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REACTION OF CARBOXAMIDE WITH Cu_2O—ISONITRILE COMPLEX; FORMATION OF A NEW CHELATED COPPER(I) COMPLEX

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Summary

Reaction of carboxamides with Cu_2O in the presence of t-butyl isocyanide gave new chelated copper(I) complexes, which probably are formed by the insertion of t-butyl isocyanide into the copper—nitrogen bond of copper(I) amide isonitrile complexes, which were initially produced from the carboxamides and Cu_2O—t-butyl isocyanide complex. The same chelated copper(I) complexes were prepared more readily by the reaction of the corresponding *N*-trimethylsilyl-carboxamides with Cu_2O—t-butyl isocyanide complex. Reactions of the copper(I) complexes thus obtained with alkylating agents, such as alkyl halides, alkyl tosylates and triethyloxonium tetrafluoroborate, also were described.

In our continuing studies on Group IB metal-catalyzed insertions of isonitrile, it has been found that (i) isonitrile insertions into the heteroatom—hydrogen bonds of amines, alcohols and thiols are catalyzed by copper, silver and gold salts such as the chlorides and cyanides (eq. 1) [1], and (ii) isonitrile insertions into the carbon—hydrogen bonds of the so-called active methylene compounds are catalyzed by Cu_2O and metallic copper (eq. 2) [2].

$$RQH + R'NC \xrightarrow{\text{Group IB metal salts}} RQCH{=}NR' \qquad (1)$$

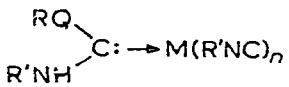
(Q = NH, O, S) (I)

$$\begin{matrix} X \\ \diagdown \\ \quad CH_2 \\ \diagup \\ Y \end{matrix} + R'NC \xrightarrow{Cu_2O,\ Cu^0} \begin{matrix} X \\ \diagdown \\ \quad CHCH{=}NR' \\ \diagup \\ Y \end{matrix} \qquad (2)$$

(II)

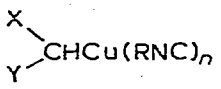
The intermediacy of carbene-coordinated metal complexes (III) recently has

been established by Balch et al. for the first type of isonitrile insertions of eq. 1 [3]. In the case of the second type of isonitrile insertion, on the other hand, an organocopper(I) isonitrile complex intermediate (IV) was isolated, which subsequently underwent isonitrile insertion into its copper—carbon bond [4].



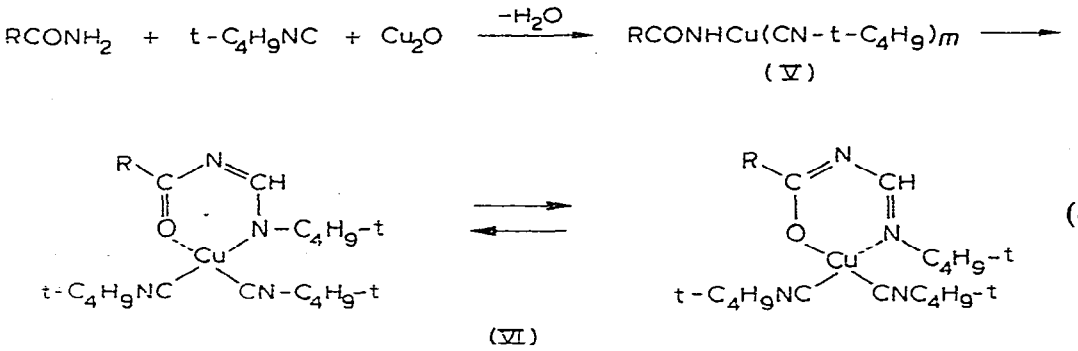
(III)

M = Cu, Ag, Au



(IV)

Herein, we wish to report a reaction of the Cu_2O—t-butyl isocyanide complex with carboxamides to produce new chelated copper(I) complexes (VI), which are assumed to be formed by isonitrile insertion into the copper—nitrogen bond of copper(I) amide—isonitrile complexes (V) initially produced from carboxamides and Cu_2O—t-butyl isocyanide complex.



