

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

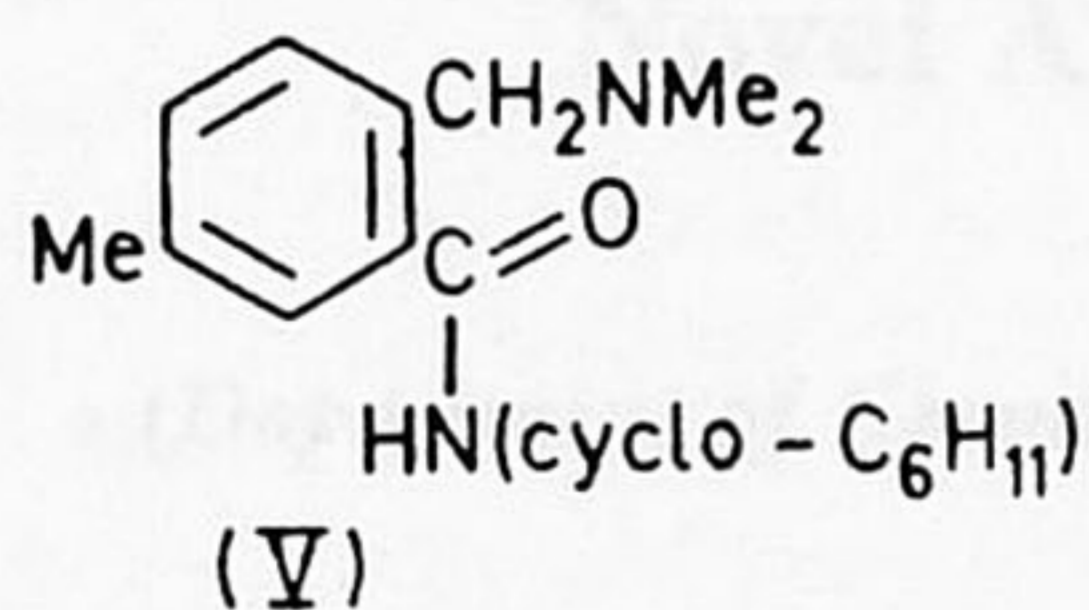
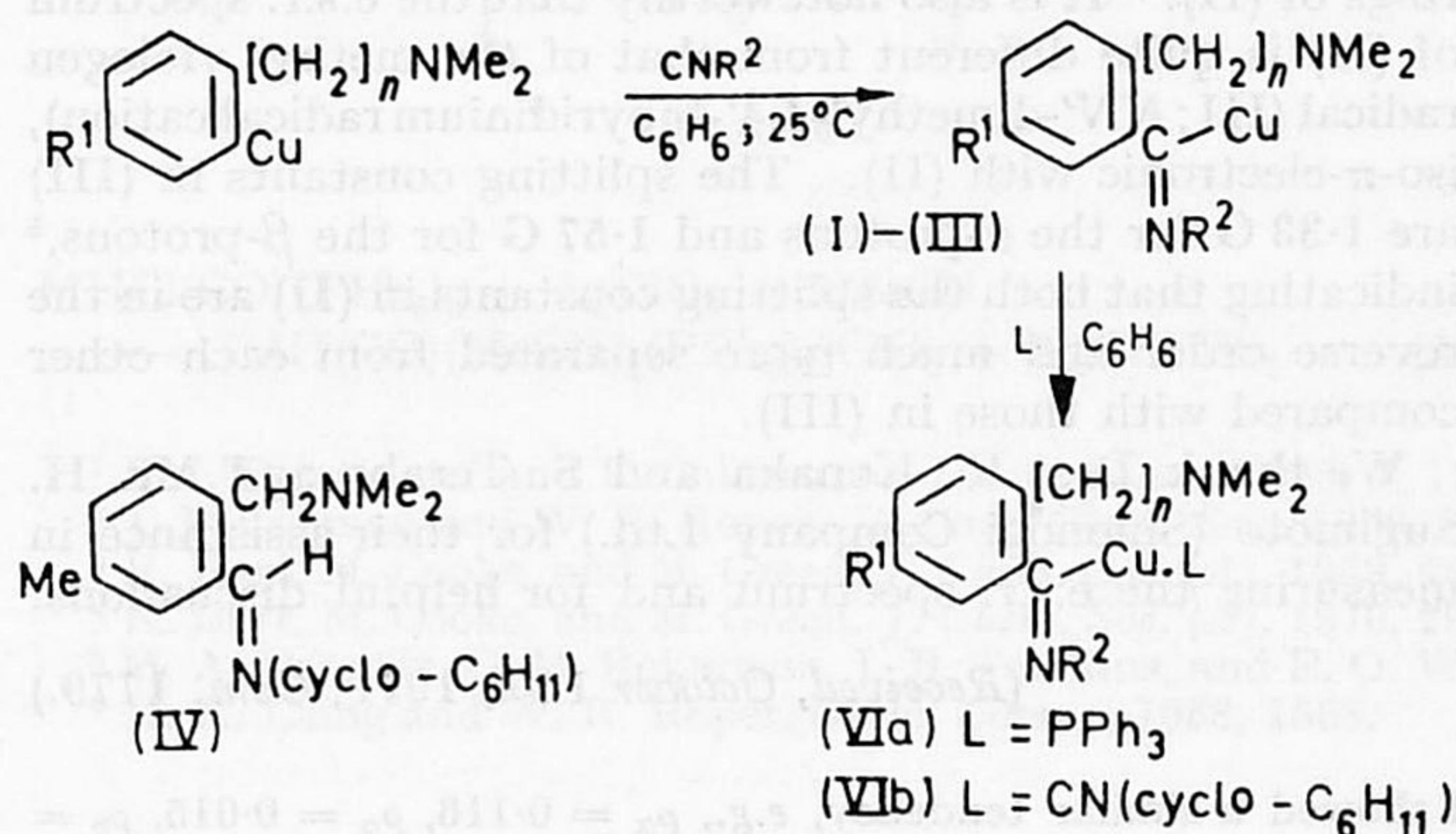
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Summary Insertion of isocyanides into the Cu-C bond of arylcopper(I) compounds affords novel, thermally stable α -cupriobenzylideneamines.

