P chemical shift in $DippPCl_2$ of +165.3 ppm is unremarkable for an $ArylPCl_2$ species. In the ^1H spectrum, there is clear indication of ^{31}P coupling to the isopropyl C*H* (5 Hz) and the *meta* C*H* (4 Hz) atoms. Similarly, the $\{^1H\}$–^{13}C spectrum displays 1:1 doublets from ^{31}P coupling to the *ipso* and *ortho* benzene ring carbon atoms and the isopropyl *C*H atoms. In addition, the signal from the benzene ring *meta* carbon atoms is line-broadened from unresolved coupling to phosphorus.

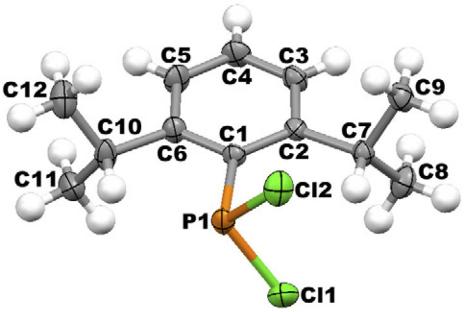


Fig. 2. Structure of $DippPCl_2$ in the crystal at −100 °C. Thermal ellipsoids are drawn at the 50% probability level. There are no significant intermolecular contacts less than the sums of van der Waals radii.

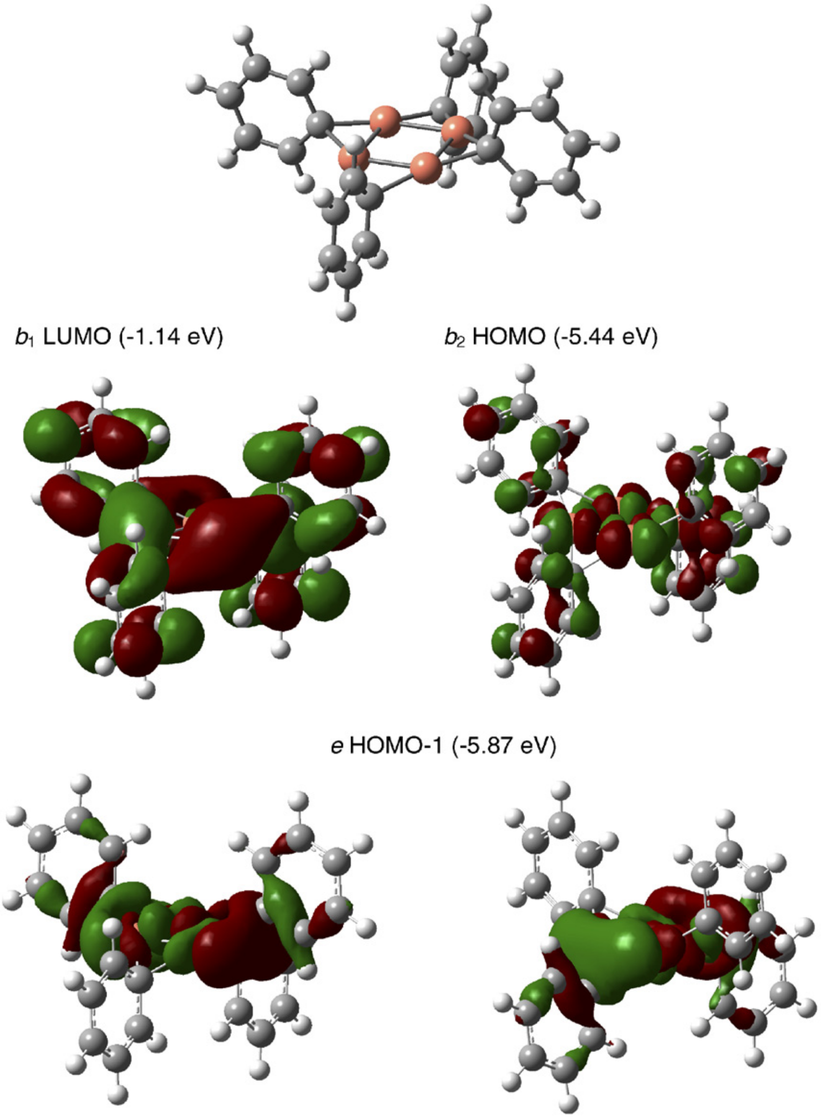


Fig. 3. Geometry optimized structure of [Cu$_4$Dipp$_4$] at the B3LYP/6-31G level of theory under D_{2d} symmetry, and surface diagrams of the LUMO, HOMO and HOMO − 1 (*e* symmetry set) Kohn–Sham orbitals. Orbitals and their energies are from a B3LYP/6-311G(2d,p) calculation.

