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XXVII *. COMPLEX FORMING REACTIONS OF POLYNUCLEAR ARYLCOPPER COMPOUNDS: C_{alk}—P BOND CLEAVAGE IN 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE (DIPHOS) BY $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ AND CRYSTAL STRUCTURE OF $[(C_6H_5)_2PCu \cdot \text{DIPHOS}]_2 \cdot 2\ C_6H_6$

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Summary

Molecular weight measurements and microwave titrations indicate that no interaction occurs between tetrameric $2\text{-}Me_2NCH_2C_6H_4Cu$ (Ar_4Cu_4) and the monodentate ligands PPh_3, CH_3CN or pyridine. However, the tetrameric structure Ar_4Cu_4 breaks down upon interaction (1/1 molar ratio ArCu/L) with the bidentate ligands (L) Diphos or *cis*-DPPEE to give the monomeric 1/1 complexes ArCu · L.

Addition of Diphos to ArCu · Diphos or conducting the reaction of Ar_4Cu_4 with Diphos in a 1/2 ratio (ArCu/Diphos) gives rise to a C_{alk}—P bond cleavage reaction resulting in the formation of dimeric $(Ph_2PCu \cdot \text{Diphos})_2 \cdot 2\ C_6H_6$, ArH and $Ph_2PCH{=}CH_2$.

The molecular structure of $(Ph_2PCu \cdot \text{Diphos})_2 \cdot 2\ C_6H_6$ has been determined by a single-crystal X-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$ and have $Z = 2$ in a unit cell of dimensions $a = 12.997(6)$, $b = 12.669(7)$, $c = 22.839(9)$ Å and $\beta = 94.48(4)°$. The structure was refined to $R = 0.048$ for 3048 independent reflections. The four copper atoms in the dimer are held together by two Ph_2P bridges. The bonding in the dimer is discussed.

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* For part XXVI, see ref. 1.

Introduction

Camus and Marsich [2] have shown that in the presence of amine and phosphine ligands polynuclear arylcopper compounds such as phenylcopper and *o*-, *m*-, and *p*-tolylcopper * form smaller aggregates with $Ar_xCu_xL_y$ stoichiometry. Alkylcopper compounds undergo break-down to mononuclear $AlkCuL_2$ complexes in which the copper atom is three-coordinate [5].

Arylcopper compounds in which the aryl group bears a coordinating substituent may be expected to show a different reactivity towards external ligands. In this type of polynuclear compounds, e.g. $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ (I) [6] and $(2\text{-}Me_2NC_6H_4Cu)_n$ (II) [7] the built-in ligand can coordinate with the copper atoms, thereby increasing the coordination number of the copper atoms from two in the unsubstituted arylcopper compounds [7] to three.

In our general study of polynuclear arylcopper compounds we have included reactions of arylcopper compounds containing built-in ligands with external coordinating ligands. We found that in contrast to its action on the simple arylcopper compounds, triphenylphosphine does not break down the structures of tetrameric I and polymeric II, whereas with 1,2-bis(diphenylphosphino)ethane (Diphos) a mononuclear copper complex is formed followed by a P—C bond cleavage in the Diphos ligand. In view of the increasing interest in the nature of the interaction of phosphines and amines with organocopper compounds which are used as intermediates in organic synthesis [8a] a more detailed discussion of our results seems timely.

We report in this paper the reactions of I and II with various mono- and bidentate phosphine and amine ligands. A $P—C_{alk}$ bond cleavage occurring upon interaction of Diphos with I will be discussed in greater detail. A preliminary communication of these results appeared in 1972 [9]. The nature of the organocopper—phosphine interaction will be placed in the broader perspective of organic synthesis based on organocopper intermediates.

Results

The reactions of tetrameric 2-[(dimethylamino)methyl]phenylcopper (I) with triphenylphosphine in a 1/1 as well as in a 1/2 ratio ($ArCu/PPh_3$) afforded reaction mixtures from which the reagents could be recovered unchanged. The absence of any interaction between the organocopper and triphenylphosphine was also obvious from molecular weight determinations of benzene solutions containing varying $ArCu/PPh_3$ ratios (see Table 1). Microwave titrations [10] confirmed the absence of complex formation between I and PPh_3. Exactly the same results were obtained when acetonitrile was used as a ligand. From the 1/1 reaction of I with acetonitrile in benzene both reagents were isolated unchanged in quantitative yields.

In contrast, I readily forms complexes with the bidentate phosphine ligands Diphos and *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-DPPEE), respectively. However, in the case of Diphos a distinct difference between the 1/1 and the 1/2 (ArCu/Diphos) reaction was observed.

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* Recently, we established that tolylcopper compounds have discrete cluster structures, e.g., *p*-tolylcopper exists in benzene as a tetramer [3] (see also ref. 4).

TABLE 1

MOLECULAR WEIGHTS IN SOLUTIONS WITH VARYING ArCu/PPh_3 RATIOS

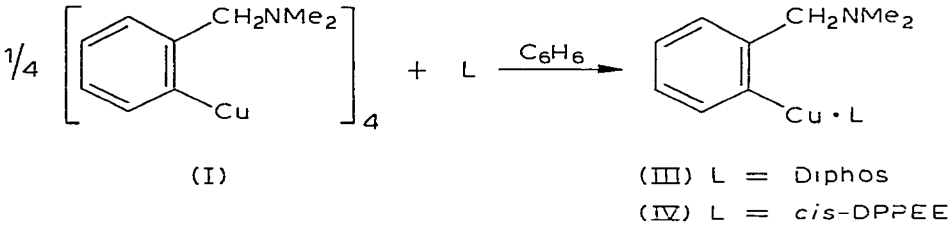
n_{found} = number of particles (found by cryoscopy)/mol "$Ar_4Cu_4 \cdot (PPh_3)_x$". $n_{calcd.}$ = number of particles when no complex formation between Ar_4Cu_4 and x PPh_3 occurs.

$Ar_4Cu_4 + x\ PPh_3$	n_{found}	$n_{calcd.}$
$x = 0$	1	1
$x = 1.3$	2.2	2.3
$x = 2.0$	2.8	3.0
$x = 3.8$	4.5	4.8
$x = 7.9$	8.1	8.9

The microwave titration curve obtained upon addition of small amounts of Diphos to a solution of I in benzene up to a Diphos/ArCu ratio of 5/1 is shown in Fig. 1. A distinct break in the curve is observed at a 1/1 molar ratio of Diphos/ArCu which points to the formation of a 1/1 complex having ArCu · Diphos stoichiometry. This was supported by molecular weight data of solutions of ArCu and Diphos in a 1/1 molar ratio. However, the results of experiments with a Diphos/ArCu ratio higher than 1 pointed to the occurrence of a complicated reaction rather than to complex formation. The results of a preparative scale study of both the 1/1 and the 2/1 reaction revealed the nature of these ArCu—Diphos reactions.

The 1/1 reaction of I with Diphos and with cis-DPPEE

The reaction of equimolar amounts of I with Diphos in benzene resulted in the formation of a homogeneous yellow solution from which a white-yellow crystalline 1/1 complex RCu · Diphos (III) was isolated in 80% yield. Similarly, the 1/1 reaction of I with *cis*-DPPEE in benzene afforded the 1/1 complex ArCu · *cis*-DPPEE (IV; 80%), which appeared to be insoluble in aromatic solvents. The use of excess of *cis*-DPPEE did not give the 2/1 complex, and the 1/1 complex IV was again isolated.



The identity of both complexes III and IV was established by elemental analysis (see Table 2). Moreover, when III was treated with a solution of DCl in ether, (2-deuteriobenzyl)dimethylamine (V) was formed quantitatively, confirming the presence of the corresponding organocopper compound in the 1/1 complex.

The decomposition temperatures of the complexes (III, 160—165°C; IV, 155—158°C) are lower than that of the parent organocopper compound I (175—180°C). Molecular weight determinations in boiling benzene revealed

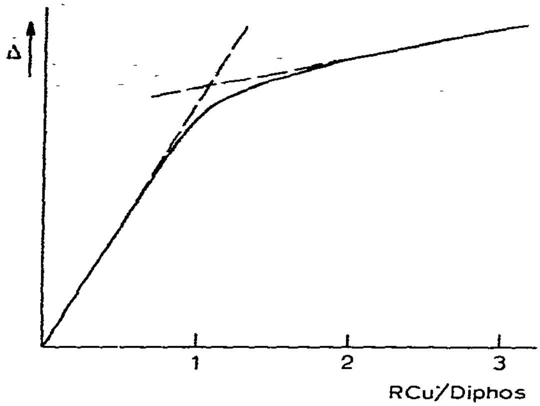


Fig. 1. Microwave titration curve for the reaction of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ with Diphos in benzene at room temperature.

that both III and IV exist in solution as monomers ArCu · L. The IR spectra (2000—400 cm^{-1}) of the complexes III and IV show some characteristic differences from that of the parent compound. In both complexes the *q*X-sensitive P—Ph vibration at about 1100 cm^{-1} shows an increase in intensity as compared with the vibrations in the region of 1030—1000 cm^{-1}. Furthermore, in the area around 700 cm^{-1} only one vibration which can be assigned to the *r*X-sensitive mode of the phenyl groups appeared to be increased in intensity. Both changes are assumed to be diagnostic for the occurrence of a metal—phosphine coordination [11]. Worthy of note is the decrease in intensity of the strong band at 838 cm^{-1} present in the free organocopper [6] which appeared in the spectrum of III as a weak and broadened band at 854 cm^{-1}. The ^1H NMR data of the parent organocopper and the two 1/1 complexes are compared in Table 3.

