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REACTION OF ARYLIMODIMAGNESIUM WITH AROMATIC BIFUNCTIONAL NITRILES: COMPETITION AND/OR COOPERATION OF FUNCTIONAL GROUPS AFFECTED BY ELECTRON-ACCEPTING ABILITY AND LOCATION†

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The reactions of aryliminodimagnesium [ArN(MgBr)$_2$, IDMg] with *p*′-substituted *p*-cyanobenzophenones, 1-cyano-9-fluorenone, *o*-, *m*- and *p*-dicyanobenzenes and *o*-, *m*- and *p*-nitrobenzonitriles were examined, and the relative yields of products were referred to the previous results of electron spin resonance studies. The products of condensation with carbonyl and nitro groups and of addition to cyano groups were formed. From the variations of the yields caused by the molar ratio of the magnesium reagent versus substrates and by the substituents of both reactants, the preferred groups were determined. The groups of *p*- and *m*-substrates are consistent with the position of highest density of free electrons in the anion radicals, whereas those of the *o*-substrates are inconsistent. The consistency indicates competition of functional groups reflecting the relative ability of single electron acceptance from the reagent, whereas the inconsistency is ascribed to cooperation of neighbouring groups for σ-complexation with the Mg atom of the reagent. The categories of competition and cooperation are discussed in relation to fundamental features and general governing factors proposed for the IDMg reactions of monofunctional substrates. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Reactions of aryliminodimagnesium [ArN(MgBr)$_2$, IDMg] with aromatic monofunctional nitro, carbonyl and cyano substrates are controlled by the efficiency of single electron transfer (SET).[1] The distribution of condensation (with NO$_2$ and Ar^{1}CO groups) or addition (to CN group) products [–N(O)=N–Ar, >C=N–Ar and –C(NH$_2$)=N–Ar; normal] and typical radical (dimerization or hydrogen abstraction) products (abnormal) were correlated with the relative electron-accepting ability (EAA) of functional groups (NO$_2$ > CO > CN) regardless of reaction manners. The IDMg reagent (having an N–Mg bond) has a weak electron-donating ability (EDA) in comparison with Grignard reagents (having a C–Mg bond).[2] According to the 'less reactive, more selective' principle, the use of mild IDMg is advantageous for elucidating factors governing the reactions of magnesium reagents.[1] In this study, IDMg was allowed to react with some bifunctional aromatic nitriles having CN and CO, CN and CN, and CN and NO$_2$ groups in an intramolecular competition manner. The relative yields of products, indicating which of two groups is preferred, were consistent or inconsistent with the reported distribution of free electrons in anion radicals of the bifunctional substrates. The reasons are discussed.

RESULTS

Intermolecular competition of two kinds of IDMgs with a benzonitrile and vice versa (Schemes 1a and 1b)

As preliminary experiments, intermolecular competition using IDMgs and benzonitriles having *p*-MeO, *p*-Me and *p*-Cl substituents was carried out. Two kinds of nitriles (or IDMgs) were allowed to react with a kind of IDMg (or nitrile). Substituent effects on EDA (*p*-MeO > *p*-Me > *p*-Cl)

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† Aryliminodimagnesium Reagents, Part XXIX. Part XXVIII; M. Okubo and Y. Omote, *J. Phys. Org. Chem.* **9**, 212 (1996).

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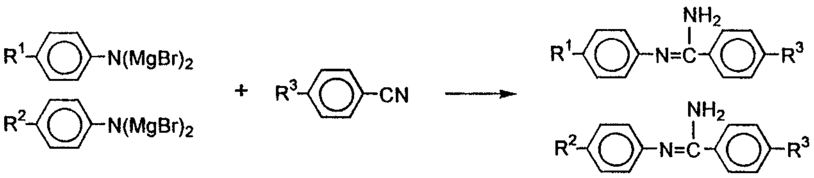
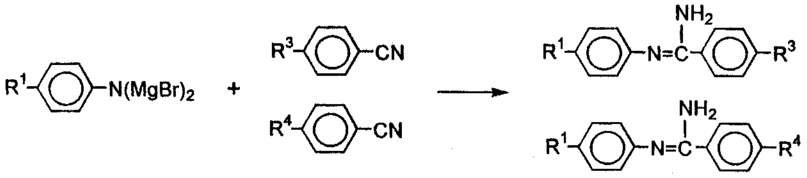