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.* NMe₂, OMe, CH₂NMe₂, and CH₂OMe).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) $n = 1$, R¹ = H, R² = cyclo-C₆H₁₁
 (IIa) $n = 1$, R¹ = Me, R² = cyclo-C₆H₁₁
 (IIb) $n = 1$, R¹ = Me, R² = Bu^t
 (III) $n = 0$, R¹ = H, R² = cyclo-C₆H₁₁

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

† 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).

¹ G. van Koten, A. J. Leusink, and J. G. Noltes, *Chem. Comm.*, 1970, 1107; G. van Koten, A. J. Leusink, and J. G. Noltes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 227.

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.

⁴ Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan* 1970, **43**, 3634; *ibid.* 1970 **43**, 2653.

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 H₂O. *E.g.* (IIa) afforded the Schiff's base (IV); $\delta(\text{N}=\text{CH})$ 8.56 p.p.m., in CCl₄; $\nu(\text{C}=\text{N})(\text{KBr})$ 1640 cm⁻¹, in 60% yield.

The reaction of (IIa) with O₂ 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 findings³ 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–NMe₂ intramolecular co-ordination is considered more likely than the formation of a larger-sized ring *via* intermolecular Cu–NMe₂ 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), $n = 1$, R¹ = Me, R² = cyclohexyl; monomeric in benzene] upon interaction of (IIa) with an equimolar amount of Ph₃P 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(PPh₃)₂Ime], but instead the 1:1 organocopper isocyanide complex was isolated as a red-brown solid [(VIb), $n = 1$, R¹ = Me, R² = cyclohexyl; $\nu(\text{C}\equiv\text{N})$ (Nujol) 2146 cm⁻¹] in 75% yield.

The isolation in 25% yield of yellow crystalline α -cuprio-*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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