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Preliminary communication

STRUCTURE OF THE $CuCl_2$ ADDUCT OF *trans*-CHLORO-1,4-BIS(*p*-METHOXYPHENYL)-1,4-DIAZA-3-METHYLBUTADIEN-2-YL-BIS(TRIPHENYLPHOSPHINE)-PALLADIUM(II)

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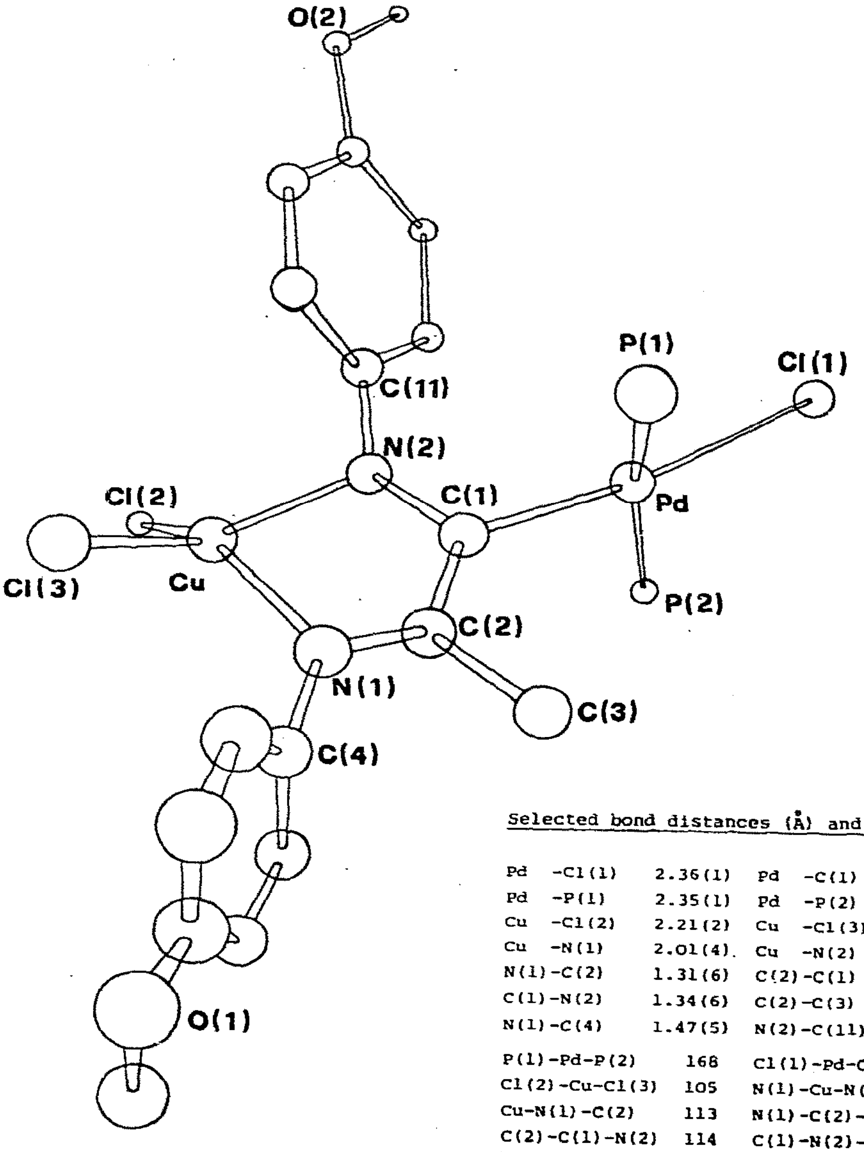
Summary

An X-ray structure analysis of the binuclear complex $[CuCl_2\{RN{=}C(Me)\text{-}C(R'){=}NR\}]$ ($R = p\text{-}C_6H_4OMe$; $R' = trans\text{-}PdCl(PPh_3)_2$) has shown that the Pd—C σ-bonded 1,4-diaza-3-methylbutadien-2-yl group acts as σ,σ-*N,N* chelating ligand with a tetragonally distorted tetrahedral geometry around the copper atom. No exchange of ancillary ligands has occurred between the two metallic centers of the molecule, which are 4.75 Å apart from each other.