Scheme 1a

Table 1a. Yield ratio of two amidines in the reaction in Scheme 1a

		Difference in EDA (R^1/R^2)		
EAA	EDA	Small ⟷ Large		
Nit (R^3)	Rg	MeO/Me	Me/Cl	MeO/Cl
Weak	MeO	65/35	57/42	67/30
↕	Me	47/17	73/26	53/16
Strong	Cl	63/32	61/30	55/31



Scheme 1b

Table 1b. Yield ratio of two amidines in the reaction in Scheme 1b

		EDA	Weak ⟷ Strong		
		Rg (R^1)	Cl	Me	MeO
	EAA	Nit			
	Small	Me/MeO	46/36	52/46	96/98
Difference in EAA (RR^{3}3/R^4)	↕	Cl/Me	64/10	71/16	96/53
	Large	Cl/MeO	77/13	97/67	99/75

are indicated by the oxidation potentials (E_{ox}) of the IDMg and ArMgBr reagents, and the effects on EAA (*p*-Cl > *p*-Me > *p*-MeO) are indicated by the reduction potentials (E_{red}) of the NO_2 and Ar^{1}CO substrates.[2] At a concentration of 5·0 mmol IDMg in 50 ml of THF, the reactions were carried out at 55 °C for 1 h. Two moles of IDMg (in total) were used in all cases in order to obtain the amidines in sufficient yields for comparison of the effects of substituents, because no effect was observable by the use of 3 mol, leading always to excellent yields.[3c] The yields of the two amidines obtained in the reactions of two kinds of IDMgs with a nitrile are given in Table 1a and yields (total 200%) obtained in the reactions of a substituted IDMg with two kinds of nitriles in Table 1b. No abnormal product was detected.

The data in Table 1a indicate a trend that the nitriles, regardless of their EAA, react preferentially with the IDMg of stronger EDA. The data of Table 1b indicate a similar trend that the magnesium reagents, regardless of their EDA, react preferentially with the nitrile of stronger EAA. The yield variation caused by the EDA of IDMg (Table 1b) seems greater than that caused by the EAA of the nitrile (Table 1a). Even with dilution using 200 ml of THF in some combinations, no lowering of the yields was observed, which suggests tight binding of reagent and substrate.

The relation of terms for SET [higher efficiency ↔ smaller ΔE (difference[2] between the potentials: $\Delta E = E_{ox} - E_{red}$) ↔ stronger EDA and/or EAA] is noted. The non-competition reaction of nitriles was characterized by the low SET efficiency,[3] i.e. weaker EDA and EAA. The character [start of reaction from formation of tight σ-complex (coordination of N atom of CN group to the $\delta+$ charged Mg

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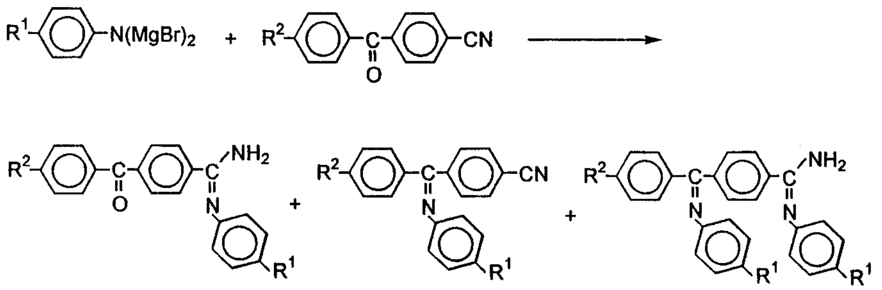

1 **2** **3**

Scheme 2

Table 2. Yields of products **1**–**3** in the reaction in Scheme 2[a]

