

K-27

A PHENOXYDICOPPER(I) COMPLEX CONTAINING A BRIDGING OXYGEN ATOM:



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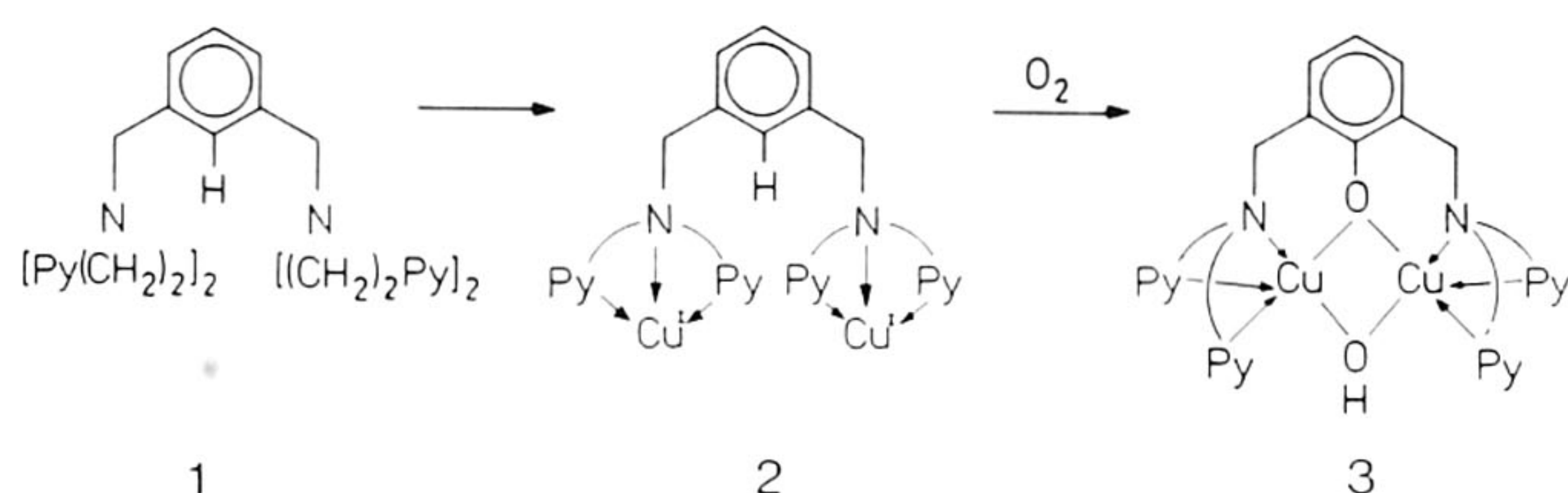
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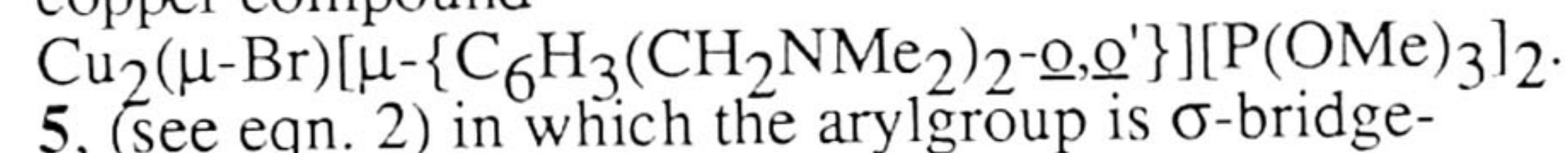
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Binuclear copper phenolates are generally regarded as important intermediates in copper-catalysed oxygenolysis reactions. This has led to extensive research into the synthesis and characterization of model compounds containing two copper centres. Many studies have also been concerned with the reactivity of these compounds and their possible application as oxygen carriers [1]. In particular, the model system **3** developed by Karlin *et al.* is intriguing as regards its formation through the insertion of an oxygen atom into an aromatic C-H bond, Eqn. 1 [2].