(V)

(VI)

(3)

In addition, the same chelated copper(I) complexes (VI) were produced more readily by the reaction of the corresponding *N*-trimethylsilylcarboxamides with the Cu_2O—t-butyl isocyanide complex.

$$RCONHSiMe_3 + t\text{-}C_4H_9NC + Cu_2O \rightarrow VI + Me_3SiOSiMe_3 \quad (4)$$

The reactions of these copper(I) complexes (VI) with alkylating agents are also described here.

Results and discussion

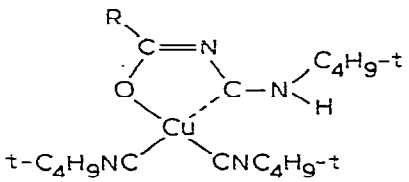
Reactions of carboxamides with Cu_2O—t-butyl isocyanide complex

Formamide was treated with Cu_2O and t-butyl isocyanide in refluxing benzene under nitrogen, and the water produced was continuously removed by azeotropic distillation. A white, solid copper(I) complex (VIa, R = H) was obtained from the reaction mixture. In a similar way, the corresponding coppper(I) complexes (VIb, R = CH_3 and VIc, R = C_6H_5) were prepared from acetamide

and benzamide, respectively. All these copper(I) complexes (VI) are gradually decomposed in air, but are stable under nitrogen.

The copper(I) complexes (VI) also were prepared by the reaction of the Cu_2O—t-butyl isocyanide complex with *N*-trimethylsilylcarboxamides. The latter are easily prepared by treating carboxamides with trimethylchlorosilane in the presence of base [5]. The latter method (eq. 4) for the preparation of copper(I) complexes (VI) has some advantages over the former one, i.e., the reaction time is remarkably shortened, and the formation of water, which may cause a partial decomposition of copper(I) complexes (VI) is avoided. In the latter case, hexamethyldisiloxane was produced instead of water as a by-product. Results are shown in Table 1.

The structure of copper(I) complexes (VI) has been established by elemental analysis, IR, NMR, molecular weight determination as well as chemical transformations. The IR spectrum of VIb shows a sharp absorption band at 2150 cm^{-1} due to the N≡C bond of the coordinated isocyanide, and strong bands at 1630 and 1590 cm^{-1}, which are assignable to the C=O and C=N double bonds of the ligand. The remarkable shift of the C=O absorption band ˙ taken to indicate a chelated structure for copper(I) complex (VIb), which is analogous to that for copper(I) acetylacetonate (ν = 1610 and 1525 cm^{-1}) [4] and the copper(II) complex of β-amino-α,β-unsaturated ketone (ν 1584 and 1530 cm^{-1}) [6]. The NMR spectrum of VIb is in accord with the proposed structure. A sharp one-proton singlet at τ 0.74 ppm, which is not exchangeable with D_2O, is ascribed to the methine proton of the N=CH—N group. The NMR spectrum, as well as the absence of absorption bands in the NH region (3000~3700 cm^{-1}), excludes the alternate structure VII containing a coordinating carbene ligand for the present chelated copper(I) complex *. Some platinum complexes having structures similar to VII have been reported [7].



(VII)

Treatment of VIb with dry HCl in ethanol afforded *N*-(*N'*-t-butyliminoformyl) acetamide and the CuCl—t-butyl isocyanide complex.

$$\text{VIb} \xrightarrow{\text{HCl in } C_2H_5OH} CH_3CONHCH{=}NC_4H_9\text{-t} + CuCl(t\text{-}C_4H_9NC)_n \qquad (5)$$

The formation of the chelated copper(I) complex (VI) may be explained as shown in Scheme 1, which involves isonitrile insertion into the copper—nitrogen bond of copper(I) amide—isonitrile complex (V) initially produced by the reaction of Cu_2O—t-butyl isocyanide complex with carboxamide or *N*-trimethylsilyl-

* The possibility of structure VII was suggested by a referee.