The 2/1 reaction of Diphos with I in benzene or toluene

As has been mentioned above molecular weight determinations of solutions with a Diphos/RCu ratio higher than one gave values much lower than expected

TABLE 2

ANALYTICAL DATA FOR THE COMPLEXES III, IV AND VI

	Analysis found (calcd.)					Mol. wt. found (calcd.)
	C	H	N	P	Cu	
III, ArCu · Diphos	70.6 (70.51)	6.3 (6.09)	2.2 (2.35)	10.2 (10.39)	10.4 (10.66)	606 (596) [a]
IV, ArCu · *cis*-DPPEE [b]	71.8 (72.08)	5.9 (5.89)	2.2 (2.21)	10.2 (9.78)	10.1 (10.03)	613 (594)
VIa, Ph_2PCu · Diphos · C_6H_6	72.6 (72.87)	5.6 (5.56)	0.0 (——)	12.4 (12.81)	8.5 (8.76)	[c]
VIb, Ph_2PCu · Diphos · toluene	73.0 (73.11)	5.8 (5.73)	0.0 (——)	12.8 (12.57)	8.5 (8.60)	[c]

[a] Ebullioscopic in benzene. [b] Calcd. for ArCu · *cis*-DPPEE · 0.5 C_6H_6. [c] See text.

TABLE 3

SOME ^{1}H NMR DATA FOR THE COMPLEXES I, III AND IV

Compound	Solvent	δ(ppm) [a]			
		NMe	NCH_2	H_6	H_3
I, Ar_4Cu_4	C_6D_6	1.90(s)	3.02(s)	8.45(d of d) $J_{5,6}$ 6 Hz $J_{4,6}$ 2 Hz	6.80(d of d) $J_{3,4}$ 7 Hz $J_{3,5}$ 1.5 Hz
	Pyridine-d_5	1.98(s)	3.12(s)	8.48(d of d)	6.49 [b]
III, ArCu · Diphos	C_6D_6	2.04(s)	3.56(s)	8.73(m)	[c]
IV, ArCu · *cis*-DPPEE	C_6D_6	1.86(s)	3.49(s)	8.65(m)	[c]

[a] TMS internal; RT; only relevant resonances are mentioned. [b] Broadened. [c] Coincide with ligand resonances.

for either further complex formation or for a mixture consisting of ArCu · Diphos and unreacted Diphos. A more detailed preparative study revealed that the overall reaction of I with Diphos in a 1/2 molar ratio, using either benzene or toluene as a solvent, can be formulated as follows.

$$\frac{1}{4}\,(ArCu)_4 + 2\ Diphos \xrightarrow[S=C_6H_6 \text{ or toluene}]{25^\circ C} \underset{\substack{(VIa),\ S = C_6H_6 \\ (VIb),\ S = CH_3C_6H_5}}{Ph_2PCu \cdot Diphos \cdot S} + \underset{(VII)}{ArH} + \underset{(VIII)}{Ph_2PCH{=}CH_2}$$

From the respective 1/2 reactions the new complexes VIa and VIb precipitate slowly from the reaction mixture as yellow crystals, which were isolated in about 70% yield. The arene VII and diphenylvinylphosphine VIII which were present in solution were identified by NMR (VII and VIII) and IR spectroscopy (VII) and by GLC analysis (VII and VIII). The formation of VIII was established by NMR spectroscopy, which showed the characteristic olefinic pattern with all chemical shifts as well as *J*(P—CH) and *J*(P—C=CH) (*trans* and *cis*) values identical to those of pure $Ph_2PCH{=}CH_2$ [12].

The identities of VIa and VIb were established by elemental analysis as well as by the results of their reactions with HCl and DCl, e.g.:

$$Ph_2PCu \cdot Diphos \cdot C_6H_6 \xrightarrow[\substack{(2)KCN/H_2O; \\ -CuCN_2^-}]{(1)HCl/Et_2O} Ph_2PH + Diphos + C_6H_6$$

NMR spectroscopy of the reaction mixture of VI with excess HCl in ether revealed the presence of Ph_2PH [δ(P—H) 5.19(d)(s) ppm; *J*(P—H) 214 Hz in C_6D_6] and Diphos [δ(PCH_2) 2.20(m) ppm]. In the NMR spectra of the mixtures obtained from the reaction of I with DCl, the characteristic doublet of the phosphine hydrogen was not present, which unambiguously proved the formation of diphenylphosphine in this reaction. Integration of the peak areas of the P—H and of the PCH_2 resonances showed that Ph_2PH and Diphos were present in a 1/1 molar ratio in the reaction mixture. The amount of benzene (100% yield) present in VIa was determined by quantitative GLC analysis directly after completion of the reaction. Similar results were obtained for the reactions of Ph_2PCu · Diphos · toluene with either HCl or DCl.

An indication for the course of the 1/2 reaction was obtained when diethyl ether was used as solvent instead of benzene or toluene. The 1/2 reaction in ether appeared to be heterogeneous, whereas a homogeneous mixture was obtained when aromatic solvent was used. The results of a careful analysis of the composition of the solution and of the precipitate after reaction have been summarized in the following equation:

$$\mathrm{ArCu} + 2\ \mathrm{Diphos}\ \xrightarrow[\mathrm{Et_2O}]{160\mathrm{h}} \begin{cases} \rightarrow \text{precipitate } [1.02\ \text{Diphos};\ 0.30\ \mathrm{Ph_2PCu};\ 0.76\ \mathrm{ArCu}] \\ \rightarrow \text{filtrate } [0.75\ \text{Diphos};\ 0.24\ \mathrm{ArH};\ 0.20\ \mathrm{Ph_2PVi}] \end{cases}$$

The composition of the precipitate suggests that although the expected complex Ph_2PCu · Diphos ($\approx$0.30, which corresponds with the amount of ArH and Ph_2PVi in solution) was formed, the 1/1 complex ArCu · Diphos ($\approx$0.70) was still present in the precipitate. The presence of characteristic absorptions of both complexes in the IR spectrum of the precipitate confirmed this view.

This result, as well as the presence of free Diphos in solution, points to the occurrence of the following reaction sequence:

$$\mathrm{ArCu} + \mathrm{Diphos} \xrightarrow{\text{fast}} \mathrm{ArCu} \cdot \mathrm{Diphos}\downarrow$$

$$\mathrm{ArCu} \cdot \mathrm{Diphos}\downarrow \rightarrow \mathrm{ArCu} \cdot \mathrm{Diphos}\ (\text{solution})$$

$$\mathrm{ArCu} \cdot \mathrm{Diphos}\ (\text{solution}) + \mathrm{Diphos} \rightarrow \mathrm{ArH} + \mathrm{Ph_2PVi} + \mathrm{Ph_2PCu} \cdot \mathrm{Diphos}\downarrow$$

The rate-determining step in this reaction is either the dissolution of the 1/1 complex or the cleavage reaction.

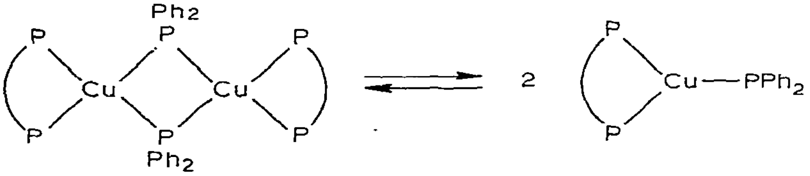
NMR spectroscopic studies of the homogeneous 1/2 reaction mixture in benzene-d_6 revealed that already after $\frac{1}{2}$ h ArCu · Diphos was absent and that formation of the cleavage products Ph_2PVi and ArH was complete. Crystallization of the yellow complex Ph_2PCu · Diphos from these solutions appeared to be slow.

That ArCu · Diphos is a key-intermediate in the cleavage reaction is further supported by the results of the 1/1 reaction of ArCu · Diphos with Diphos. From this reaction a yellow-green solid was isolated, the IR spectrum of which was identical to that of pure Ph_2PCu · Diphos · C_6H_6. Moreover, the facts that (i) elemental analysis showed the solid to contain no nitrogen, and (ii) Diphos and Ph_2PH were formed in a 1/1 molar ratio when the solid was decomposed with HCl in ether, confirmed the formation (74% yield) of the cleavage product Ph_2PCu · Diphos · C_6H_6.

