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Kinetic study of the amination of Grignard reagents and cuprates with *O*-methylhydroxylamine

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ABSTRACT: Substituent effects on the rate of electrophilic amination of phenylmagnesium bromides, magnesium diphenylcuprates and catalytic phenylzinc cyanocuprates with *O*-methyhydroxylamine in THF were investigated in a competitive kinetic study. Rate data and Hammett substituent constants are discussed on the basis of proposed mechanisms for the substitution reactions of these organometallics with an electrophilic amino transfer reagent.

KEYWORDS: Grignard reagents; magnesium cuprates; zinc cyanocuprates; electrophilic amination; *O*-methylhydroxylamine; competitive kinetics; Hammett plots

INTRODUCTION

Electrophilic amination of carbanions, i.e. formation of C—N bonds using electrophilic amino transfer reagents, is an important synthetic methodology (Scheme 1).[1,2] Several methods have been reported for the non-symmetric and symmetric synthesis of amines[3–6] and α-aminocarbonyl compounds[7,8] from organometallic compounds and α-metallocarbonyl compounds, respectively. A number of sp^{3}N- or sp^{2}N-containing reagents are used as $NH_2^{\delta+}$ synthons. *O*-Methyl-, *O*-alkyl (or *O*-aryl)-, *O*-sulfonyl-, *O*-acyl- and *O*-phosphinylhydroxylamines (**1**–**5**) and their *N*-substituted derivatives, *N*,*O*-bis(trimethylsilyl)hydroxylamine (**6**), *N*-(tert-butoxycarbonyl)-*O*-tosylhydroxylamine (**7**) and oxaziridines (**8**) react with carbanions directly. *O*-Sulfonyloximes (**9**) produce imines which are hydrolyzed to amines. Amination with azides (**10**), arene diazonium salts (**11**) and diazene dicarboxylates (**12**) form intermediates which require reductive work-up to produce amines.

However, most of the work on the electrophilic amination of carbanions has concentrated on the synthetic potential of the amino transfer reagents. Mechanistic investigations of the amination of carbanions are limited and to the best of our knowledge, the kinetic investigation of the reaction of *N*-aryl derivatives of *O*-pivaloylhydroxylamine (**4**) ($R^1 = t$-Bu) with *N*,*N*-dimethylaniline as a carbon nucleophile is the only published kinetic report.[9] We therefore planned to investigate the kinetics of electrophilic amination of organomagnesium, -lithium, -zinc and -copper reagents and to establish structure–reactivity relationships.

Beak's group had already carried out a series of detailed mechanistic studies of the amination of organolithiums[10,11] with *O*-alkyl- and *O*-arylhydroxylamines **1** and **2** and their *N*-alkyl derivatives, and also the amination of α-lithionitriles[12] with *N*,*N*-dialkyl derivatives of *O*-phosphinylhydroxylamines **5** ($R^1 = C_6H_5$). They found strong evidence favoring (i) the initial deprotonation of *O*-(organyl)hydroxylamines **1** and **2** by organolithiums leading to the formation of *N*-lithiated species **13**, (ii) ruling out a nitrene intermediate and (iii) a mechanism involving an initial complex **14** with the N—OR bond being polarized, thus leading to the transition state **15**, in which the displacement occurs via a concerted S_N2-like mechanism [Scheme 2(a)]. They also provided the first experimental information about the geometry of transition state **15** of neutral sp^{3}N [Scheme 2(b)].

Theoretical calculations by Boche and Wagner,[13] Armstrong *et al.*[14] and McKee[15] indicated that the *N*-lithium derivatives of **1** and **2** ('nitrenoids') actually react with organolithiums. Their results are consistent with the importance of Li bridging in the initial complex **13**. Experimental evidence was also provided[16] for the formation of *N*-lithio and *N*,*N*-dilithio derivatives of **1** to act as amino transfer reagents in the amination of phenyllithium with **1**. Radhakrishna *et al.* considered[17] various mechanisms for the amination of Li enolates of esters with 2,4-dinitrophenylhydroxylamine **2**