TABLE I

REACTION OF CARBOXAMIDE WITH Cu_2O AND t-BUTYL ISOCYANIDE

Carboxamide	Method [a]	Reaction time (h)	Copper(I) complex VI	Yield (%)
$HCONH_2$	A	4	VIa	70
CH_3CONH_2	A	5	VIb	83
	B	3	VIb	90
$PhCONH_2$	A	15	VIc	80
	B	9	VIc	83

[a] Method A: Reaction of carboxamide with Cu_2O/t-C_4H_9NC;
Method B: Reaction of *N*-trimethylsilylcarboxamide with Cu_2O/t-C_4H_9NC.

carboxamide, and the subsequent rapid migration of the copper moiety from carbon to the adjacent nitrogen atom (VIII → VI).

SCHEME 1

$$RCONH_2 \text{ (or } RCONHSi(CH_3)_3) \xrightarrow{Cu_2O/t\text{-}C_4H_9NC} RCONCHCu(t\text{-}C_4H_9NC)_m \xrightarrow{t\text{-}C_4H_9NC}$$

(V)

$$RCONHC(=N\text{-}t\text{-}C_4H_9)\text{-}Cu(t\text{-}C_4H_9NC)_n \longrightarrow VI$$

(VIII)

In some cases, intermediate V was trapped by reaction with an alkyl halide. For instance, the reaction mixture of acetamide and the Cu_2O—t-butyl isocyanide complex was treated with n-octyl bromide to afford *N*-n-octylacetamide in 33% yield, together with *N*-(*N'*-t-butyliminoformyl)-*N*-n-octylacetamide. (IXb-5).

Alkylation of copper(I) complexes (VI)

Alkylation of copper(I) complexes (VI) was performed by stirring a benzene solution of VI with alkylating agents, such as alkyl halide, alkyl tosylate and triethyloxonium tetrafluoroborate, at room temperature with or without a small amount of t-butyl isocyanide *. Copper(I) complexes (VIa and VIb : R = alkyl) derived from aliphatic amides were treated with alkylating agents to furnish *N*-alkyl-*N*-(*N'*-t-butyliminoformyl)amides (IX) in moderate yields.

$$VI + R'X \xrightarrow{R = H, CH_3} RCON(R')CH{=}N\text{-}C_4H_9\text{-}t \quad (IX) \qquad (6)$$

$$VI + R'X \xrightarrow{R = Ph,\ 2\text{-furyl}} IX + RCON{=}CH{-}N(R')C_4H_9\text{-}t \quad (X)$$

* The presence of a small amount of t-butyl isocyanide remarkably accelerated alkylation of copper(I) complex VII.

TABLE 2

ALKYLATIONS OF COPPER(I) COMPLEXES (VI)

Copper(I) complex (VI)	Alkylating agents (R'X)	Product (yield, %)	
		RCON(R')CH=NC$_4$H$_9$-t (IX)	RCON=CHN(R')(C$_4$H$_9$-t) (X)
VIa	MeOTs	IXa-1: R = H, R' = CH$_3$ (50)	
VIa	n-PrBr	IXa-2: R = H, R' = n-Pr (67)	
VIb	CH$_3$I	IXb-1: R = CH$_3$, R' = CH$_3$ (52)	
VIb	(C$_2$H$_5$)$_3$OBF$_4$	IXb-2: R = CH$_3$, R' = C$_2$H$_5$ (42)	
VIb	n-PrBr	IXb-3: R = CH$_3$, R' = n-Pr (87)	
VIb	n-BuBr	IXb-4: R = CH$_3$, R' = n-Bu (80)	
VIb	n-OctBr	IXb-5: R = CH$_3$, R' = n-Oct (60)	
VIc	MeOTs	IXc-1: R = Ph, R' = CH$_3$ (9)	Xc-1: R = Ph, R' = CH$_3$ (83)
VIc	n-PrBr	IXc-2: R = Ph, R' = n-Pr (20)	Xc-2: R = Ph, R' = n-Pr (76)
VIc	n-BuBr	IXc-3: R = Ph, R' = n-Bu (13)	Xc-3: R = Ph, R' = n-Bu (70)
VId [a]	n-PrBr	IXd-1: R = C$_4$H$_3$O, R' = n-Pr (34)	Xd-1: R = C$_4$H$_3$O, R' = n-Pr (55)