Structure of (Ph_2PCu · Diphos)$_2$ · 2 C_6H_6

The complex Ph_2PCu · Diphos crystallizes with 1 mol of crystal benzene or toluene. The same melting point (185—187°C) was observed for both complexes, indicating that upon heating the same solid was formed. TGA analysis of the two solids confirmed this picture, i.e. complex VIa looses benzene at 47.3°C (97%); complex VIb looses toluene at 34.5°C (73%). The IR spectra of the heated (up to 80°C) samples (in nujol) appeared to be identical. That benzene (or toluene) was evolved upon heating could be concluded from a comparison of the IR spectra of Ph_2PCu · Diphos · C_6H_6 (or $C_6H_5CH_3$) and Ph_2PCu · Diphos. The absorption at about 675 cm^{-1} found in the IR spectrum of the former compound was absent in the spectrum of the heated sample.

Both complexes are stable in the atmosphere and are slightly soluble in benzene but insoluble in ether. Molecular weight determinations (ebullioscopy) of benzene solutions (0.9—3.9 × 10^{-2} *M*) of either VIa or VIb gave values of *n* of 1.3—1.4. This can be explained in terms of an equilibrium mixture of the dimer and monomer:



In the dimer the copper atoms are four coordinate, whereas in the monomer the copper atom is three coordinate. Three coordinate copper is found in a number of other complexes, e.g. $(Ph_3P)_2CuBr$, $(Ph_3P)_3Cu_2X_2$ (X = Cl, I) and $(Ph_3PCuX)_4$ ("step" structure: X = Cl, Br) [13]. In view of the general interest in complexes in which the Ph_2P ligand acts as a 3-electron donor the structure of $Ph_2PCu \cdot$ Diphos $\cdot C_6H_6$ (VIa) has been determined by X-ray analysis *.

The crystals are monoclinic, space group $P2_1/c$ and have $Z = 2$ in a unit cell of dimensions $a = 12.997(6)$, $b = 12.669(7)$, $c = 22.839(9)$ Å and $\beta = 94.48(4)°$. The structure was refined to $R = 0.048$ for 3048 independent reflections. The adopted numbering scheme together with the bond distances for the non-hydrogen atoms is shown in Fig. 2, whereas the bond angles are tabulated in Table 4. Thermal vibrational ellipsoids are shown in the ORTEP-drawing (Fig. 3).

The unit cell contains two dimeric units, mutually separated by normal Van der Waals distances, as is shown in the ac-projection in Fig. 4. The molecule of benzene of crystallization occupies interstitial sites in the structure.

It may be seen from the stereoscopic drawing (Fig. 5) that the approximate molecular symmetry is $2/m$, which is higher than the site symmetry $\bar{1}$.

The C—H bond distances range from 0.87 to 1.07 Å. Their average along with some other averages are given in Table 5. The averages given for the benzene rings should be compared with the ideal value of 1.394(5) Å (cf. ref. 16).

The four-coordinate copper atoms are held together by two Ph_2P bridges. The Cu—P distances in the central Cu_2P_2 unit are equal (mean 2.363 Å) and are only slightly longer than the Cu—P(Diphos) bonds (mean 2.301 Å). The Cu---Cu distance correlates very well with the Cu—P—Cu bond angle as was shown by Mingos and Mason in their qualitative discussion of M—M bond distances in polynuclear complexes with bridging groups [14]. Recently, Summerville and Hoffmann [17] have discussed the factors which influence the geometry and electronic structure of metal complexes of the M_2L_6 type. In the present complex the Cu—P—Cu bridge bond angle is enlarged from the ideal value of 70.5 to 90°. The P(2)—Cu—P(2') angle is also 90°. The expected opening-up of the P—Cu—P-

(Continued on p. 450)

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* Preliminary details of this structure have already been used in theoretical studies [14,15].

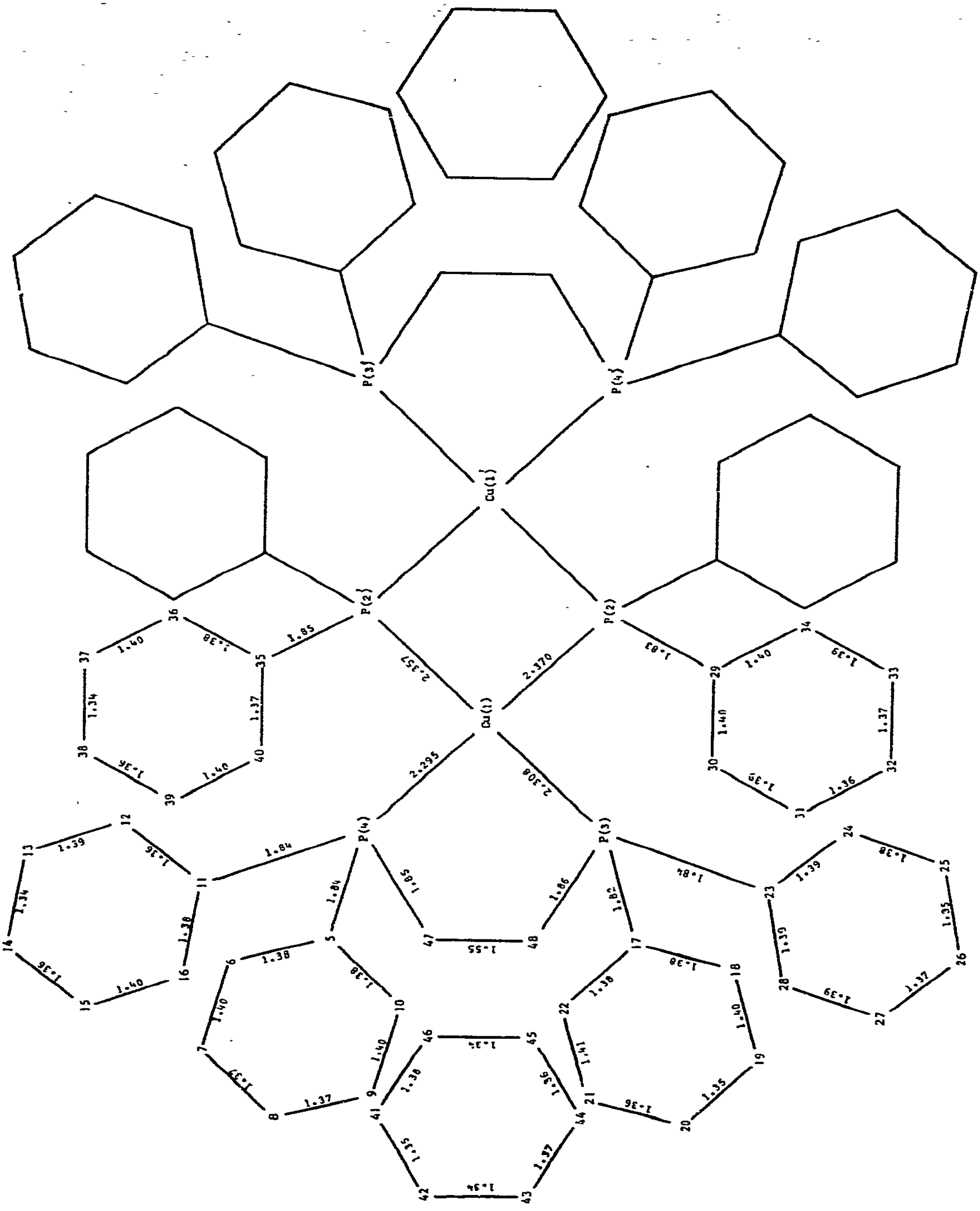

Fig. 2. Numbering scheme and bond lengths (Å). The standard deviations are: Cu—P, 0.002 Å; P—C, 0.005 Å and C—C, 0.01 Å.