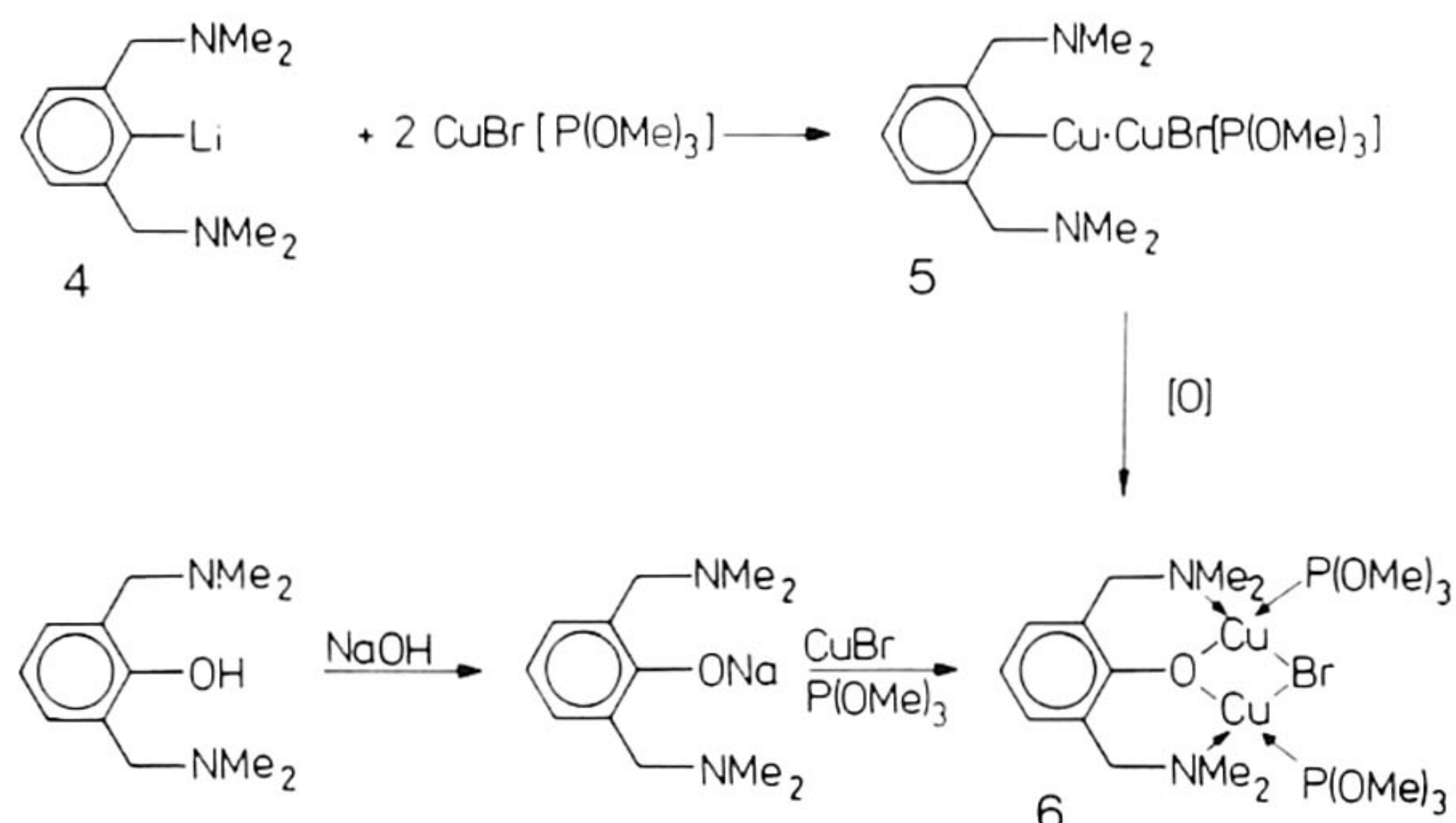
(1)