[a] VId: R = cyclo-C$_4$H$_3$O. Complex VId was prepared by the reaction of 2-furoic acid amide with Cu$_2$O-t-C$_4$H$_9$NC complex and was used without purification.

Reaction of copper(I) complex (VIb) with trimethylchlorosilane, however, gave *N*-(*N'*-t-butyliminoformyl)acetamide in a moderate yield instead of the expected product *N*-trimethylsilyl-*N*-(*N'*-t-butyliminoformyl)acetamide. It is likely that *N*-trimethylsilyl-*N*-(*N'*-t-butyliminoformyl)acetamide was formed first and then was hydrolyzed rapidly by the moisture in the air to give *N*-(*N'*-t-butyliminoformyl)acetamide.

The alkylation of copper(I) complex VIc (R = aryl) derived from an aromatic carboxylic amide, on the other hand, afforded two isomeric alkylated products (IX and X) with X predominating. The products IX and X were identified by elemental analyses, IR and NMR spectra, and their hydrolysis products *.

Results of alkylation of VI are summarized in Table 2.

Attempts to trap the copper(I) complexes (VI) with other electrophiles such as α,β-unsaturated carbonyl and nitrile compounds were not successful.

Experimental

Reagents

t-Butyl isocyanide was prepared by Ugi's procedure [8]. 2-Furamide was prepared by ammonolysis of 2-furoic acid [9]. *N*-Trimethylsilylacetamide and *N*-trimethylsilylbenzamide were prepared by a reported method [5]. Cu$_2$O was a commercial reagent and was dried in vacuum prior to use. All other reagents and solvents were commercial reagents and were purified by conventional methods and distilled under nitrogen.

Reaction of acetamide with Cu$_2$O and t-butyl isocyanide

A mixture of 1.77 g (30 mmol) of acetamide, 2.43 g (17 mmol) of Cu$_2$O and

* Alkaline hydrolysis of IX gave RCONHR' and t-C$_4$H$_9$NHCHO, while alkaline hydrolysis of X gave RCONH$_2$ and (t-C$_4$H$_9$)(R')NCHO.

13.2 ml (120 mmol) of t-butyl isocyanide in 30 ml of benzene was refluxed for 5 h under a nitrogen atmosphere, removing the water produced by azeotropic distillation. The mixture was filtered and the filtrate was evaporated. The residual white solid was recrystallized from benzene/hexane (1/2) to give 7.17 g (83%) of copper(I) complex VIb, which gradually decomposed on exposure to air. The structure of VIb was convincingly confirmed by elemental analysis, IR and NMR spectra, and a chemical transformation.

VIb: Anal. Found: C, 54.84; H, 8.08; N, 15.50. $C_{17}H_{31}N_4OCu$ calc.: C, 55.04; H, 8.42; N, 15.10%. IR (KBr disk) 2150, 1630, 1590, 1362, 1295 cm^{-1}; NMR (C_6D_6 with TMS): τ (ppm) 0.74 (s, 1H), 7.52 (s, 3H), 8.22 (s, 18H), 8.55 (s, 9H).

Copper(I) complex VIb (1.85 g, 5 mmol) was added to one equivalent of dry HCl in ethanol (5 ml) at room temperature and stirred for 30 min. Ten ml of ether were added to the reaction mixture. Filtration was followed on distillation of the filtrate to give *N*-(*N'*-t-butyliminoformyl)acetamide (b.p. 115°C/1 mmHg) in 43% yield [Anal. Found: C, 59.01; H, 9.67; N, 19.98. $C_7H_{14}N_2O$ calcd.: C, 59.12; H, 9.92; N, 19.70%. IR (neat): 1690, 1650 cm^{-1}; NMR (CCl_4 with TMS): τ (ppm) 1.05 (s, 1H), 1.75 (s, 1H), 7.80 (s, 3H), 8.65 (s, 9H)]. Mass spectrum: *m/e* 142 (M^+).