TABLE 4

BOND ANGLES WITH STANDARD DEVIATIONS [a]

P(2)—Cu(1)—P(2′)	90.31(6)	P(2)—C(29)—C(30)	125.2(4)
P(2)—Cu(1)—P(3)	117.77(7)	P(2)—C(29)—C(34)	117.2(4)
P(2′)—Cu(1)—P(3)	116.26(7)	C(30)—C(29)—C(34)	117.7(5)
P(2)-Cu(1)—P(4)	121.83(6)	C(29)—C(30)—C(31)	121.8(6)
P(2′)—Cu(1)—P(4)	124.56(6)	C(30)—C(31)—C(32)	118.7(6)
P(3)—Cu(1)—P(4)	89.90(7)	C(31)—C(32)—C(33)	121.6(7)
Cu(1)—P(2)—Cu(1′)	89.69(6)	C(32)—C(33)—C(34)	120.1(6)
Cu(1)—P(2)—C(29)	113.7(2)	C(29)—C(34)—C(33)	120.1(6)
Cu(1′)—P(2)—C(29)	111.4(2)	P(2′)—C(35)—C(36)	121.0(4)
Cu(1)—P(2)—C(35′)	117.8(2)	P(2′)—C(35)—C(40)	120.2(4)
Cu(1′)—P(2)—C(35′)	124.9(2)	C(36)—C(35)—C(40)	118.8(5)
C(29)—P(2)—C(35′)	100.1(2)	C(35)—C(36)—C(37)	119.8(6)
Cu(1)—P(3)—C(17)	124.6(2)	C(36)—C(37)—C(38)	121.1(7)
Cu(1)—P(3)—C(23)	119.0(2)	C(37)—C(38)—C(39)	120.2(7)
Cu(1)—P(3)—C(48)	102.7(2)	C(38)—C(39)—C(40)	119.6(7)
C(17)—P(3)—C(23)	102.7(2)	C(35)—C(40)—C(39)	120.6(6)
C(17)—P(3)—C(48)	102.9(2)	C(42)—C(41)—C(46)	121.0(8)
C(23)—P(3)—C(48)	101.4(3)	C(41)—C(42)—C(43)	120.3(8)
Cu(1)—P(4)—C(5)	121.0(2)	C(42)—C(43)—C(44)	120.0(8)
Cu(1)—P(4)—C(11)	122.2(2)	C(43)—C(44)—C(45)	119.2(8)
Cu(1)—P(4)—C(47)	103.8(2)	C(44)—C(45)—C(46)	121.8(9)
C(5)—P(4)—C(11)	101.3(2)	C(41)—C(46)—C(45)	117.7(8)
C(5)—P(4)—C(47)	101.6(2)	P(4)—C(47)—C(48)	108.2(4)
C(11)—P(4)—C(47)	104.0(2)	P(3)—C(48)—C(47)	109.4(4)
P(4)—C(5)—C(6)	122.3(4)		
P(4)—C(5)—C(10)	118.5(4)		
C(6)—C(5)—C(10)	119.2(5)		
C(5)—C(6)—C(7)	120.0(6)		
C(6)—C(7)—C(8)	120.2(6)		
C(7)—C(8)—C(9)	120.4(6)		
C(8)—C(9)—C(10)	119.5(6)		
C(5)—C(10)—C(9)	120.6(5)		
P(4)—C(11)—C(12)	124.8(4)		
P(4)—C(11)—C(16)	115.7(4)		
C(12)—C(11)—C(16)	119.4(5)		
C(11)—C(12)—C(13)	120.3(6)		
C(12)—C(13)—C(14)	120.8(7)		
C(13)—C(14)—C(15)	119.9(7)		
C(14)—C(15)—C(16)	120.3(6)		
C(11)—C(16)—C(15)	119.3(6)		
P(3)—C(17)—C(18)	123.6(4)		
P(3)—C(17)—C(22)	117.9(4)		
C(18)—C(17)—C(22)	118.5(5)		
C(17)—C(18)—C(19)	120.0(6)		
C(18)—C(19)—C(20)	120.8(7)		
C(19)—C(20)—C(21)	120.3(7)		
C(20)—C(21)—C(22)	120.1(7)		
C(17)—C(22)—C(21)	120.3(6)		
P(3)—C(23)—C(24)	119.6(4)		
P(3)—C(23)—C(28)	123.4(4)		
C(24)—C(23)—C(28)	117.0(5)		
C(23)—C(24)—C(25)	121.8(6)		
C(24)—C(25)—C(26)	120.5(6)		
C(25)—C(26)—C(27)	119.3(6)		
C(26)—C(27)—C(28)	121.0(6)		
C(23)—C(28)—C(27)	120.3(6)		

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[a] Indicates an atomic position related by inversion through (0, 0, 0) to the atomic positions in Table 6.

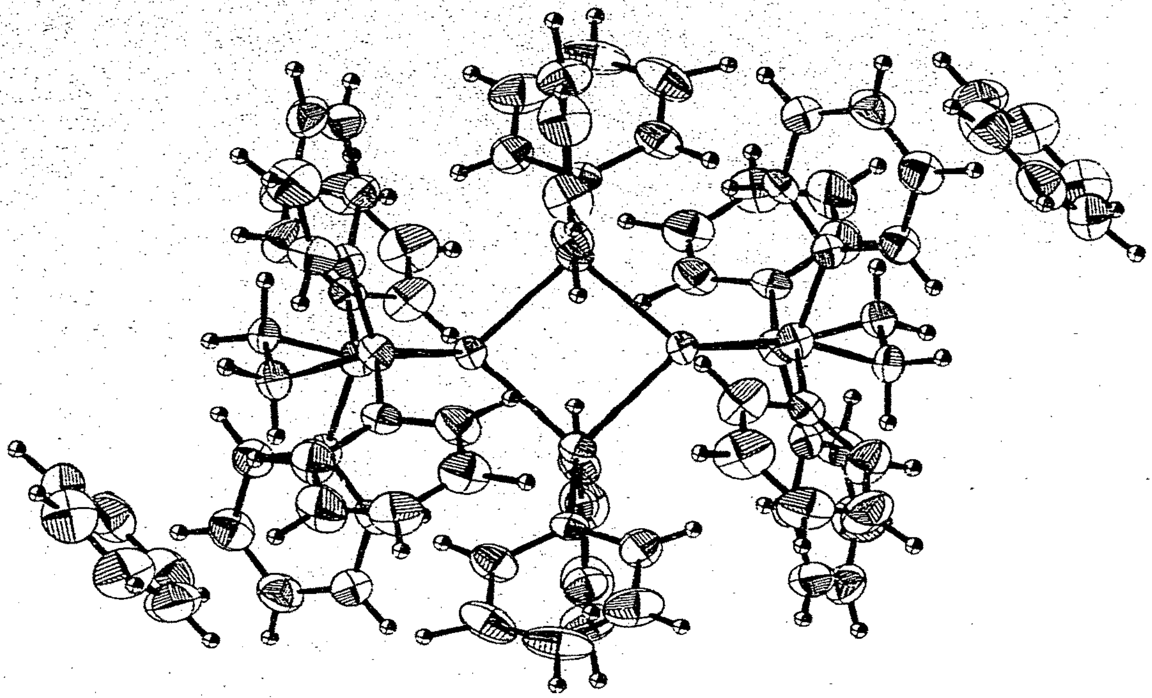


Fig. 3. ORTEP-drawing showing the 40% probability ellipsoids. Hydrogen atoms are represented by artificial small spheres. The pseudo two-fold axis of the molecule is indicated.

(Diphos) bond angle which amounts in VIa to 90° is not observed. This finding reflects the approximately constant value of about 90° for the bite of the Diphos ligand (e.g. in $Cu_2(CF_3CN_4)_2(Diphos)_3$ [18] and $Cu_2(N_3)_2Diphos_3$ [19] this angle is 90°). These geometrical features contrast with, for example, those of the complex (*o*-$Me_2NC_6H_4AsMe_2$)CuI_2Cu($Me_2AsC_6H_4NMe_2$-*o*) [20] for which acute Cu—I—Cu angles and a short Cu—Cu distance have been found. The present data indicate that the geometrical features of the bridging region are obviously not primarily determined by the chelate bite size of the bidentate ligands in these complexes.

TABLE 5

SOME IMPORTANT AVERAGE BOND LENGTHS

Benzene rings			
C(5)—C(10)	1.384(7)	C—H (phenyl)	0.94(1)
C(11)—C(16)	1.371(10)	C—H (methylene)	0.97(1)
C(17)—C(22)	1.380(9)		
C(23)—C(28)	1.378(7)		
C(29)—C(34)	1.389(6)		
C(35)—C(40)	1.378(8)		
C(41)—C(46)	1.354(7)		
P—C	1.840(3)		