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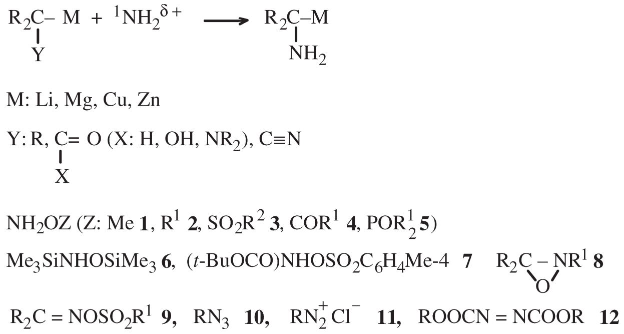
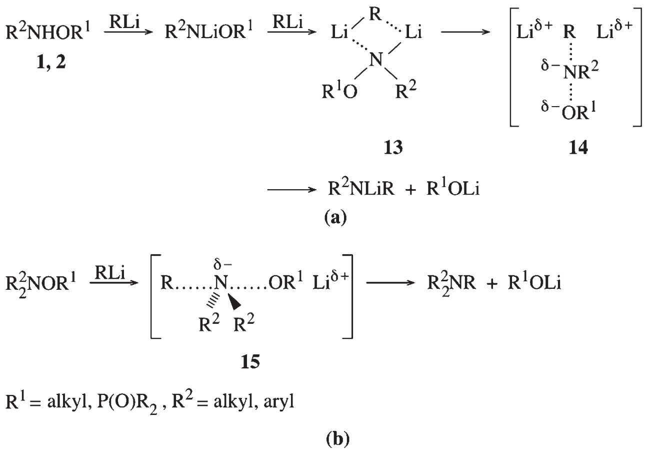


Scheme 1



Scheme 2

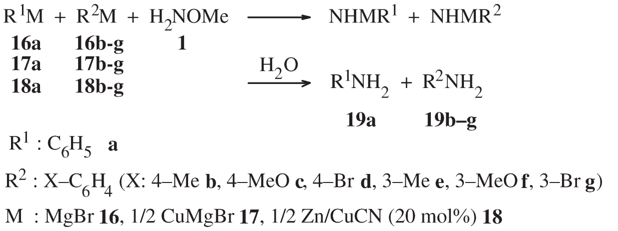
($R^1 = C_6H_3(NO_2)_2$-2,4) and the experiments suggested that the mechanism might involve a direct displacement by the nucleophile on electrophilic nitrogen. For the amination of higher order lithium cuprates with **6**, Casarinl *et al.* offered a mechanism which is in accordance with Beak *et al.*'s approach.[18] The crystal structure of *N*-lithio-*N*-(tert-butoxycarbonyl)-*O*-tosylhydroxylamine (**7**) was reported by Boche *et al.*[19]

Stimulated by our work on the competitive kinetic study of the amination of phenyl carbanions with acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**9**) ($R^1 = C_6H_2Me_3$-2,4,6),[20] we tried to find kinetic support for the polar S_N2-like mechanism for the amination of carbanions with **1**.

In this paper, we report competitive kinetic studies and Hammett correlations for the amination of a series of substituted phenylmagnesium bromides, magnesium-derived organocuprates and zinc-derived cyanocuprates with **1** and we also discuss the mechanistic differences between these three reactions on the basis of the experimental results.

RESULTS AND DISCUSSION

For the purpose of determining structural and metal effects in the electrophilic amination of substituted phenylmetals with **1**, we carried out competitive experiments by reacting a pair of phenyl and 3- or 4-substituted phenylmetal with a limited amount of **1**. As source of the carbanions, we used Grignard reagents, stoichiometric bromomagnesium cuprates and catalytic zinc cyanocuprates (Scheme 3). The reaction temperatures for the amination of these organometallics with **1** were already optimized[16,21,22] as −15 to 0 °C for organolithiums, Grignard reagents and bromomagnesium cuprates and room temperature for CuCN-catalyzed mono- or diorganozinc reagents. Since Beak *et al.*'s results[10] on the reaction of organolithiums provided a reminder of the need for caution in the interpretation of results due to the composition of aggregates, we omitted the amination of organolithiums with **1** for competitive kinetics.



Scheme 3

In preliminary experiments on model amination reactions with the pair of C_6H_5MgBr (**16a**) and 4-MeC_6H_4MgBr (**16b**), the pair of $(C_6H_5)_2CuMgBr$ (**17a**) and $(4\text{-}MeC_6H_4)_2CuMgBr$ (**17b**) and the pair of $(C_6H_5)_2Zn$ (**18a**) and $(4\text{-}MeC_6H_4)_2Zn$ (**18b**) in the presence of CuCN, we optimized the ratio $[R^1M]:[R^2M]:[1]$ as 5:5:1 and 2.5:2.5:1 and 4:4:1, respectively. We also observed that the competitive kinetic method can be used to find the relative reactivities of carbanions in a phenylmetal series since the differences between the reaction rates of R^1M and R^2M are not large and the amounts of R^1NH_2 and R^2NH_2 are much higher than the experimental error.