Run No.	R^1	R^2	Molar ratio	Temperature (°C)	Yield/% **1**	Yield/% **2**	Yield/% **3**	Recovery (%)	Hydrolysis (%)
1	MeO	MeO	2·5	55	Trace	38	58	—	—
2	MeO	MeO	2·5	r.t.	Trace	58	19	4	—
3	Me	MeO	2·5	55	—	38	55	—	—
4	Me	MeO	2·5	r.t.	6	41	Trace	38	—
5	Me	MeO	1·0	55	—	—	—	92	—
6	Cl	Meo	2·5	55	Trace	33	54	—	—
7	Cl	MeO	2·5	r.t.	Trace	—	—	97	—
8	MeO	Me	2·5	55	—	32	54	—	6
9	MeO	Me	2·5	r.t.	16	56	13	13	—
10	MeO	Me	2·0	55	4	9	72	10	—
11	Me	Me	2·5	55	—	36	62	—	—
12	Me	Me	2·5	r.t.	Trace	65	15	—	—
13	Ne	Ne	2·0	55	—	42	56	—	—
14	Cl	Me	2·5	55	—	52	47	—	—
15	Cl	Me	2·5	r.t.	Trace	Trace	Trace	78	—
16	MeO	Cl	2·5	55	Trace	14	72	—	9
17	MeO	Cl	2·5	r.t.	—	30	18	41	10
18	Cl	Cl	2·5	55	—	39	52	—	—
19	Cl	Cl	2·5	r.t.	—	—	—	94	—

[a] Reaction mixture were stirred for 3 h in THF. E_{red} of substrate, R^2=MeO − 1·646 V: R^2=Me − 1·629 V: R^2=Cl − 1·552 V.

atom, as governing step) followed by SET inside the complex[3]] is supported by the trends given above, and will be referred to in the following discussion.

Intramolecular competition and/or cooperation of cyano, carbonyl and nitro groups

Some IDMg reactions with bifunctional nitro and carbonyl compounds have been examined previously. The two NO_2 groups of dinitrobenzenes compete and lead mainly to self-decomposition via vigorous SET.[4] The NO_2 and CO groups of *p*-nitrobenzophenone compete, and the former group of stronger EAA is preferred.[4] The involvement of SET is supported by comparison with previous ESR results: the anion radicals of *m*- and *p*-nitroacetophenones[5] and *o*-, *m*- and *p*-nitrobenzophenones[6] have the highest free electron (spin) density on the NO_2 groups. Diphenyl diketone (benzil) reacts via the generation of the anion radical of an Mg chelate (very tight σ-complex),[7,8] implying that two CO groups cooperate. It should be noted that two groups compete or cooperate depending on their relative EAA and location.

The following discussion on the features of IDMg reactions with bifunctional substrates having at least one CN group will be based on the reported result[5] that the anion radicals of *m*-and *p*-cyanoacetophenones have the highest spin density on the CO group. Undoubtedly from all the ESR results cited,[5,6] the spin density in anion radicals of nitrobenzonitriles, although it is not reported, must be highest on the NO_2 group.

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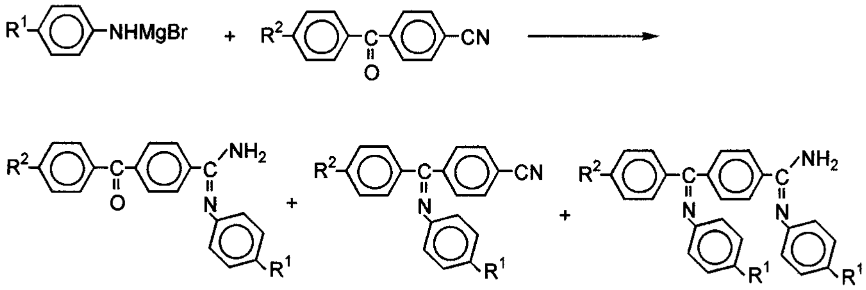