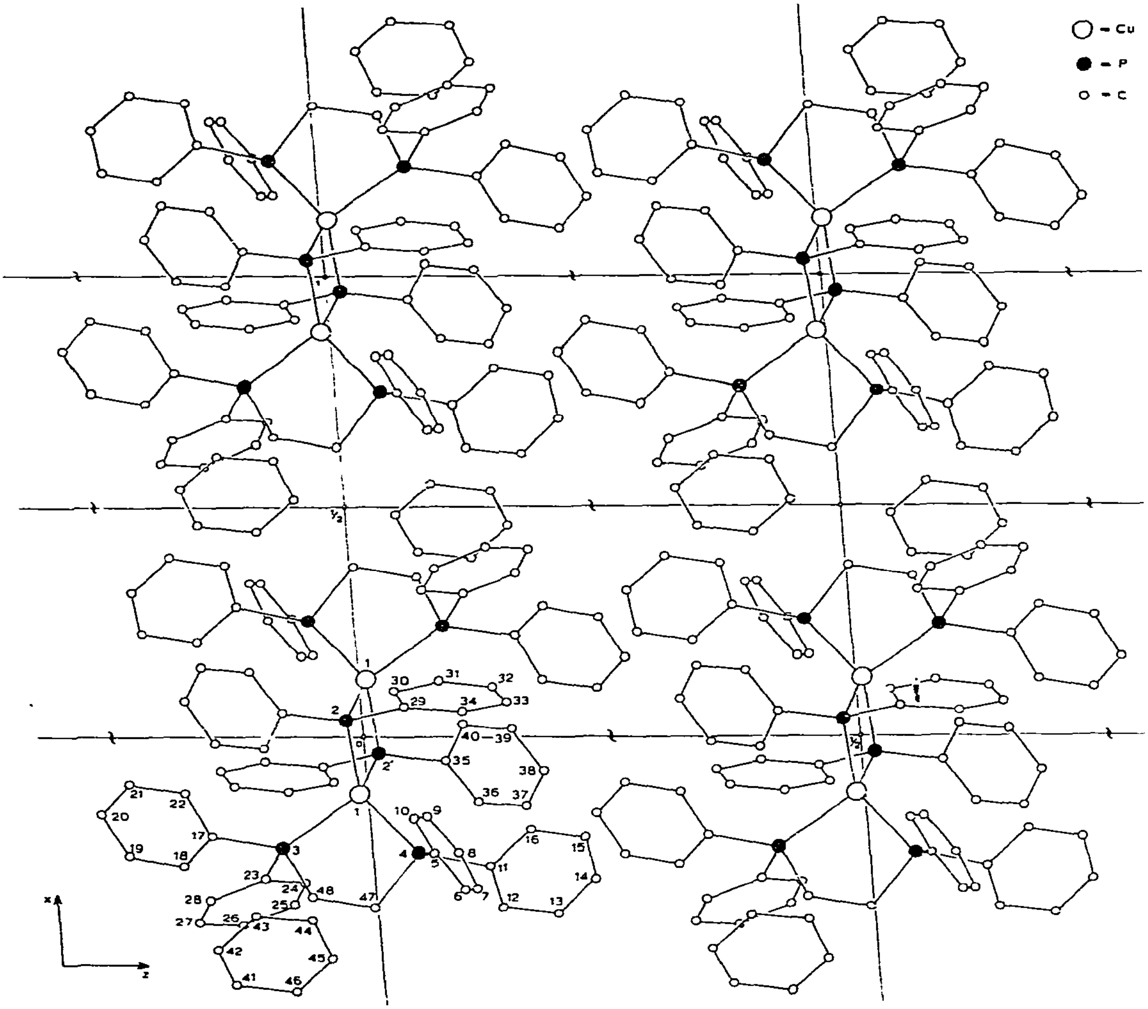


Fig. 4. Packing of the molecules as viewed along the *b*-axis.

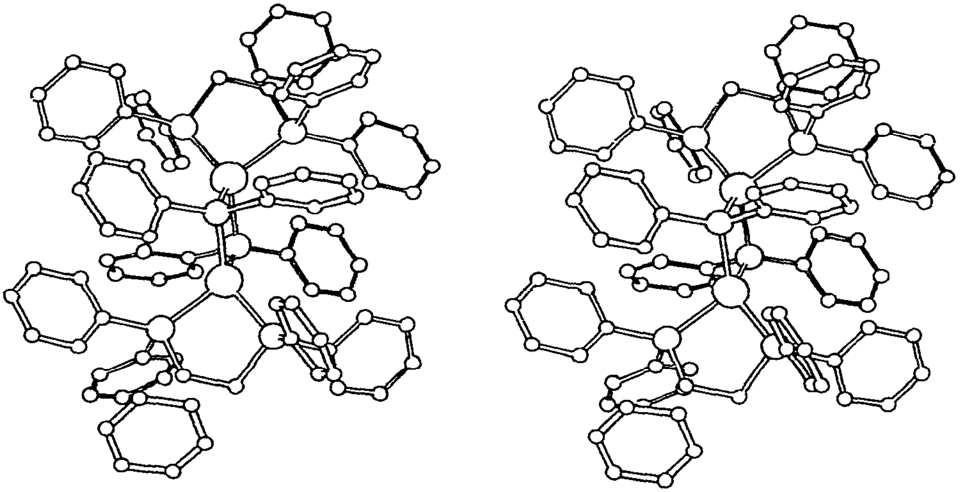


Fig. 5. Stereoscopic drawing of the dimer and two benzene molecules.

Discussion

Elucidation of the difference in reactivity of arylcopper compounds towards phosphines and amines should include a discussion of the bonding in arylcopper clusters. During the last ten years the structures of a number of arylcopper compounds have been solved by X-ray structure determinations or made plausible on the basis of spectroscopic data. Examples are the solid state structures of 5-Me-2-$Me_2NCH_2C_6H_4Cu$ tetramer [6], $(2\text{-}Me_2NC_6H_4)_4Cu_6X_2$ (X = Br [21] or $C{\equiv}C{-}C_6H_4CH_2$-4 [22]), the tentative structure of 3-$CF_3C_6H_4Cu$ octamer [23], and the structures in solution of the mixed metal cluster compounds $(C_6H_5)_6Cu_4Mg \cdot Et_2O$ [24] and $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag or Au) [25]. The structures of these soluble arylcopper derivatives have as a common structural feature a central copper (or copper metal) core to which the aryl groups are bound via *2e—3c* bonds.

In view of the fact that direct unassisted metal—metal bonding can be excluded a maximum number of three bridging or non-bridging ligands can be bound to each metal atom. A trigonal coordination symmetry is present in 2-$Me_2NCH_2C_6H_4Cu$ tetramer, i.e., each copper atom takes part in two aryl—Cu bonds while the third coordination site at Cu is occupied by the built-in ligand Me_2NCH_2—. However, each Cu atom will be two-coordinate when such a coordinating group is absent [7]. This coordination symmetry has, for example, been found in Me_3SiCH_2Cu tetramer [26], while in the hexanuclear clusters $(2\text{-}Me_2NC_6H_4)_4Cu_6X_2$ both trigonal and a digonal coordination are present [21,22].

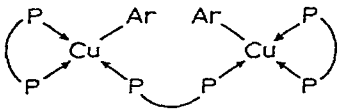
Information concerning the structure of the insoluble arylcopper compounds is limited, but on the basis of the available data for the soluble compounds we have proposed an oligomeric or polymeric structure consisting of patterns of copper atoms to which the aryl groups are bound via *2e—3c* bonds [7].

The generalizations for the bonding around copper, either digonal (*sp* or *ds* hybridization) or trigonal (sp^2 hybridization) [6,21], offer a basis for an explanation of the interaction of phosphines or amines with organocopper compounds.

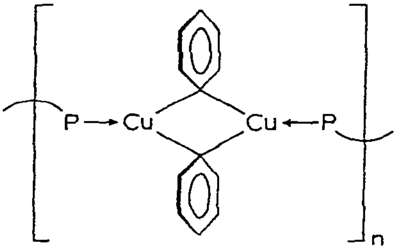
Interaction of ligands with ArCu with conservation of the cluster structure

The present data point to a high stability towards break-down by complex formation of arylcopper compounds containing a built-in ligand at the *ortho* position with respect to the Cu—C bond. Thus the 2-Me_2NCH_2 and 2-Me_2N substituted phenylcopper aggregates are stable towards monodentate ligands like PPh_3, $CH_3C{\equiv}N$ and pyridine. This means that the formation of complexes of the type $Ar_4Cu_4 \cdot xPPh_3$, which can be considered to be the first step towards break-down of the cluster structure, do not take place. Evidently the three-coordinate bonding situation around copper in the Ar_4Cu_4 compound I is a stable one, and ligand exchange between the Me_2NCH_2 group and PPh_3 is not energetically favoured.

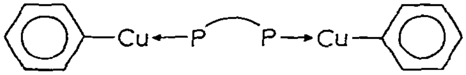
Another class of organocopper compounds which do not undergo break-down by interaction with phosphines are the mixed-metal clusters, e.g. $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag or Au) [25]. In these compounds the IB metal is two-coordinate, while the built-in ligands coordinate with lithium. Since no interac-



a: $(ArCu)_2 \cdot Diphos_3$



b: $Ph_2Cu_2 \cdot Diphos$



c: $(PhCu)_2 \cdot Diphos$

Fig. 6. Possible structures of arylcopper—Diphos complexes resulting from partial or total break-down of the polynuclear structure of Ar_nCu_n.

tion occurs, phosphine complexes can even be used as starting materials for synthesis [27], e.g.:

$$2\ BrMPPh_3 + 4\ 2\text{-}Me_2NCH_2C_6H_4Li \rightarrow 2\ LiBr + 2\ PPh_3 + (2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$$

In this class of compounds it is most probably the high electron density located on the IB metal [28] which prevents formation of stable phosphine—metal bonds.