Acknowledgments

We thank the Natural Sciences and Engineering Research Council (Canada) and the University of Lethbridge for financial support and for the purchase of the X-ray diffractometers and NMR spectrometers employed in this study. R. Macdonald (University of Alberta) is thanked for obtaining X-ray data on [Cu$_4$Dipp$_4$].

Appendix A. Supplementary material

CCDC 614243 and 614244 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.004.

References

[1] Abbreviations used in this paper. Mes: 2,4,6-trimethyphenyl. Dipp: 2,6-diisopropylphenyl. Tripp: 2,4,6-triisopropylphenyl. RT: room temperature, 22 °C unless otherwise specified. EI: electron impact. DMS: dimethyl sulphide. Ph: phenyl. Me: methyl. Et: ethyl. dppe: bis(diphenylphosphino)ethane. THF: tetrahydrofuran.

[2] (a) [Cu(dppe)$_2$][CuMes$_2$] P. Leoni, M. Pasquali, C.A. Ghilardi, J. Chem. Soc., Chem. Commun. (1983) 240;
(b) [Li(THF)$_4$][Cu-(CH$_2$SiMe$_3$)$_2$] C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Organomet. Chem. 263 (1984) C23;
(c) [Li(12-crown-4)$_2$][CuMe$_2$] or [CuPh$_2$] H. Hope, M.M. Olmstead, P.P. Power, J. Sandell, X. Xu, J. Am. Chem. Soc. 107 (1985) 4337;
(d) Li$_2$Cu$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)$_4$ G. van Koten, J.T.B.H. Jastrzebski, F. Muller, C.H. Stam, J. Am. Chem. Soc. 107 (1985) 697;

(e) Li_2Cu_2-$Ph_4(OEt_2)_2$ N.P. Lorenzen, E. Weiss, Angew. Chem. 102 (1990) 322;

(f) Li_2Cu_2-$Ph_4(OEt_2)_2$ N.P. Lorenzen, E. Weiss, Angew. Chem., Int. Ed. Engl. 29 (1990) 300;

(g) $Li_2Cu_2Ph_4(DMS)_3$ M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 112 (1990) 8008.

[3] (a) $Li_6(OEt_2)_3Cu_4(CCPh)_{10}$ F. Olbrich, J. Kopf, E. Weiss, Angew. Chem. 105 (1993) 1136;

(b) $Li_6(OEt_2)_3Cu_4(CCPh)_{10}$ F. Olbrich, J. Kopf, E. Weiss, Angew. Chem., Int. Ed. Engl. 32 (1993) 1077;

(c) $Li_3(CuPh_2)(CuPh_3)(DMS)_4$ and $Li_5(CuPh_2)_3(CuPh_3)(DMS)_4$ M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 112 (1990) 8008;

(d) For detailed reviews of the field see: J.T.B.H. Jastrzebski, G. van Koten, in: N. Krause (Ed.), Modern Organocopper Chemistry, Wiley–VCH, Weinheim, 2002, p. 1;

(e) E. Nakamura, S. Mori, Angew. Chem., Int. Ed. 39 (2000) 3750.

[4] F. Jäkle, I. Manners, Organometallics 18 (1999) 2628.

[5] A.L. Keen, M. Doster, H. Han, S.A. Johnson, Chem. Commun. (2006) 1221.

[6] A. Sundararaman, L.N. Zakharov, A.L. Rheingold, F. Jäkle, Chem. Commun. (2005) 1708.

[7] E.M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, Organometallics 8 (1989) 1067.

[8] D. Nobel, G. van Koten, A.L. Spek, Angew. Chem. 101 (1989) 211; Angew. Chem., Int. Ed. 28 (1989) 208.

[9] J.A.J. Jarvis, R. Pearce, M.F. Lappert, J. Chem. Soc., Dalton Trans. (1977) 999.

[10] A. Sundararaman, R.A. Lalancette, L.N. Zakharov, A.L. Rheingold, F. Jäkle, Organometallics 22 (2003) 3526.

[11] H. Eriksson, M. Håkansson, S. Jagner, Inorg. Chim. Acta 277 (1988) 233.