1 **2** **3**

Scheme 3

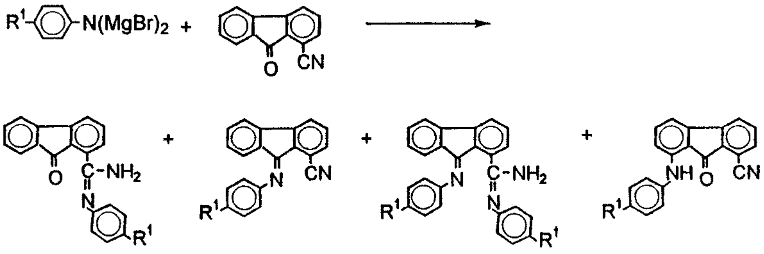
Table 3. Yields of products in the reaction in Scheme 3

Run No.	R^1	R^2	Temperature (°C)	Yield (%) **1**	**2**	**3**	Recovery (%)
1	Me	MeO	55	52	Trace	41	—
2	Me	MeO	r.t.	58	8	—	23
3	Cl	MeO	55	59	8	30	—
4	Me	Me	55	26	Trace	65	—
5	Me	Me	r.t.	53	—	—	44
6	Me	Cl	55	30	—	68	—
7	Me	Cl	r.t.	36	—	—	62

[a] The reaction mixture was stirred for 3 h in THF.

The discussion will also be referred to the known facts and features of general meaning on IDMg reactions:[8–14] determination of relative EAA of substrates the E_{red} values of which are unobservable,[9] basic character of IDMg reaction with diaryl ketones,[10] nuclear substitution and/or decomposition of substrates of strong EAA,[8, 11, 12] general need for aggregate excess moles of the magnesium reagents (IDMg and RMgX) for product formation,[13] action and role of hexamethylphosphoramide (HMPA) (having a very strong coordinating ability) added (in a calculated amount) to IDMg solution[13] and oxidation and decomposition of IDMg molecule in reactions of efficient SET.[14]

On the basis of consistency and/or inconsistency in the position of highest spin density with the most reactive site, a set of two categories of the positional effects of functional



1^{fl} **2**^{fl} **3**^{fl} **4**^{fl}

Scheme 4

Table 4. Yields of products in the reaction in Scheme 4[a]

Run No.	Molar ratio	Temperature (°C)	Yield (%) **1**^{fl}	**2**^{fl}	**3**^{fl}	**4**^{fl}	Recovery (%)
1	2·5	55	31	—	36	21	11
2	2·5	r.t.	—	—	6	—	93
3	1·5	55	—	10	—	—	20
4 (NH)	3·0	55	53	6	18	—	6
5 (NH)	3·0	r.t.	10	—	trace	—	82

[a] The reaction mixture was stirred for 3 h.

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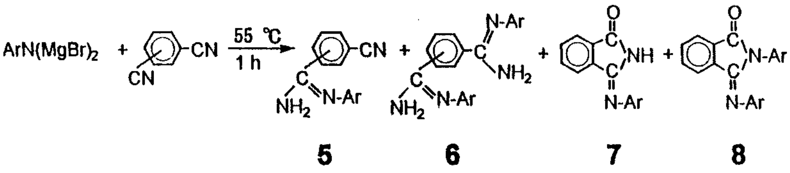
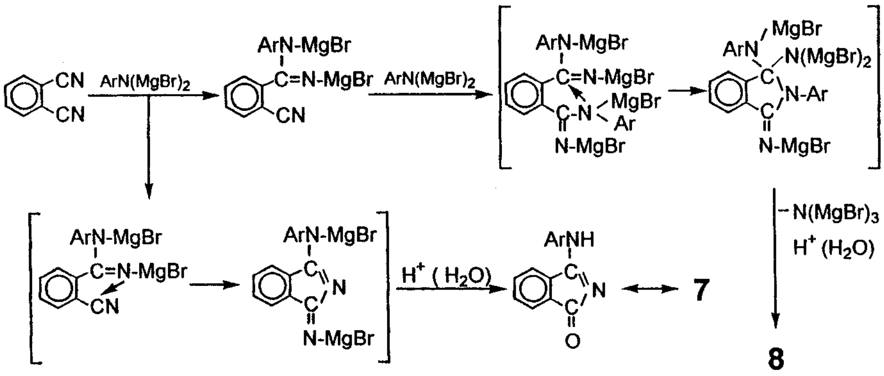