Interaction of ligands with ArCu resulting in break-down of the cluster structure

Complex formation between Ar_4Cu_4 (I) and the bidentate ligands Diphos and *cis*-DPPEE does occur *. The tetranuclear cluster structure with electron deficient Cu—C bonds is broken down by the bidentate ligand, thus producing monomeric 1/1 complexes ArCu · L containing electron precise Cu—C bonds. The copper atom in these monomeric complexes is at least three-coordinate while the low-field shifts of the benzylic protons and the NMe protons (see

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* It must be noted that the use of isocyanides results in insertion of the isocyanide ligand into the Cu—C bonds of the arylcopper compounds. Whether in these reactions complex formation preceeds the insertion reaction is not known in great detail at this moment [29]. A strong indication for a stepwise insertion is the isolation of $[2\text{-}Me_2NCH_2C_6H_4C(NMe)]_3(2\text{-}Me_2NCH_2C_6H_4)Cu_4$ in which the tetranuclear cluster contains three inserted isocyanide molecules [30].

Table 3) point to an interaction of the CH_2NMe_2 ligand with Cu which renders this atom four-coordinate.

Analogous reactions of arylcopper compounds which do not contain coordinating substituents do not give 1/1 complexes, but instead produce complexes with a stoichiometry $(RCu)_2 \cdot Diphos_3$ [2]. In this case the copper atoms are most probably tetra-coordinate by coordination with a chelating and a bridging Diphos molecule (see Fig. 6a). Molecular weight measurements indicated that the bridging Diphos molecule coordinates rather weakly. Other examples of such structures have been reported, i.e., $(CuCF_3CN_4)_2 \cdot Diphos_3$ [18] and $(CuN_3)_2 \cdot Diphos_3$ [19]. Furthermore, partial break-down has been observed by Camus and Marsich [2] in the reaction of phenylcopper with Diphos. The stoichiometry of the isolated complex $(PhCu)_2 \cdot$ Diphos can be explained in terms of a breakdown of the polymeric structure of phenylcopper into smaller aggregates which still contain electron deficient aryl-to-copper bonds (see Fig. 6b) or to a structure containing 2*e*—2*c* bonded phenyl groups (Fig. 6c).

The results presented also offer an explanation for the observed P—C bond cleavage which Diphos undergoes by reaction with I. The first step in this reaction is the formation of the 1/1 complex ArCu · Diphos (III). Subsequently, the $-PPh_2$ group of a second equivalent of Diphos competes with the built-in NMe_2 ligand for the fourth coordination site forming a complex of the type IX, which obviously has low stability. In this complex cleavage of the P—C bond with formation of ArH, $Ph_2PCH{=}CH_2$ and $Ph_2PCu \cdot$ Diphos-dimer occurs via a concerted mechanism involving nucleophilic attack at the ethylenic proton β to the coordinated PPh_2 group [9,8b] * (see Fig. 7). Such a P—C bond cleavage has recently been reported to occur upon boiling the dithiocarboxylatocopper compound $(RCSSCu)_2 \cdot Diphos_3$ in CS_2 [32]. Also in this reaction the group bound to copper abstracts a hydrogen atom bound to the carbon β with respect to the coordinating PPh_2 group of a second Diphos molecule.

We have proposed that formation of $(CuCl_2)_2 \cdot Diphos_3 \cdot DCE_2$, arene and vinyl chloride from the reaction of 1,2-dichloroethane (DCE) with $(RCu)_2 \cdot Diphos_3$ complexes [2] proceeds in the same way [9]. In this reaction the formation of an ArCu · Diphos · DCE complex in which a Cl atom of DCE competes for the fourth coordination site at Cu would constitute the first step.

The importance of the nature of the aryl group in the arylcopper compound for this P—C bond cleavage process can be deduced from the fact that whereas $2\text{-}Me_2NC_6H_4Cu$ polymer reacts with Diphos to give the 1/1 complex $2\text{-}Me_2NC_6H_4Cu \cdot$ Diphos the reaction with excess Diphos takes place only very slowly. After 130 h cleavage very little cleavage had occurred.

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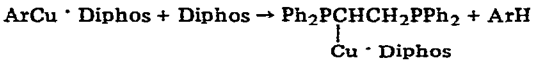
* No evidence has been found for the occurrence of the alternative route:

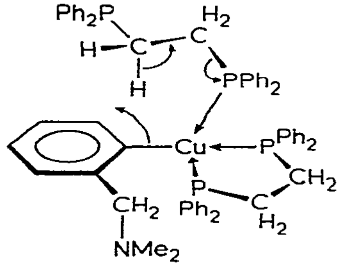


$$ArCu \cdot Diphos + Diphos \rightarrow \underset{\displaystyle Cu \cdot Diphos}{Ph_2P\underset{|}{C}HCH_2PPh_2} + ArH$$

(X)

which involves Cu—H exchange resulting in formation of X followed by elimination of $Ph_2PCu \cdot$ Diphos.

Reactions involving Cu—H exchange between arylcopper compounds and compounds containing acidic protons affording stable copper-conjugated base complexes have been described by Marsich and Camus [31].



(XI)

Fig. 7. Proposed mechanism for the C_{alk}—P bond cleavage in the reaction of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ with Diphos.

Conclusions

The present work provides further proof for the complex nature of the interaction of phosphines with organocopper compounds. In this respect the variety of structures found so far bears resemblance to the array of structures of copper halide—phosphine complexes reported during the past few years. X-Ray studies have shown that species which have essentially the same stoichiometry can have very different structures. Examples are the step and cubane structures established for ($CuX \cdot PPh_3$) in which X is a halide anion [13]. Because phosphines are often used as additional ligands in organocopper reagents used for synthetic purposes [8a] the importance of a better understanding of the interaction of organocopper compounds with phosphines is obvious. In general, attempts at asymmetric synthesis by using chiral phosphines in combination with organocopper intermediates must be expected to fail, because in solutions containing organocopper compounds and phosphines a wide variety of mono- and polynuclear organocopper—phosphine complexes rather than distinct organocopper—phosphine species will be present. It is important to realize that asymmetric synthesis using organocopper reagents in combination with chiral phosphines may also fail simply because the chiral phosphine (or amine) does not react with the organocopper species. This is particularly true for organocopperlithium compounds, which have a prominent position as intermediates in C—C coupling reactions [25,30].

Both organocopper and organic copper compounds are capable of P—C bond cleavage in coordinated Diphos to afford Ph_2PCu complexes. A large number of R_2P-bridged bimetallic compounds have been obtained via routes involving for example reaction of R_2PX with carbonyl metallates [33] and reaction of R_2PH with metal carbonyls [34]. A few reactions of P—C bond cleavage in triphenylphosphine coordinated to transition metals have been reported [35]. Recently, Blickensderfer and Kaesz [36] reported a P—C bond cleavage in coordinated PPh_3 leading to a series of Ph_2P-bridged heterometallic complexes. Another example involves the reaction of osmium and iridium carbonyl derivatives with PPh_3, which proceeds under rather severe conditions [37].

Experimental

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen.

2-[(Dimethylamino)methyl]phenylcopper tetramer and 2-(dimethylamino)-phenylcopper polymer were prepared by published methods [6,7].

^{1}H NMR spectra were recorded on a Varian Associates HA-100 spectrometer and IR spectra on a Perkin-Elmer Grating Infrared Spectrometer Nr. 577. Elemental analyses were carried out in the Analytical Department of the TNO Institute.

Synthesis of 2-[(dimethylamino)methyl]phenylcopper—Diphos (III)

A solution of 1,2-bis(diphenylphosphino)ethane (Diphos: 4.46 mmol) in benzene (30 ml) was added at 25°C to a solution of I in benzene (4.46 mmol in 30 ml). The yellow solution was stirred for 24 h. Concentration of the solution to about 10 ml followed by slow addition of ether (30 ml) gave a light-yellow precipitate of III. The precipitate was washed with ether (2 × 20 ml) and dried in vacuo. Yield 80%. Elemental and spectroscopic data are listed in Tables 2 and 3. M.p. 165°C (with dec.).

Reaction of III with D(H)Cl in ether. A solution of 1.90 mmol of HCl in ether was slowly added to a suspension of III (0.43 g) in ether (5 ml). The white precipitate was filtered off, extracted with ether (2 × 5 ml), with H_2O (O_2-free, 2 × 5 ml), and dried in vacuo. (For further work-up procedure see below.)

The filtrate and the combined ether and water extracts were acidified with 2 ml of HCl solution (4 *N*). The layers were separated and the water layer made alkaline with solid NaOH. The water layer was extracted with ether and the ether extracts dried over Na_2SO_4. Quantitative GLC analysis (decane as internal standard) of the ether solution revealed that N,N-dimethylbenzylamine was formed in 60% yield. The amine was isolated pure via an acid/base work-up. IR spectroscopy (neat) confirmed the identity of the N,N-dimethylbenzylamine, and from the reaction in which DCl was used pure 2-deuterio-N,N-dimethylbenzylamine was obtained (cf. ref. 38 for analogous reactions).