Recent studies have shown that the organometallic compound $RN{=}C(Me)\text{-}C(R'){=}NR$ ($R = p\text{-}C_6H_4OMe$; $R' = trans\text{-}PdCl(PPh_3)_2$), DAB, containing a Pd—C σ-bonded 1,4-diaza-3-methylbutadien-2-yl group [1,2], gives a series of monomeric 1/1 adducts with transition metal chlorides MCl_2 (M = Fe, Co, Ni, Zn, Pd, Cd, Pt) [3,4]. In some cases (M = Pd, Pt) transfer of PPh_3 from the Pd center of R′ to M has been observed [4].

In view of our interest [3—5] in this type of binuclear complexes we have determined the crystal structure of $[CuCl_2(DAB)]$ in order to obtain information about (i) the type of bonding and the effects of coordination on the diazabutadienyl moiety, (ii) the configuration around the copper atom, (iii) the possible rearrangement of the molecule with exchange of ancillary ligands between the two metallic centers.

Red-brown crystals of $[CuCl_2(DAB)]$, which were obtained from CH_2Cl_2/ethyl ether solution, are monoclinic, space group $P2_1/n$ and have $Z = 4$ in a unit cell of dimensions a 14.250(6), b 20.375(8), c 19.181(7) Å and β 102.95(4)°. The intensities of 2184 independent reflections to θ_{max} 15° were measured, of which only 1279 obeying the condition $I > 2\sigma(I)$ were used in subsequent calculations. The high proportion of very weak reflections may be attributed to the small crystal used and to large thermal motion. The structure was refined to $R = 0.10$ with w based on $\sigma(F_0)$ and function minimized $\Sigma w(|F_0| - |F_c|)^2$. Because the number of observations was insufficient to give a reasonable observation-to-parameter ratio, it was necessary to treat the eight phenyl rings as rigid groups and to refine only palladium and copper atoms anisotropically*.



Selected bond distances (Å) and angles (°)

Pd -Cl(1)	2.36(1)	Pd -C(1)	2.00(5)
Pd -P(1)	2.35(1)	Pd -P(2)	2.33(1)
Cu -Cl(2)	2.21(2)	Cu -Cl(3)	2.18(2)
Cu -N(1)	2.01(4)	Cu -N(2)	2.00(4)
N(1)-C(2)	1.31(6)	C(2)-C(1)	1.44(7)
C(1)-N(2)	1.34(6)	C(2)-C(3)	1.56(7)
N(1)-C(4)	1.47(5)	N(2)-C(11)	1.41(5)
P(1)-Pd-P(2)	168	Cl(1)-Pd-C(1)	173
Cl(2)-Cu-Cl(3)	105	N(1)-Cu-N(2)	80
Cu-N(1)-C(2)	113	N(1)-C(2)-C(1)	117
C(2)-C(1)-N(2)	114	C(1)-N(2)-Cu	114

Fig. 1. Molecular geometry of [$CuCl_2$(DAB)]. The phenyl groups of PPh_3 ligands are omitted for clarity.

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*Cell dimensions and diffraction intensities were measured on a Philips PW 1100 diffractometer with monochromated Mo-K_α radiation. The solution and refinement were carried out using SHELX-76 System. Final atomic fractional coordinates, thermal parameters and the structure factor tables have been deposited.