A survey of literature methods for studying the competitive kinetics of organometallics revealed that competition experiments based on finding the yields of products[23–25] have been more frequently used than those based on finding the relative rates of reagents.[26–33]

Thus, in the reaction of B with equimolar and larger amounts of A^1 and A^2 to provide C^1 and C^2 (first-order reaction in A is assumed):

$$A^1 + B \xrightarrow{k_1} C^1$$

$$A^2 + B \xrightarrow{k_2} C^2$$

The competitive rate ratios are calculated by using Eqn (1):[26,27]

$$\frac{k_2}{k_1} = \frac{\%\ \text{yield of}\ C^2}{\%\ \text{yield of}\ C^1} \qquad (1)$$

or Eqn (2):[22–24]

$$\frac{k_2}{k_1} = \frac{\log([A^2]_t/[A^2]_0)}{\log([A^1]_t/[A^1]_0)} \qquad (2)$$

where $[A]_t$ and $[A]_0$ are the concentrations of the competitive reactants at time t (the end of the reaction or a definite reaction time) and their initial concentrations, respectively.

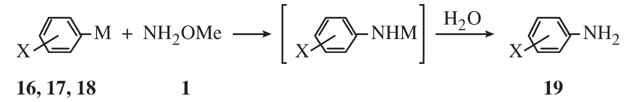
We found that calculation of rate ratios using Eqn (2) at a series of reaction times gives the most reproducible and accurate results in the competitive amination of phenyl carbanions. However, rather than measuring $[R^1M]_t$ and $[R^2M]_t$, we were interested in the competitive formation of product amines R^1NH_2 (**19a**) and R^2NH_2 (**19b–g**) and we expressed Eqn (2) in terms of amine amounts by assuming the simplification $[RM]_t = [RM]_0 - [RNH_2]_t$ and then leading to Eqn (3):

$$\frac{k_2}{k_1} = \frac{\log\{([R^2M]_0 - [R^2NH_2]_t)/[R^2M]_0\}}{\log\{([R^1M]_0 - [R^1NH_2]_t)/[R^1M]_0\}} = \frac{\log\{1 - ([R^2NH_2]_t/[R^2M]_0)\}}{\log\{1 - ([R^1NH_2]_t/[R^1M]_0)\}} \tag{3}$$

In the competitive amination of pairs of C_6H_5M and XC_6H_4M (M: **16, 17** and **18**) with **1**, the amounts of amines were found by GLC analysis. In the case of M = MgBr (**16**) and M = ZnCl/'CuCN' (**18**), carrying out the reactions in the presence of an internal standard, taking 5–7 samples at 4, 5 or 10 min intervals, calculating the amine amounts $(R^1NH_2)_t$ and $[R^2NH_2]_t$ in each sample and taking the average of the k_1/k_1 values, led to a mean deviation of 4–7%, which is in the error limit of GLC analysis. However, in the case of M = 1/2 CuMgBr (**17**), the reproducibility for the quantitative analysis of amines seemed low, possibly owing to the heterogeneous reaction. Therefore, the method used in the competition experiments with acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**9**)[20] was applied, i.e. a number of competition experiments for the same pair of bromomagnesium cuprates were carried out in different reaction flasks and the reactions were quenched at different time points. This method gave more reproducible results. We also used Eqn (1) to calculate competitive rate ratios and found that these values are in accordance with those found by using Eqn (3).

The competitive rate ratios k_2/k_1, i.e. k_X/k_H for the amination of substituted phenylmagnesium bromides (**16**), bromomagnesium cuprates (**17**) and catalytic chlorozinc-cyano cuprates (**18**) with (**1**), are given in Table 1.