During our investigations into the structure of arylcopper(I) compounds we have isolated a dinuclear copper compound



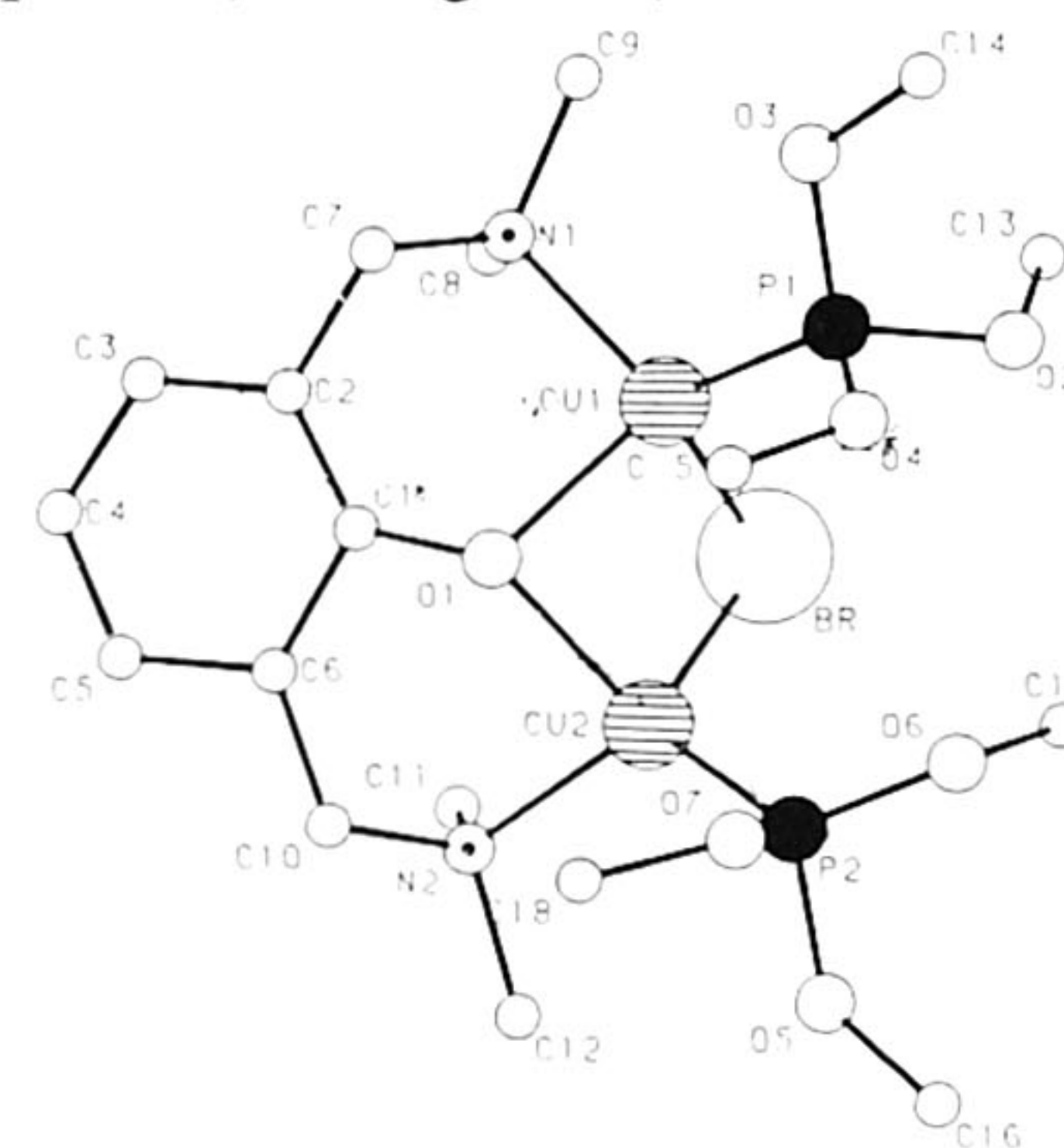
(2)