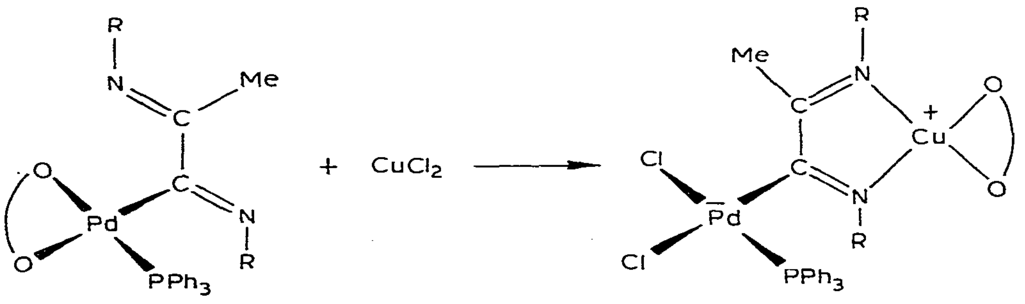
The molecular geometry of [$CuCl_2$(DAB)] as well as some selected bond distances and angles in the molecule are shown in Fig. 1.

The crystal structure consists of discrete monomeric [$CuCl_2$(DAB)] units in which both metallic centers are four-coordinated. The distance between copper and the nearest non-bonded chlorine atom is greater than 4 Å, too large for a Cl-bridging bond. The configuration about palladium(II) exhibits the same distortion from square-planar towards tetrahedral arrangement of the four donor atoms as was observed in the free ligand DAB [2]. The configuration about copper(II) is tetragonally distorted tetrahedral, the 1,4-diaza-3-methylbutadien-2-yl group acting as a σ,σ-*N,N* chelating ligand with an N(1)—Cu—N(2) angle of 80.0°, very close to those reported for complexes of organic 1,4-diazabutadienes [6,7]. This is in line with the pseudo-tetrahedral geometry assigned to the binuclear adducts [MCl_2(DAB)] (M = Fe, Co, Ni) on the basis of their magnetic moments and electronic spectra [3]. The N=C—C=N fragment is virtually planar, its mean plane being almost normal (82.6°) to P(1)— Cl(1)—P(2)—C(1), whereas the dihedral angle with the plane Cl(2)—Cu—Cl(3) is 58.0°. The Pd and Cu centers are 4.75 Å apart from each other and are out of the N(1)—C(2)—C(1)—N(2) plane by +0.07 and −0.30 Å, respectively.

In this structure short-range palladium—hydrogen interactions are likely to occur, as can be inferred from the Pd—C(12) (3.23 Å) and Pd—C(3) (3.37 Å) distances above and below the mean coordination plane P(1)—Cl(1)—P(2)—C(1). This would account for the marked deshielding of the *ortho* protons of *p*-C_6H_4OMe substituent in position 1 and of the methyl protons in position 3, observed in the ^1H NMR spectrum of [$ZnCl_2$(DAB)] [3]. The phenyl rings of the N-substituents do not interact with the π-system of the diazabutadiene moiety, as they are rotated by 69.4° and 45.2° out of the N=C—C=N plane, and together form a dihedral angle of 27.5°.

Apart from the conformational change, the bond distances of the N=C—C=N unit seem to be little influenced by coordination, but the high e.s.d.'s do not allow a more accurate comparison at this stage of data refinement.

Even the geometry around palladium(II) is not affected by complex formation. In this part of the molecule, however, a significant shortening of the Pd—Cl bond occurs, from 2.41(1) Å of DAB [2] to 2.36(1) Å of [$CuCl_2$(DAB)], indicat-



(1)

(R = *p*-C_6H_4OMe ; O—O = 2,4-pentanedionate) ing a reduced *trans*-influence of the coordinated 1,4-diaza-3-methylbutadien-2-yl group. In the IR spectra this is paralleled by the higher frequency shift (30—40 cm^{-1}) of ν(Pd—Cl) upon coordination [3].

The molecular structure of [$CuCl_2$(DAB)] confirms the previous formulation of this compound [3] and rules out any exchange of ancillary ligands between the two metallic centers, such as that which occurs in reaction 1 [8].

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