α-Cupriobenzylideneamines, a Novel Class of Thermally Stable Organocopper Compounds

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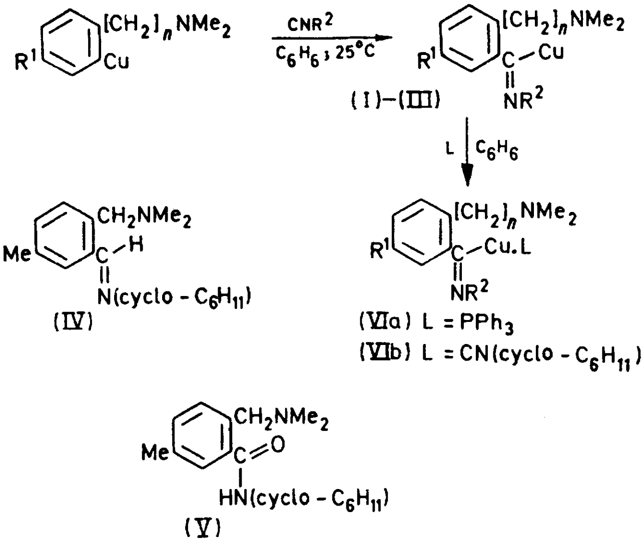
Summary Insertion of isocyanides into the Cu-C bond of arylcopper(I) compounds affords novel, thermally stable α-cupriobenzylideneamines.

Recently we reported the isolation and characterization of thermally, oxidatively, and hydrolytically stable arylcopper(I) compounds which contain, preferably in the *ortho* position, hetero-atom containing substituents (*e.g.* NMe_2, OMe, $CH_2{\cdot}NMe_2$, and $CH_2{\cdot}OMe$).[1] We have now found that these compounds readily react with isocyanides to afford α-cupriobenzylideneamines instead of organocopper isocyanide complexes.† The observed insertion reaction represents a novel reaction type in organometallic chemistry of Group IB elements.

Compared with alkylcopper compounds, which decompose below 20 °C,[2] compounds (I)—(III) display a remarkable thermal stability (decomp. 100—200 °C) probably as a result of copper–hetero-atom co-ordinative bonding. However, these compounds are susceptible towards hydrolysis and oxidation.



(I) $n = 1$, $R^1 = H$, $R^2 =$ cyclo-C_6H_{11}
(IIa) $n = 1$, $R^1 = Me$, $R^2 =$ cyclo-C_6H_{11}
(IIb) $n = 1$, $R^1 = Me$, $R^2 = Bu^t$
(III) $n = 0$, $R^1 = H$, $R^2 =$ cyclo-C_6H_{11}

The identity of the yellow solids, (I)—(III) (isolated in 50—90% yield after recrystallization from ether, pentane, or benzene) have been established by elemental analysis, and n.m.r. and i.r. spectroscopy. Moreover, the insertion of CNR into the Cu–C(aryl) bond yielding a Cu—C(=NR) bond was confirmed by the isolation of the corresponding Schiff bases from degradation of the respective compounds (I)—(III) with H_2O. *E.g.* (IIa) afforded the Schiff's base (IV); δ(N=CH) 8·56 p.p.m., in CCl_4; ν(C=N)(KBr) 1640 cm^{-1}, in 60% yield.

The reaction of (IIa) with O_2 in ether affords (V) in 60% yield and traces of the Schiff's base (IV). The cleavage of a Cu–C bond by oxygen yielding a carbonyl group is in striking contrast with earlier findings[3] that oxidation of organocopper compounds RCu with oxygen gives the symmetric coupling products R–R.

Thermal degradation of (IIa) dissolved in quinoline at 200 °C yielded Schiff's base (IV) (61% yield) instead of the expected symmetric dimer.

The structure of the α-cupriobenzylideneamines (I)—(III) is under investigation. Molecular-weight determinations (by cryometry) at various concentrations indicate compound (IIa) to be dimeric in benzene. A six-membered ring structure formed by intermolecular co-ordination of two Cu–C=N units with the possibility of additional Cu–NMe_2 intramolecular co-ordination is considered more likely than the formation of a larger-sized ring *via* intermolecular Cu–NMe_2 co-ordination. The breakdown of the dimeric structure under the influence of suitable ligands is illustrated by the almost quantitative formation of a yellow 1 : 1 organocopper–triphenylphosphine complex [(VIa), $n = 1$, $R^1 = Me$, $R^2 =$ cyclohexyl; monomeric in benzene] upon interaction of (IIa) with an equimolar amount of Ph_3P in benzene at room temperature.

The 1 : 1 reaction of (IIa) with cyclohexyl isocyanide at 60 °C did not result in a further insertion reaction [*cf.* ref. 4 for the occurrence of repeated insertion reactions with isocyanide of *trans*-$Pd(PPh_3)_2IMe$], but instead the 1 : 1 organocopper isocyanide complex was isolated as a red-brown solid [(VIb), $n = 1$, $R^1 = Me$, $R^2 =$ cyclohexyl; ν(C≡N) (Nujol) 2146 cm^{-1}] in 75% yield.

The isolation in 25% yield of yellow crystalline α-cupric-*N*-cyclohexylbenzylideneamine (dimeric in benzene) from the 1 : 1 reaction of purified phenylcopper with cyclohexyl isocyanide indicates that the insertion of isocyanides into Cu–C bonds is a general reaction for arylcopper compounds.

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† Recently the isolation of the 1 : 1 complex of π-cyclopentadienylcopper(I) with methyl isocyanide has been reported (F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 5114).

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[2] *E.g.*: H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, 1952, **17**, 1630.

[3] *E.g.*: R. J. De Pasquale and C. Tamborski, *J. Org. Chem.*, 1969, **34**, 1736: A Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1968, **90**, 2186.

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