Table 1. Competitive rate ratios for the amination of substituted phenylmagnesium bromides **16a–g**, bromomagnesium cuprates **17a–g** and catalytic chlorozinc cyanocuprates **18a–g** with **1**



M: MgBr **16**, 1/2 CuMgBr **17**, 1/2 Zn/CuCN (20 mol%) **18**

X	σ[a]	k_X/k_H[b] M:MgBr[c]	M:1/2 CuMgBr[c]	M:1/2 Zn/'CuCN'[d]
4-Me	−0.17	1.38	3.30	2.54
4-MeO	−0.27	0.40	4.15	0.55
4-Br	0.23	0.57	18	0.54
H	0.00	1.00	1.00	1.00
3-Me	−0.07	1.36	1.31	1.70
3-MeO	0.12	0.92	0.23	1.04
3-Br	0.39	0.45	0.80	0.29

[a] Substituent constants are taken from Ref. 34.
[b] The values were calculated from the competition experiments using Eqn (3). The relative error of the values does not exceed 7%.
[c] Reactions were carried out in THF at −15 °C.
[d] Reactions were carried out in THF at 25 °C.

The plots of log (k_X/k_H) against Hammett substituent constants are given in Fig 1. A reasonably good linear relationship was obtained for each reaction. However the point for the 4-MeO substituent gives a downward deviation for the reactions of Grignard reagents [Fig. 1(A)] and also for zinc cyanocuprates [Fig. 1(C)]. This deviation is attributed to the inadequacy of applying σ constants of the hydrogen bond accepting substituents for reactions carried out in an aprotic solvent.[29,31] In addition, upward deviations with 3-Br and 4-Br substituents were observed for the reaction of the magnesium cuprate [Fig. 1(B)]. Except for these points lying significantly off the linear plots, we obtained values of $\rho = -0.95$ (r = 0.975) for the amination of Grignard reagents, $\rho = -3.28$ ($r = 0.965$) for the amination of magnesium cuprates and $\rho = -1.67$ ($r = 0.978$) for the amination of zinc cyanocuprates. The reaction constants are essentially a measure of the susceptibility of the amination of organometallics to polar effects[35–37] and the linearity of Hammett plots also supports the assumption of first-order reaction in organometallics for the calculation of competitive rate ratios.[26,27]

The signs of the reaction constants are all negative, indicating the development of neutral charge at the reaction centre,[35,36] i.e. the carbon atom of the C–metal bond, leading to higher reaction rates in the aminations of carbanions substituted with electron-donating substituents. However, it is necessary to be cautious in interpreting the magnitudes of the reaction constants, since they can be particularly informative when substituent effects are compared involving reactions which take place with the same mechanism.[35]

The above kinetic data demonstrated that the mechanism proposed for the amination of RLi reagents with **1** can also be proposed for the amination of RMgBr reagents with **1**. Electrons of the carbanion attack the electrophilic nitrogen of *N*-bromomagnesium methoxyamide leading to an S_N2-like transition state (**20**) (Scheme 4). Beak and co-workers established that endocyclic and exocyclic restriction tests support the structure of transition state **14** (Scheme 2) offered for the amination of RLi reagents with **1**.[10–12]

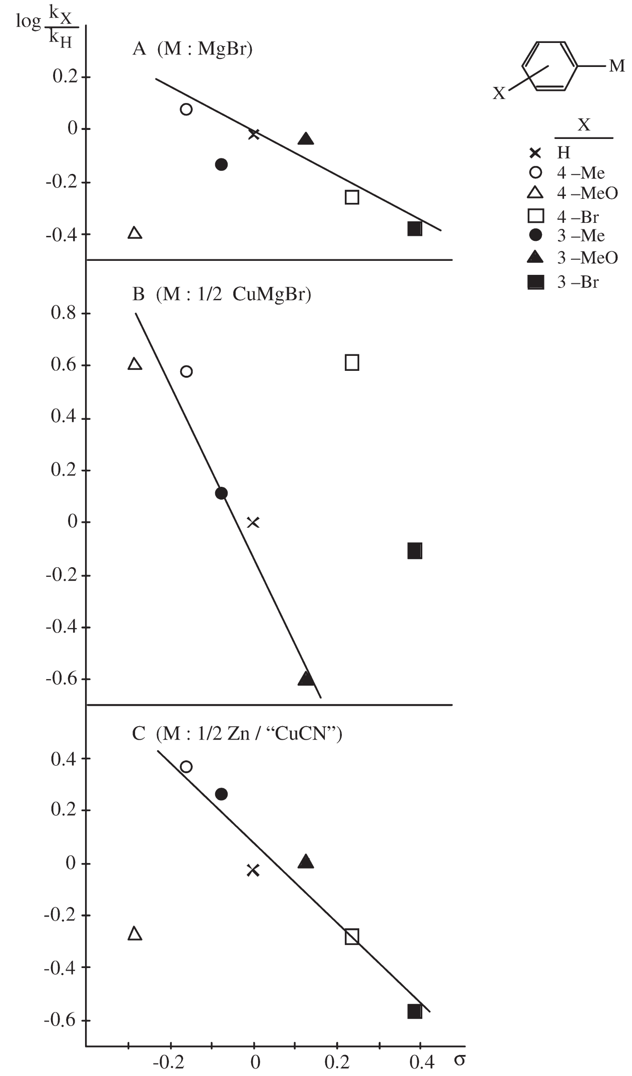
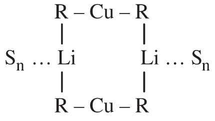