Copper(I) complex VIa was prepared in similar fashion by the reaction of formamide with Cu_2O and t-butyl isocyanide.

VIa: Anal. Found: C, 53.88; H, 8.33; N, 15.92. $C_{16}H_{29}N_4OCu$ calcd.: C, 53,83; H, 8.19; N, 15.70%. IR (KBr disk): 2150, 1595, 1270, 1200 cm^{-1}; NMR (C_6D_6 with TMS); τ (ppm) 0.70 (s, 1H), 1.70 (s, 1H), 8.50 (s, 9H), 8.90 (s, 18H).

Reaction of benzamide with Cu_2O and t-butyl isocyanide

A mixture of 3.63 g (30 mmol) of benzamide, 2.43 g (17 mmol) of Cu_2O and 13.2 ml (120 mmol) of t-butyl isocyanide in 30 ml of benzene was refluxed vigorously for 15 h, removing the water produced by azeotropic distillation. The reaction mixture was filtered and the filtrate was distilled in vacuo to remove benzene. The residual white solid was recrystallized from benzene to afford copper(I) complex VIc in 80% yield.

VIc: Anal. Found: C, 60.42; H, 7.55; N, 12.90. $C_{22}H_{33}N_4OCu$ calcd.: C, 61.01; H, 7.68; N, 12.94%. IR (KBr disk): 2150, 1640, 1590, 1550, 1200 cm^{-1}; NMR (CD_3CN with TMS): τ (ppm) 1.22 (s, 1H), 1.70~1.95 (m, 2H). 2.43~2.80 (m, 3H), 1.48 (s, 18H), 1.30 (s, 9H).

Reaction of N-trimethylsilylbenzamide with Cu_2O and t-butyl isocyanide

A mixture of 5.79 g (30 mmol) of *N*-trimethylsilylbenzamide, 2.43 g (17 mmol) of Cu_2O and 13.2 ml (120 mmol) of t-butyl isocyanide was refluxed for 9 h under nitrogen. After insoluble materials were removed by filtration, and excess t-butyl isocyanide was distilled in vacuo, the residual white solid was recrystallized from benzene to given an 83% yield of copper(I) complex VIc.

Similarly, copper(I) complex VIb was prepared by the reaction of *N*-trimethylsilylacetamide with Cu_2O and t-butyl isocyanide.

General procedure for alkylation of copper(I) complexes VIa and VIb

The general procedure for alkylation of copper(I) complex VIa or VIb is

exemplified by the reaction of VIb with n-propyl bromide. A mixture of 1.1 g (3 mmol) of VIb, 0.36 ml (4 mmol) of n-propyl bromide and 66 μl (0.6 mmol) of t-butyl isocyanide in 5 ml of benzene was stirred at room temperature for 4 h under nitrogen. As the reaction proceeded, copper(I) bromide—t-butyl isocyanide complex was gradually precipitated. The reaction mixture was triturated with ether and filtered to remove the copper(I) bromide—t-butyl isocyanide complex. The filtrate was concentrated and distilled to give crude *N*-propyl-*N*-(*N'*-t-butyliminoformyl)acetamide (IXb-3, b.p. 95—110°C/2 mmHg) in 83% yield. An analytically pure sample of IXb-3 was obtained by preparative GlC.

IXb-3: Anal. Found: C, 65.08; H, 10.68; N, 15.11%. $C_{10}H_{20}N_2O$ calcd.: C, 65.17; H, 10.94; N, 15.20%. IR (neat): 1630 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.70 (br, 1H), 6.30 (t, 2H), 7.81 (s, 3H), 8.3—8.9 (m, 2H), 8.75 (s, 9H), 9.2 (t, 3H).