The white precipitate was suspended in a mixture of 0.8 g KCN in benzene/water (20/10). This mixture was heated to 60°C for 2 h. The benzene and water layers were separated. The benzene layer was washed with water (5 ml), dried over Na_2SO_4, and concentrated, to give white solid Diphos (0.3 g). The NMR and IR spectra were identical with those of a pure sample of Diphos.

Synthesis of 2-[dimethylamino)methyl]phenylcopper—cis-DPPE (IV)

A solution of *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-DPEE; 2.12 mmoles) in benzene (10 ml) was slowly added at room temperature to a solution of I (2.12 mmoles) in benzene (20 ml). The colour of the solution changed from yellow ro red. After 2 h a yellow solid precipitated from the solution, which was stirred for another 72 h. The yellow-ochre precipitate was filtered off, washed with benzene (2 × 5 ml) and dried in vacuo. Elemental analysis confirmed the isolation of a 1/1 complex ArCu · DPEE (IV) containing a small amount of benzene (see Tables 2 and 3). M.p. 135°C (dec.).

Reaction of ArCu · Diphos (III) with Diphos

A benzene solution of Diphos (0.705 mmoles in 10 ml) was added to a suspension of III (0.705 mmoles) in benzene (10 ml). The precipitate dissolved slowly to give a yellow solid. Stirring was continued for 10 days. The yellow solution was concentrated, yielding a yellow solid, which was extracted with pentane (20 ml) and then with ether (2 × 10 ml), and dried in vacuo. Yield 74%. Its IR spectrum was identical with a spectrum of pure $Ph_2PCu \cdot$ Diphos $\cdot C_6H_6$, and correct elemental analyses (N absent) were obtained.

Reaction of the yellow solid with HCl. HCl in ether (0.40 ml, 1.89 *N*) was added to a well-stirred suspension of the yellow solid (see above) in ether (5 ml). The resulting white precipitate was isolated by filtration. The filtrate contained no products (GLC analysis). The white solid (about 0.16 g) was added to a mixture of KCN (0.4 g) in benzene/water (5/10 v/v) which completely dissolved after heating the mixture at 60°C for 4 h. The benzene layer was separated, dried over Na_2SO_4, and concentrated. NMR spectroscopy of the resulting white residue revealed the formation of Diphos and Ph_2PH in 1/0.8 molar ratio. (NMR data see text).

Reaction of I with Diphos in 1/2 molar ratio

A mixture of 7.05 mmoles of I and 14.10 mmoles of Diphos in benzene (100 ml) was stirred for 96 h at room temperature. During this time a yellow crystalline solid precipitated. This solid was isolated by filtration. Degradation experiments (see above, 1/1 reaction) established its identity as $PPh_2Cu \cdot$ Diphos C_6H_6 (VIa).

The filtrate was concentrated in vacuo. The residue (containing unreacted Diphos and other products) was extracted with pentane. The amount of N,N-dimethylbenzylamine (VII; 69.7%) in this extract was determined by GLC analysis. VII was removed from the pentane extract by subsequent acid/base workup resulting in a pentane extract containing exclusively $Ph_2PCH{=}CH_2$ (VIII; 50%), which was identified by NMR spectroscopy and GLC analysis.

Structure determination and refinement [14]

Yellow crystals of VIa are monoclinic with $a = 12.997(6)$, $b = 12.669(7)$, $c = 22.839(9)$ Å and $\beta = 94.48(4)°$, $V = 3749.1$ Å^3, $Z = 2$, $D_{calcd.} = 1.285$ g cm^{-3}, $F(000) = 1512$ and $\mu(\text{Cu-}K_\alpha) = 22.5$ cm^{-1}.

A suitable specimen, measuring 0.56 × 0.25 × 0.13 mm, was mounted in a Lindemann capillary (in dry nitrogen atmosphere), with its macroscopic twofold axis (b-axis) parallel to the spindle axis. The observed extinctions ($0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$) on preliminary Weissenberg and precession photographs indicated the space group to be $P2_1/c$, C_{2h}^5. Accurate values of the unit cell parameters and the crystal orientation matrix were determined at ambient room temperature from a least-squares treatment of the angular settings of 18 reflections, carefully centered on an Enraf-Nonius CAD4 diffractometer equipped with a scintillation counter using Cu-K_α radiation (λ 1.54051 Å) [39], and estimated standard deviations were derived from these settings following a procedure described by Duisenberg [40].

The intensity data were collected in the ω-scan mode using nickel filtered Cu-K_α-radiation (λ 1.5418 Å) for all independent reflections up to $2\theta = 100°$. The applied scan angle was $\Delta\omega = 1.00 + 0.42 \tan(\theta)°$. The background was measured in an additional scan area of $\Delta\omega/4°$ on both sides of the main scan and with the same scan speed. The intensity of every reflection was measured at the

(Continued on p. 460)

TABLE 6

FINAL REFINED PARAMETERS [a] IN THE NON-HYDROGEN ATOMS

Atom	X/A	Y/B	Z/C	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	−12321(6)	3772(6)	−738(3)	443(5)	475(5)	114(1)	34(5)	13(2)	−2(3)
P(2)	3624(10)	12355(11)	−1458(6)	540(10)	495(9)	139(3)	7(8)	15(4)	7(5)
P(3)	−23933(11)	3768(12)	−8922(6)	598(10)	587(10)	136(3)	30(9)	3(4)	2(4)
P(4)	−24924(11)	10736(11)	4609(6)	554(10)	592(11)	135(3)	30(9)	35(4)	−23(5)
C(5)	−2530(4)	2496(4)	622(2)	48(4)	52(4)	13(1)	4(3)	2(2)	−3(2)
C(6)	−3310(5)	2947(5)	913(3)	69(5)	65(5)	20(2)	4(4)	6(2)	−7(2)
C(7)	−3296(5)	4035(5)	1031(3)	87(6)	73(5)	27(2)	10(4)	9(2)	−14(3)
C(8)	−2505(5)	4647(5)	865(3)	91(6)	63(5)	32(2)	8(5)	−3(3)	−8(3)
C(9)	−1725(5)	4210(5)	575(3)	67(5)	74(5)	33(2)	−3(4)	2(2)	7(3)
C(10)	−1744(4)	3125(4)	449(3)	60(4)	48(4)	24(2)	18(4)	3(2)	1(2)
C(11)	−2807(4)	508(4)	1166(2)	59(4)	57(4)	13(1)	9(4)	6(2)	−0(2)
C(12)	−3714(5)	37(6)	1263(3)	74(5)	121(7)	20(2)	−15(5)	7(2)	13(3)
C(13)	−3853(6)	−422(7)	1806(3)	90(6)	130(8)	31(2)	−29(6)	12(3)	18(3)
C(14)	−3096(6)	−409(6)	2238(3)	136(7)	99(6)	19(2)	−3(6)	24(3)	9(3)
C(15)	−2189(6)	77(7)	2154(3)	136(7)	138(8)	15(1)	−17(6)	−3(3)	11(3)
C(16)	−2031(5)	544(6)	1611(3)	89(6)	123(7)	16(1)	−22(5)	1(2)	3(3)
C(17)	−2143(4)	948(4)	−1600(2)	69(4)	51(4)	10(1)	0(4)	−4(2)	1(2)
C(18)	−2807(5)	1643(6)	−1906(3)	79(5)	108(6)	22(2)	10(5)	3(2)	17(3)
C(19)	−2572(6)	2020(7)	−2456(3)	113(7)	138(8)	28(2)	24(6)	−2(3)	38(3)
C(20)	−1696(6)	1726(6)	−2690(3)	124(7)	112(7)	16(1)	−3(6)	4(3)	16(3)
C(21)	−1026(6)	1058(6)	−2394(3)	110(6)	91(6)	22(2)	1(5)	20(3)	2(3)
C(22)	−1238(5)	677(5)	−1838(3)	91(5)	76(5)	20(2)	15(5)	12(2)	8(2)
C(23)	−3080(4)	−851(4)	−1103(2)	48(4)	54(4)	16(1)	8(3)	−1(2)	−1(2)