Figure 1. Variations of reactivities with Hammett σ values in the amination reactions of substituted phenylmetals with *O*-methylhydroxylamine **1** in THF. (A) Amination of substituted phenylmagnesium bromides **16a–g** at $-15\,^{\circ}C$; (B) amination of substituted bromomagnesium diphenylcuprates **17a–g** at $-15\,^{\circ}C$; (C) amination of substituted diphenylzincs in the presence of 20 mol% CuCN **18a–g** at $25\,^{\circ}C$

For the amination of organocuprates $R_2CuMgBr$ derived from RMgBr and cyanocuprates RCu(CN)ZnR derived from R_2Zn, an oxidative addition–reductive elimination mechanism can be proposed on the basis of reported substitution mechanisms for cuprates.[38–41] In our work, $R_2CuMgBr$ reagents were obtained by stoichiometric transmetallation of RMgBr reagents with CuI,[39,40,42] and RCu(CN)ZnR reagents were obtained by *in situ* transmetallation of R_2Zn reagents with CuCN catalysis.[43,44] In the amination of $R_2CuMgBr$ and catalytic RCu(CN)ZnR reagents, *N*-magnesium methoxyamide and *N*-zinc methoxyamide, i.e. NHM(OMe) (M = MgBr or ZnR), are expected to form by deprotonation of **1**, and then act as an electrophilic nitrogen source rather than **1**. For the amination of $R_2CuMgBr$ and RCu(CN)ZnR reagents, it seemed less speculative to propose the mechanism involving reactive intermediates in the reactions of cuprates offered by Nakamura and Yoshikai.[45]

Amination of $R_2CuMgBr$ (**17**) or catalytic RCu(CN)ZnR reagents (**18**) can take place by rate-determining addition of the *N*-metallated derivative of **1**, i.e. **1-M**, to the cuprate to give the Cu(III) intermediate **21** and followed by reductive elimination of **21** to the product *N*-metallated amine **19-M** and an RCu compound or the CuCN catalyst (Scheme 5).[38–40,43]

In order to propose a transition state, the contact ion pair structure **22** of lithium organocuprates[45] may be taken into account for the structure of bromomagnesium cuprates $R_2CuMgBr$.[40] Zinc cyanocuprates are tentatively described as RCu(CN)ZnCl; however, the role of Cu—CN bond formation is accepted owing to their higher reactivity than that of zinc organocuprates.[40,41,43] Hence the structure of a lower order lithium cyanocuprate **23**[46,47] may be assumed for the structure of zinc cyanocuprates.



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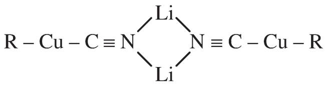
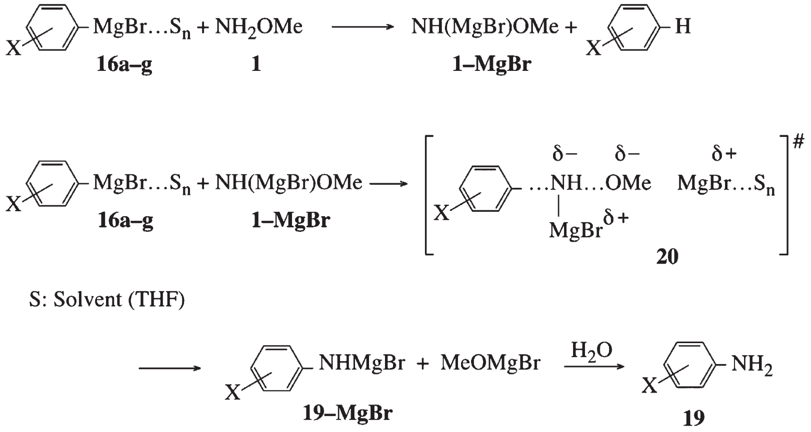