Other combinations of copper(I) complexes VIa and VIb and alkylating agents such as alkyl halide, alkyl tosylate and triethyloxonium tetrafluoroborate were carried out according to the procedure mentioned above.

IXa-1: Anal. Found: C, 58.97; H, 9.80; N, 19.52. $C_7H_{14}N_2O$ calcd.: C, 59.12; H, 9.92; N, 19.70%. IR (neat): 1710, 1650 cm^{-1}; NMR ($CDCl_3$ with TMS); τ (ppm) 1.40 (s, 1H), 2.10 (s, 1H), 6.83 (s, 3H), 9.10 (s, 9H).

IXa-2: Anal. Found: C, 63.31; H, 10.43; N, 16.18. $C_9H_{18}N_2O$ calcd.: C, 63.49; H, 10.66; N, 16.46%. IR (neat): 1710, 1650 cm^{-1}; NMR (CCl_4 with TMS): τ (ppm) 1.44 (s, 1H), 2.07 (s, 1H), 6.32 (t, 2H), 8.2—8.7 (m, 2H) 8.81 (s, 9H), 9.12 (t, 3H).

IXb-1: Anal. Found: C, 61.38; H, 10.11; N, 17.69. $C_8H_{16}N_2O$ calcd.: C, 61.50; H, 10.32; N, 17.93%. IR (neat): 1635 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 2.2—2.7 (br, 1H), 6.85 (s, 3H), 7.80 (s, 3H), 8.80 (s, 9H).

IXb-2: Anal. Found: C, 63.58; H, 10.52; N, 16.68. $C_9H_{18}N_2O$ calcd.: C, 63.49; H, 10.66; N, 16.46%. IR (neat): 1630 cm^{-1}; NMR (CCl_4 with TMS): τ (ppm) 1.80 (br, 1H), 6.24 (q, 2H), 7.82 (s, 3H), 8.81 (s, 9H), 8.93 (t, 3H).

IXb-4: Anal. Found: C, 66.68; H, 11.30; N, 14.28. $C_{11}H_{22}N_2O$ calcd.: C, 66.62; H, 11.18; N, 14.13%. IR (neat): 1680, 1640 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.65 (br, 1H), 6.30 (t, 2H), 7.82 (s, 3H), 8.25—9.00 (m, 4H), 8.80 (s, 9H), 9.19 (t, 3H).

IXb-5: Anal. Found: C, 70.79; H, 11.64; N, 10.71. $C_{15}H_{30}N_2O$ calcd.: C, 70.81; H, 11.89; N, 11.01%. IR (neat): 1630 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.80 (br, 1H), 6.31 (t, 2H), 7.72 (s, 3H), 8.00—9.30 (m, 15H), 8.72 (s, 9H).

General procedure for alkylation of copper(I) complexes VIc and VId

The general procedure for alkylation of copper(I) complex VIc or VId is exemplified by the reation of VIc with n-propyl bromide. A mixture of 1.3 g (3 mmol) of VIc, 0.36 ml (4 mmol) of n-propyl bromide and 66 μl (0.6 mmol) of t-butyl isocyanide in 5 ml of benzene was stirred at room temperature for 4 h under nitrogen. As the reaction proceeded, copper(I) bromide—t-butyl isocyanide complex was gradually precipitated. The reaction mixture was triturated with ether and filtered. The filtrate was concentrated and distilled to afford *N*-propyl-*N*-(*N'*-t-butyliminoformyl)benzamide (IXc-2, 20% yield, b.p. 120°C/0.6 mmHg) and *N*-(t-butyl-n-propylaminomethylidene)benzamide (Xc-2, 76%

yield, b.p. 200°C/0.6 mmHg). Analytically pure samples of IXc-2 and Xc-2 were obtained by preparative GLC.