bonded to two copper atoms by the C atom which is ortho to both $-\text{CH}_2\text{NMe}_2$ substituents [3]. Interestingly, attempts to crystallize **5** led to isolation of the phenoxydicopper(I) title compound, presumably as a result of the inadvertent introduction of traces of oxygen. Compound **6** can also be prepared via an alternative route involving the reaction of $\text{Na}[\text{OC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o']$ with CuBr in the presence of $\text{P}(\text{OMe})_3$ [4]. The $^1\text{H NMR}$ spectrum of **6** shows singlets for the NMe_2 and CH_2 groups and the presence of equivalent $\text{P}(\text{OMe})_3$ groups [$^3\text{J}(\text{P},\text{H}) = 11.8 \text{ Hz}$]. An X-ray structural determination of this compound has been carried out and Fig. 1. shows the molecular structure found and the adopted numbering scheme. The structure reveals **6** to be a dinuclear monomeric molecule in which a single phenoxy-oxygen atom is symmetrically bridging two virtually equivalent copper atoms ($\text{Cu-O} = 2.10(2)$ and $2.11(2) \text{ \AA}$). Furthermore, each copper atom is coordinated by one N-donor of a $-\text{CH}_2\text{NMe}_2$ group ($\text{Cu-N} = 2.17(2)$ and $2.20(2) \text{ \AA}$, resp.), one $\text{P}(\text{OMe})_2$ ligand ($\text{Cu-P} =$

$2.146(8)$ and $2.143(8) \text{ \AA}$, resp.) and a symmetrically bridging bromine atom ($\text{Cu-Br} = 2.557(4)$ and $2.520(5) \text{ \AA}$, resp.). These ligands are so positioned as to provide each copper atom with a slightly distorted tetrahedral coordination sphere (see Figure 1).

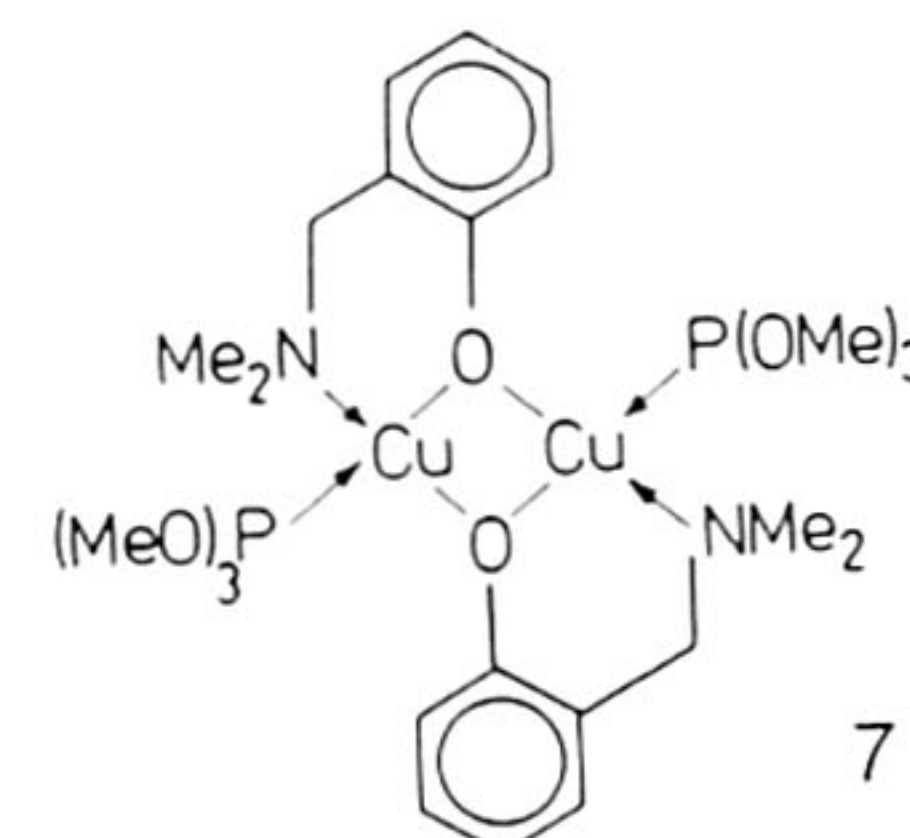
Figure 1.