23

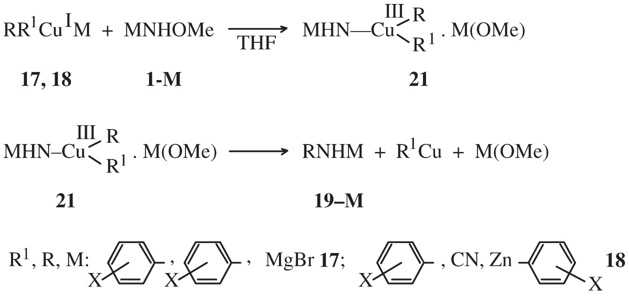
Nakamura and Yoshikai[45] suggested a reaction pathway for the substitution of a carbon electrophile with a lithium organocuprate cluster. In the amination of $R_2Cu(CN)Li_2$ reagents, Casarini *et al.* proposed that removal of the proton by one of the R ligands is concerted with an intramolecular substitution path.[18] Taking these pathways into consideration, we thought that the oxidative addition involves a two-electron nucleophilic attack of the copper atom of **17** and **18** to the electrophilic nitrogen of the *N*-metallated derivatives of **1**, i.e. **1-MgBr** or **1-ZnR**, to give transition states **24** and **25** in which a Cu—N coordination and N–metal bonding take place (Scheme 6). Formation of the C—N bond by reductive elimination gives the product.

The coordination ability of the cyano group with both the Cu(III) and Zn ions leads to the delivery of the R group to the electrophilic nitrogen and formation of CuCN in the catalytic turnover. The difference between the reaction constants for the amination of $R_2CuMgBr$ and RCu(CN)ZnR reagents ($\rho = -3.28$ and -1.67, respectively) does not suggest that the characteristics of the rate-determining transition states are much different for these reactions. However, the susceptibility of the reaction to substituent effects seems larger in the case of $R_2CuMgBr$ reagents. This result appears to be consistent with the difference in the extent of C—N bond formation in the transition states of these reactions. It is known that the ligands on Cu(I) favor oxidative addition if they are σ-donor–π-acceptor ligands.[38] As the σ-donor properties of the ligands R and CN for a soft acid center such as Cu(I) decrease in the order R > CN, the C—N bond formation rate and the dependence of the rate on the substituent effects are expected to be higher in the amination of



Scheme 4

R_2Cu^- anion compared with the $RCu(CN)^-$ anion, which also has one R group less to be aminated. However, we still think that the C—N coupling in the transition states proposed for substitution of cuprates with electrophilic nitrogen need support from other mechanistic studies. The much smaller reaction constant for the amination of RMgBr reagents (−0.95) compared with those for the amination of cuprates possibly reflects the small extent of C—N bond formation in the transition state **20**, although the substituents on the R group are able to interact with the reaction center more easily than they interact in the transition state **21** of the amination of cuprates.



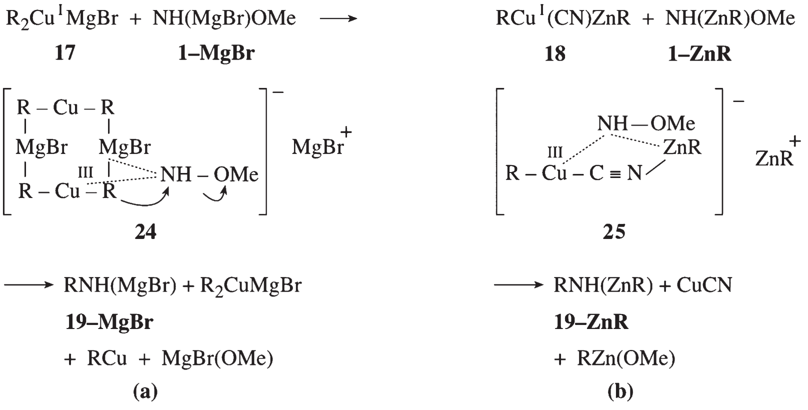
Scheme 5

In conclusion, the above competitive rate data obtained in amination reactions of phenylmagnesium bromides, phenylmagnesium-derived organocuprates and phenylzinc-derived catalytic cyanocuprates with *O*-methylhydroxylamine exhibit linear Hammett plots. The reaction constants of these plots are consistent with the proposed S_N2-type amination mechanisms of these reactions.