Scheme 5

Table 5. Yields of products in the reaction in Scheme 5.[a]

Run No.	Substrate	Ar=RC$_6$H$_4$ R	Molar ratio	Yield (%) 5	6	7	8	Overall yield (%)
1	*o*-	*p*-Meo	4·0	—	—	—	100	100
2	*o*-	*p*-Me	4·0	—	—	—	92	92
3	*o*-	*p*-Me	2·0	—	—	46	49	95
4	*o*-	*p*-Me	1·0	—	—	64	13	77
5	*o*-	*p*-Cl	4·0	—	—	78	17	95
6	*m*-	*p*-MeO	4·0	59	40	—	—	99
7	*m*-	*p*-MeO	6·0	57	34	—	—	91
8	*m*-	*p*-Me	4·0	76	21	—	—	97
9	*m*-	*p*-Me	2·0	52	41	—	—	93
10	*m*-	*p*-Me	1·0	40	1	—	—	41
11	*m*-	*p*-Cl	4·0	67	26	—	—	93
12	*p*-	*p*-MeO	4·0	44	40	—	—	84
13	*p*-	*p*-MeO	6·0	19	37	—	—	56
14	*p*-	*p*-Me	4·0	54	46	—	—	100
15	*p*-	*p*-Me	2·0	62	27	—	—	89
16	*p*-	*p*-Me	1·0	94	1	—	—	95
17	*p*-	*p*-Cl	4·0	45	40	—	—	85

[a] Concentration of IDMg=200 mmol 1. [b] The reaction mixture was stirred for 1 h at 55 °C in THF. E_{red}: *p*-, −1·802 V; *o*-, −1·881 V; *m*-, unobservable.



Scheme 6

groups originating from fundamental nature of the SET governance in IDMg reactions is proposed in the final section.

CO and CN groups (Schemes 2–4)

p′-R^2-substituted *p*-cyanobenzophenones were allowed to react with *p*-R^{1}C$_6$H$_4$-IDMg (mainly a 2·5 molar amount; R^1=R^2=MeO, Me, Cl) at 55 °C and at room temperature (Scheme 2). The products are an amidine (**1**) formed via IDMg addition to CN group, an anil (**2**) formed via IDMg condensation with CO group and an anil-amidine (**3**) formed via addition–condensation. As Table 2 (runs 1–19) shows, the yields of **1**–**3** vary according to the substituents of the reactants and the reaction conditions.

The effects of molar ratio and temperature are shown in

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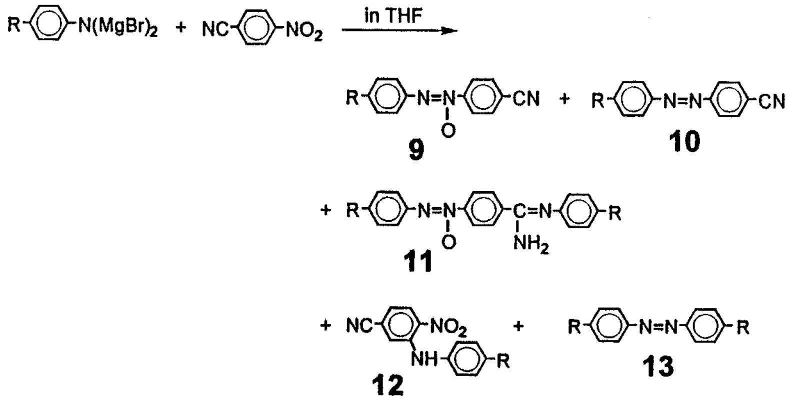

Scheme 7

Table 6. Yields of products in the reaction in Scheme 7

Run No.	R	Molar ratio	HMPA	Temperature (°C)	Yield (%) 9	10	11	12	13	Recovery (%)
1	MeO	2·0	0	0	63	3	9	—	4	4
2	MeO	2·0	0[a]	0	68	9	6	—	6	—
3	MeO	4·0	0	0	38	9	17	—	6	5
4	MeO	3·0	×	r.t.	34	8	—	—	9	—
5	Me	2·0	0	0	75	Trace	11	—	3	—
6	Me	4·0	0	0	54	Trace	14	Trace	1	—
7	Me	3·0	×	r.t.	69	5	—	—	10	—
8	Cl	2·0	0	0	17	Trace	3	10	1	69
9	Cl	4·0	0	0	15	Trace	2	13	Trace	62
10	Cl	2·0	0	55	63	Trace	8	5	2	—
11	Cl	4·0	0	55	54	Trace	12	4	2	—
12	Cl	3·0	×	r.t.	23	19	—	—	5	—

[a] 0 = Present; × = absent.