The selective aromatic hydroxylation involving the conversion of a Cu(I)-C bond in **5** into a Cu(I)-OC bond in **6** is remarkable. Although the mechanism of this reaction is not known it can be anticipated that part of the RCu(I) aggregate serves as an electron source with formation of either $\text{R}\cdot$ and Cu(0) or $2\text{R}\cdot$, 2Cu(I) , and O_2^{2-} . In subsequent steps bound O_2^{2-} can disproportionate to afford O^{2-} and O with the latter inserting into the Cu(I)-C bond.

Oxygenation reactions of aryl compounds are usually found only with copper(I) [2], most likely as a result of the high reactivity of the Cu(I)-phenoxy unit. Not surprisingly, therefore, the phenoxy copper compound **6** is found to be extremely air sensitive. A further new phenoxy copper compound, **7**, related to **6** but which now contains an aryl ligand with only one coordinating ortho CH_2NMe_2 group has been prepared from the reaction of $\text{Na}[\text{OC}_6\text{H}_4\text{-}2\text{-CH}_2\text{NMe}_2]$ and CuBr in the presence of $\text{P}(\text{OMe})_3$. The dinuclear structure proposed for **7** is shown in Figure 2. The present study has shown that

Figure 2.



phenoxydicopper(I) units can be stabilized by a combination of ligands including intramolecular coordination of either one or two ortho CH_2NMe_2 aryl ligand substituents.

Further work on the scope and mechanism of the reactions by which **6** and **7** are formed is in progress.

- [1] K.D. Karlin, J. Zubieta (eds.): Biological & Inorganic Copper Chemistry, Volume II; Adenine Press, New York, 1986.
- [2] K.D. Karlin, R.W. Cruse, Y. Gultneh, J.C. Hayes, J. Zubieta, J. Am. Chem. Soc. **106**, 3272 (1986).
- [3] E. Wehman, G. van Koten, C.J.M. Erkamp, D.M. Knotter, J.T.B.H. Jastrzebski, C.H. Stam, manuscript in preparation.
- [4] Under a N_2 atmosphere 3.8 mmol of CuBr , was slowly added portionwise to a mixture of 1.9 mmol of $\text{C}_6\text{H}_3\text{OH}(\text{CH}_2\text{NMe}_2)_2\text{-}o,o'$, 1.9 mmol of NaOH and 3.8 mmol of $\text{P}(\text{OMe})_3$ in 10 ml of MeOH at room temperature. The resulting suspension was filtered and subsequently the filtrate was concentrated *in vacuo*. The white precipitate which had formed was filtered off, washed with Et_2O , and dried *in vacuo* giving **3** (70%). $^1\text{H NMR}$ (C_6D_6): 2.33 (12H, s, NMe_2); 3.05 (4H, s, CH_2); 3.56 (18H, d, OMe, $^3\text{J}(\text{P},\text{H}) = 11.8 \text{ Hz}$); 6.6-6.8 (H, m, ArH); 6.9-7.1 ppm (2H, m, ArH).
- [5] $a = 10.142$; $b = 28.157$, $c = 9.609 \text{ \AA}$; space group $\text{P}_{2,2,2}$, $R_f = 0.094$.