This study also provides an example for the kinetic investigation of substituent effects in the substitution reactions of Grignard reagents and stoichiometric or catalytic cuprates with an electrophilic amino transfer substrate. We are currently investigating the mechanisms of the reactions of organometallic compounds with electrophilic nitrogen transfer reagents of different types.

EXPERIMENTAL

All reactions involving air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe–septum cap techniques.[48] GLC analyses were performed on a Unicam 610 gas chromatograph equipped with a flame ionization detector and a DB-1 glass capillary column packed with dimethyl polysiloxane. Quantitative analysis



Scheme 6

was performed using an internal standard technique. THF was distilled from sodium benzophenone dianion under nitrogen immediately before use. All substituted bromobenzenes and bromobenzene and authentic samples of substituted anilines and aniline are commercially available and were purified using literature procedures. Magnesium turnings for Grignard reactions (Fischer) was used without purification. Zinc chloride (Aldrich) was dried under reduced pressure (2 mmHg) at 100 °C for 2h and dissolved in THF prior to use. Copper(I) iodide (Fischer)[49] and copper(I) cyanide[50] (Aldrich) were purified according to the published procedures, dried at 60–90 °C under reduced pressure for 4 and 8 h, respectively, and kept under dry nitrogen for at least 2 months without any noticeable change.

Grignard reagents RMgBr (**16a–g**) were prepared in THF by conventional standard methods and their concentrations were found prior to use by a modified Watson and Eastham method.[51] Bromomagnesium diorganocuprates $R_2CuMgBr$ (**17a–g**) were prepared by addition of 2 mol equiv. of a Grignard reagent to a suspension of 1 mol equiv. of CuI in THF at 0 °C and stirring at that temperature for 15–30 min.[42] Diorganozincs R_2Zn (**18a–g**) were prepared by addition of 2 mol equiv. of a Grignard reagent to a solution of 1 mol equiv. of $ZnCl_2$ in THF at -5 to 0 °C and stirring at that temperature for 15 30 min.[43,44]

O-Methylhydroxylamine was prepared and purified by the method of Hjeds.[52]

The general procedure for the competitive amination of a substituted phenylmetal with phenylmetal was as follows. Into a flame-dried, two-necked, round-bottomed flask equipped with a stirring bar and kept at -15 °C, a substituted phenylmagnesium bromide (**16b–g**) (20 mmol) and phenylmagnesium bromide (**16a**) (20 mmol) were placed with syringes. Internal standard was added. The reaction was initated by rapid addition of **1** (4 mmol in 5 cm^3 of THF). Aliquots (5–7) were withdrawn from the homogeneous solution at 4 or 5 min intervals and hydrolyzed with saturated NH_4Cl solution containing 20% NH_3. The aqueous phase was extracted with diethyl ether and the product mixtures were analyzed by GLC. The competitive amination of a pair of diorganozincs in the presence of CuCN catalyst was carried out by following the same procedure, except that the reaction was carried out at 25 °C. Preparation of **18b–g** (2 mmol) and **18a** (2 mmol) from **16b–g** (2 mmol) and **16a** (2 mmol) using $ZnCl_2$ (2 mmol) was carried out in the same reaction flask; 20 mol% CuCN (0.359 g; 0.4 mmol) was added, the temperature was allowed to rise to 25 °C and the green homogeneous solution was stirred for 15 min before addition of **1** (0.25 mmol). Aliquots were withdrawn at 5 or 10 min intervals. A different procedure was applied for the competitive amination of a pair of bromomagnesium diorganocuprates. Preparation of **17b–g** (1 mmol) and **17a** (1 mmol) from **16b–g** (1 mmol) and **16a** (1 mmol) using CuI (0.5 mmol for each) was carried out separately, and each cuprate was added to the flask kept at -15 °C by means of a cannula. Following the addition of internal standard and **1** (0.2 mmol), the reaction mixture was stirred for an appropriate time (4, 8, 12, ..., 40 or 5, 10, 15, ..., 45 min) and then hydrolyzed.

Acknowledgements

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