IXc-2: Anal. Found: C, 73.01; H, 8.90; N, 11.19. $C_{15}H_{22}N_2O$ calcd.: C, 73.13; H, 9.00; N, 11.37%. IR (neat): 1640 cm^{-1}; NMR (CCl_4 with TMS): τ (ppm) 2.18 (s, 1H), 2.67 (s, 5H), 6.14 (t, 2H), 8.20—8.80 (m, 2H), 8.94 (s, 9H), 9.15 (t, 3H).

Xc-2: Anal. Found: C, 73.00; H, 8.77; N, 11.51. $C_{15}H_{22}N_2O$ calcd.: C, 73.13; H, 9.00; N, 11.37%. IR (neat): 1620, 1560 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.16 (s, 1H), 1.62—2.10 (m, 2H), 2.45—2.90 (m, 3H), 6.30—6.70 (m, 2H), 8.10—8.80 (m, 2H), 8.60 (s, 9H), 9.12 (t, 3H).

Other combinations of copper(I) complex VIc or VId and alkylating agents were carried out according to the procedure mentioned above.

IXc-1: Anal. Found: C, 71.33; H, 8.12; N, 12.59. $C_{13}H_{18}N_2O$ calcd.: C, 71.52; H, 8.31; N, 12.83%. IR (neat): 1635 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 2.20 (s, 1H), 2.65 (s, 5H), 6.80 (s, 3H), 8.92 (s, 9H).

Xc-1: Anal. Found: C, 71.40, H, 8.11; N, 12.55. $C_{13}H_{18}N_2O$ calcd.: C, 71.52; H, 8.31; N, 12.83%. IR (neat): 1638, 1560 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.15 (s, 1H), 1.60—2.00 (m, 2H), 2.45—2.90 (m, 3H), 6.82 (s, 3H), 8.55 (s, 9H).

IXc-3: Anal. Found: C, 73.58; H, 9.01; N, 10.55. $C_{16}H_{24}N_2O$ calcd.: C, 73.80; H, 9.29; N, 10.76%. IR (neat): 1640 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 2.20 (s, 1H), 2.72 (s, 5H), 6.14 (t, 2H), 8.20—8.90 (m, 4H), 8.91 (s, 9H), 9.15 (s, 3H).

Xc-3: Anal. Found: C, 73.85; H, 9.23; N, 10.79. $C_{16}H_{24}N_2O$ calcd.: C, 73.80; H, 9.29; N, 10.76%. IR (neat): 1640, 1560 cm^{-1}; NMR (CCl_4 with TMS): τ (ppm) 1.16 (s, 1H), 1.60—2.00 (m, 2H), 2.43—2.92 (m, 3H), 6.30—6.70 (m, 2H), 8.10—8.80 (m, 4H), 8.62 (s, 9H), 9.12 (t, 3H).

IXd-1: Anal. Found: C, 66.18; H, 8.68; N, 11.98. $C_{13}H_{20}N_2O_2$ calcd: C, 66.06; H, 8.53; N, 11.86%. IR (neat): 1630 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.60 (s, 1H), 2.50—2.60 (m, 1H), 3.02 (d, 1H), 3.55 (dd, 1H), 6.10 (t, 2H), 8.00—8.80 (m, 2H), 8.77 (s, 9H), 9.11 (t, 3H).

Xd-1: Anal. Found: C, 66.24; H, 9.34; N, 11.95. $C_{13}H_{20}N_2O_2$ calcd.: C, 66.06; H, 8.53; N, 11.86%. IR (neat): 1630, 1590, 1550 cm^{-1}; NMR ($CDCl_3$ with TMS): τ (ppm) 1.30 (s, 1H), 2.55—2.70 (m, 1H), 3.05 (d, 1H), 3.20 (dd, 1H), 6.35—6.80 (m, 2H), 8.10—8.80 (m, 2H), 8.70 (s, 9H), 9.07 (t, 3H).

In the alkylation of copper(I) complexes VI, isolation of VI is not needed. Copper(I) complexes VI, which were generated *in situ* in benzene by the reaction of the corresponding carboxamide with Cu_2O and t-butyl isocyanide, were treated with alkylating agents to afford the products IX or X in moderate yields.

References

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