[12] H. Eriksson, M. Ortendahl, M. Hakansson, Organometallics 15 (1996) 4823.

[13] M. Niemeyer, Organometallics 17 (1998) 4649.

[14] R. Lingnau, J. Strähle, Angew. Chem., Int. Ed. 27 (1988) 436.

[15] A. Haaland, K. Rypdal, H.P. Verne, W. Scherer, W.R. Thiel, Angew. Chem., Int. Ed. 33 (1994) 2443.

[16] H. Eriksson, M. Håkansson, Organometallics 16 (1997) 4243.

[17] R.T. Boeré, Y.K. Zhang, J. Organomet. Chem. 690 (2005) 2651.

[18] R.R. Schrock, M. Wesolek, A.H. Liu, K.C. Wallance, J.C. Dewan, Inorg. Chem. 27 (1988) 2050.

[19] R.T. Boeré, J.D. Masuda, Can. J. Chem. 80 (2002) 1607.

[20] Bruker SMART V 5.631, Bruker AXS Inc., 2003.

[21] G.M. Sheldrick, SHELXTL, Version 6.14, Bruker AXS Inc., Madison, WI, 2003.

[22] M.J. Frisch et al., GAUSSIAN-98, Revision A.9, Gaussian Inc., Pittsburgh, PA, 1998.

[23] Z.-M. Xie, R.H. Neilson, Organometallics 2 (1983) 921.

[24] (a) J.B. Lambert, J.-H. So, J. Org. Chem. 56 (1991) 5960;

(b) D.J. Brauer, F. Bitterer, F. Dörrenbach, G. Heßler, O. Stelzer, C. Krüger, F. Lutz, Z. Naturforsch. B 51 (1996) 1183.

[25] Errors in averaged derived parameters refer to *standard deviations* of the values from the mean; we note that in most cases these deviations are *larger* than the e.s.d.'s from the refinement.

[26] R.J. Wehmschulte, M.A. Khan, S.I. Hossain, Inorg. Chem. 40 (2001) 2756.

[27] P. Kilian, A.M.Z. Slawin, J.D. Woollins, Chem.-Eur. J. 9 (2003) 215.

[28] S.A. Reiter, S.D. Nogai, H. Schmidbaur, Dalton Trans. (2005) 247.

[29] E. Niecke, M. Nieger, R. Pietschnig, Phosphorus Sulfur Silicon Relat. Elem. 147 (1999) 325.

[30] P. Kilian, H.L. Milton, A.M.Z. Slawin, J.D. Woollins, Inorg. Chem. 43 (2004) 2252.

[31] G.P. Matveicheva, T.L. Krasnova, G.M. Apal'kova, A.I. Gusev, V.A. Sharapov, E.F. Bugerenko, E.A. Chernyshev, Zh. Obshch. Khim. (Russ.) (Russ. J. Gen. Chem.) 55 (1985) 1433.

[32] H. Schumann, F.H. Gorlitz, M. Schafers, Acta Crystallogr., Sect. C 49 (1993) 688.

[33] R.K. Bansal, N. Gupta, S. Singh, K. Karaghiosoff, P. Mayer, M. Vogt, Tetrahedron Lett. 45 (2004) 7771.

[34] T.R. van den Ancker, P.C. Andrews, S.J. King, J.E. McGrady, C.L. Raston, B.A. Roberts, B.W. Skelton, A.H. White, J. Organomet. Chem. 607 (2000) 213.

[35] S.S. Al-Juaid, S.M. Dhaher, C. Eaborn, P.B. Hitchcock, C.A. McGeary, J.D. Smith, J. Organomet. Chem. 366 (1989) 39.

[36] Y. Ehleiter, G. Wolmershauser, H. Sitzmann, R. Boese, Z. Anorg. Allg. Chem. 622 (1996) 923.

[37] C. Jones, P.C. Junk, A.F. Richards, M. Waugh, New J. Chem. (Nouv. J. Chim.) 26 (2002) 1209.

[38] A. Schmidpeter, H. Noth, G. Jochem, H.-P. Schrodel, K. Karaghiosoff, Chem. Ber. 128 (1995) 379.

[39] V. Plack, J.R. Goerlich, A. Fischer, H. Thonnessen, P.G. Jones, R. Schmutzler, Z. Anorg. Allg. Chem. 621 (1995) 1080.

[40] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) S1.