C(24)	−3142(4)	−1652(5)	−693(3)	55(4)	68(5)	20(1)	−3(4)	2(2)	4(2)
C(25)	−3649(5)	−2589(5)	−830(3)	84(6)	69(5)	31(2)	−8(4)	11(3)	5(3)
C(26)	−4096(5)	−2757(5)	−1375(3)	63(5)	76(6)	38(2)	−10(4)	3(3)	−16(3)
C(27)	−4045(7)	−1988(6)	−1792(3)	122(8)	99(7)	27(2)	−10(6)	−14(3)	−19(3)
C(28)	−3538(5)	−1087(5)	−1662(3)	106(6)	68(5)	19(2)	−8(5)	−14(2)	−1(2)
C(29)	660(4)	2221(4)	430(2)	45(4)	51(4)	14(1)	6(3)	2(2)	−2(2)
C(30)	994(5)	3249(5)	336(3)	75(5)	64(5)	19(2)	−7(4)	4(2)	−7(2)
C(31)	1194(6)	3955(5)	796(3)	109(6)	71(5)	28(2)	−22(5)	4(3)	−18(3)
C(32)	1077(6)	3622(6)	1355(3)	114(7)	113(7)	23(2)	9(6)	−7(3)	−30(3)
C(33)	755(5)	2622(6)	1469(3)	106(6)	115(7)	13(1)	22(5)	4(2)	−2(2)
C(34)	528(5)	1917(5)	1010(2)	76(5)	69(5)	18(1)	18(4)	2(2)	−3(2)
C(35)	−517(4)	−2049(4)	805(2)	59(4)	37(4)	12(1)	−3(3)	−1(2)	−3(2)
C(36)	−1396(5)	−1982(5)	1102(3)	72(5)	79(5)	21(2)	1(4)	11(2)	5(2)
C(37)	−1499(6)	−2617(6)	1594(3)	136(7)	96(6)	26(2)	−24(6)	26(3)	4(3)
C(38)	−751(7)	−3296(5)	1784(3)	199(10)	63(5)	19(2)	−13(6)	12(3)	11(2)
C(39)	129(7)	−3370(5)	1499(3)	153(8)	76(6)	22(2)	29(6)	−9(3)	9(3)
C(40)	250(5)	−2733(5)	1007(2)	98(6)	71(5)	17(1)	11(4)	4(2)	12(2)
C(41)	−5402(7)	3401(7)	−1476(4)	129(8)	134(8)	31(2)	4(7)	−1(3)	−18(4)
C(42)	−4569(7)	3919(7)	−1644(3)	138(8)	134(8)	29(2)	−16(7)	17(3)	−8(3)
C(43)	−3866(6)	4304(6)	−1243(4)	115(7)	92(7)	43(3)	−28(6)	4(3)	3(3)
C(44)	−3999(7)	4189(7)	−657(4)	128(8)	115(7)	30(2)	28(6)	−18(3)	−7(3)
C(45)	−4846(7)	3677(7)	−493(4)	117(8)	112(7)	34(2)	36(6)	18(3)	11(3)
C(46)	−5548(6)	3259(6)	−889(4)	77(6)	97(7)	49(3)	7(5)	5(3)	−2(3)
C(47)	−3690(4)	900(4)	−22(2)	42(4)	65(5)	17(1)	4(4)	4(2)	−2(2)
C(48)	−3460(4)	1208(5)	−655(2)	55(4)	69(5)	14(1)	8(4)	−2(2)	−0(2)

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[a] All values in the table are multiplied by 10^4 except for the Cu and P atom parameters which are multiplied by 10^5. Estimated deviations in the least significant digit(s) are in parentheses. The expression for the anisotropic temperature factor is: $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23})\}$

highest possible speed and then, if necessary, at a speed designed to achieve 1500 counts above background. A maximum of 90 s was placed on the measurement time. The horizontal and vertical detector apertures were 3 and 4 mm, respectively, and the distance from the crystal to the aperture 174 mm. The intensities of a total of 3679 reflections were obtained of which 631 with values less than 0. Only the remaining 3048 reflections were used in the structural analysis. The reflection 1 2 $\bar{4}$ was monitored every 20 reflections as a standard reflection. The fluctuations were less than 2% and there was no indication for decay during the measurements. A smooth curve through the points was applied to the intensity data to correct for the intermediate fluctuations.

The data were corrected for Lorentz and polarisation factors (*Lp*), but no correction for absorption was applied.

The crystal structure was solved by a variant of the symbolic addition procedure [14]. The phases of 479 reflections with $E > 1.3$, for the most probable direct methods solution, were used for the calculation of a preliminary Fourier map. The Cu and P atoms were easily located from this map. A second Fourier map was then calculated with new coefficients, with the now known heavy atom contribution subtracted in order to clean up the map from heavy atom ripples. The remaining non-hydrogen atoms could be located from it, except for those of the benzene molecule which were found after one cycle of structure factor and difference Fourier calculation. The structure was refined assuming thermal motion for all non-hydrogen atoms by a block-diagonal least-squares procedure. Unit weights were used in the preliminary stages of the refinement. The structure refinement converged to $R_F = 0.072$. At this stage a difference Fourier synthesis was calculated and fourty hydrogen atom positions inferred. The refinement was continued, including the refinement of the non-hydrogen atom positional parameters. The isotropic *B*-values of the hydrogen atoms were fixed on the value 3.0 Å^2. The *R*-values at this point were $R_F = 0.053$ and $R_{wF} = 0.054$.

At this point an empirical relative weighting scheme was introduced: $w = (6.0 - 0.116|F_o| + 0.00167|F_o|^2)^{-1}$ that was obtained from an analysis of $\langle(F_o - F_c)^2\rangle$ against $|F_o|$.

Convergence was reached at $R_F = 0.048$ and $R_{wF} = 0.067$ for 3048 reflections. All shifts were less than the corresponding standard deviations when refinement was stopped. The final refined parameters are listed in Tables 6 and 7. A final difference Fourier synthesis showed no peaks higher than 0.3 *e* Å^{-3}, apart from some peaks near the Cu atom due to absorption effects.

Scattering factors used in this analysis are those of Doyle and Turner [41] for Cu and P, of Allmann [42] for carbon and of Stewart [43] for H. Anomalous dispersion corrections for Cu and P were taken from a compilation by Rietveld [44].

Part of the calculations were carried out on an Electrologica E1-X8 computer and part on a CDC Cyber 73 computer at the computer center of the University of Utrecht. Among the programs that were used in this structural analysis were the local programs CAD 4 Tape (for handling of the diffractometer output by D. Kaas), Audice (a direct methods procedure by A.L. Spek), Fourier (by D. Kaas), least-squares (D. Kaas), stereo (for stereoscopic drawings by D. Kaas), ORTEP (thermal ellipsoid drawing by C.K. Johnson) and an extended version

TABLE 7

REFINED HYDROGEN ATOM POSITIONS [a]

Atom	*X/A*	*Y/B*	*Z/C*
H[C(6)]	−386(4)	252(5)	102(2)
H[C(7)]	−389(4)	435(4)	126(2)
H[C(8)]	−245(4)	534(5)	96(2)
H[C(9)]	−115(4)	457(5)	46(2)
H[C(10)]	−118(4)	286(5)	26(2)
H[C(12)]	−429(4)	−0(5)	95(2)
H[C(13)]	−453(4)	−70(5)	182(2)
H[C(14)]	−317(4)	−79(5)	259(2)
H[C(15)]	−166(4)	4(5)	243(2)
H[C(16)]	−142(4)	88(5)	155(2)
H[C(18)]	−347(4)	187(4)	−174(2)
H[C(19)]	−301(4)	248(5)	−265(2)
H[C(20)]	−153(4)	208(5)	−303(2)
H[C(21)]	−28(4)	92(5)	−252(2)
H[C(22)]	−71(4)	22(5)	−163(2)
H[C(24)]	−279(4)	−155(4)	−33(2)
H[C(25)]	−367(4)	−306(5)	−58(2)
H[C(26)]	−443(4)	−338(4)	−146(2)
H[C(27)]	−435(4)	−209(4)	−214(2)
H[C(28)]	−353(4)	−45(4)	−196(2)
H[C(30)]	113(4)	346(4)	−4(2)
H[C(31)]	152(4)	467(5)	73(2)
H[C(32)]	123(4)	411(5)	164(2)
H[C(33)]	62(4)	238(5)	182(2)
H[C(34)]	26(4)	119(5)	108(2)
H[C(36)]	−196(4)	−160(4)	96(2)
H[C(37)]	−212(4)	−266(5)	175(2)
H[C(38)]	−87(4)	−374(5)	208(2)
H[C(39)]	84(4)	−373(5)	166(2)
H[C(40)]	92(4)	−271(5)	85(2)
H[C(41)]	−588(4)	310(4)	−175(2)
H[C(42)]	−443(4)	389(5)	−203(2)
H[C(43)]	−329(4)	467(5)	−133(2)
H[C(44)]	−351(4)	445(4)	−40(2)
H[C(45)]	−493(4)	359(4)	−11(2)
H[C(46)]	−622(4)	296(5)	−82(2)
H[C(47)]	−389(4)	15(5)	1(2)
H[C(47)]	−429(4)	122(5)	11(2)
H[C(48)]	−409(4)	110(5)	−90(2)
H[C(48)]	−324(4)	193(4)	−66(2)

[a] All values in the table are multiplied by 10^4.

of the X-ray system (by Stewart et al. and implemented by the Dutch X-Ray-System group) for several other calculations * [45].

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* The function minimized was $\Sigma(w(|F_o|-|F_c|)^2)$. The refinement was on F. The unweighted and weighted residuals are defined as follows:

$R_F = (\Sigma|F_o| - |F_c|)/(\Sigma|F_o|)$

$R_{wF} = [(\Sigma w(|F_o| - |F_c|)^2)/(\Sigma|F_o|^2)]^{1/2}$

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