[b] Equimolar amount of HMPA based on Mg.

runs 3–5, 8–10 and 11–13. Equimolar IDMg leads to no product even at 55 °C, and more than 2 mol are needed for a sufficient yield.[13] With the use of 2·5 mol, the yield of **2** plus **3** predominates over **1** (formed in trace or small amounts) while the formation of **3** is depressed at room temperature. From comparison of the yields of **2** and **3** in runs 1–18 (at 55 °C and room temperature), it is clear that the CO group (more strongly electron-accepting although sterically more crowded than the CN group) is preferred to give **2**. The generated product **2** having CN and arylimino groups must have a weaker EAA than the starting CO–CN substrate (suggested from the reported examples[2b, 9]), and undergoes efficient IDMg addition to the CN group to give **3**. The poor yield of **1** seems slightly improved at room temperature (runs 4 and 9), probably because a lower temperature promotes aggregation of IDMg molecules to favour α-complexation with the CN group.

As shown in Table 2, the relative yields are affected in an ambiguous manner by the substituent of the substrate, but in a clear manner by the substituent of IDMg. The weaker *p*-Cl IDMg[2] (Runs 7, 15 and 19) leads to a high recovery at room temperature, while the stronger *p*-MeO IDMg (runs 8, 16 and 17) gives benzhydrol (diarylmethanol, in a small amount) via hydrogen abstraction from solvent molecules by the ketyl radical, generated via efficient SET due to the apparently small E_{red} (see footnote to Table 2).

Undoubtedly, the condensation with the CO group precedes the addition to the CN group. Exclusive formation of **1** is expected with the use of anilinomagnesium (ArNHMgBr), which is capable of addition to CN group but incapable of condensation with CO group.[3, 10] By the use of 2·5 mol (Table 3, Scheme 3), the yield of **1** was improved in the expected manner, but the formation of **2** and **3** was, unexpectedly, not excluded. The reason is given later.

In the reaction of 1-cyano-9-fluorenone [Scheme 4 ($R^1 = Me$), Table 4], the expected $\mathbf{1}^{fl}$ and $\mathbf{3}^{fl}$ were formed. In addition, product **4**$^{\text{fl}}$ of nuclear substitution at the 8-position was formed, reflecting the efficient SET[8, 11, 12] [due to the apparently small E_{red} (− 1·218V)]. Distinct from the data of Table 2, the higher yield of **1**$^{\text{fl}}$ and no formation of **2**$^{\text{fl}}$ in run 1 (using 2·5 mol of IDMg) clearly implies a preference for the CN group. The reason is discussed later.

Two CN groups (Scheme 5, Table 5)

The IDMg reaction of *p*- and *m*-dicyanobenzenes leads to mono- and bisamidines (**5** and **6**). The *o*-isomer (phthalodinitrile) gives the arylimino derivative of cyclic benzopyrrolidindione (**7**) and its *N*-aryl derivative (**8**). The formation of **7** and **8** (runs 1–5) may be initiated by IDMg addition (single and/or double): cyclization accompanies the release of NH_3 unit and/or hydrolysis of the precursors (Scheme 6). The formation of symmetrical azobenzenes via oxidative coupling of IDMg is negligible, implying that the reactions are mild.

As Table 5 shows, the product yields vary with the molar ratio of the reactants: variations in the yields of **5** and **6** formed from the *p*- and *m*-substrates (E_{red} of the latter is unobservable but may be larger than 2.0 V[3]) are first noted. The data for runs 6, 8, 11, 12, 14 and 17 indicate that 4 mol of IDMg (more than 2 mol of IDMg per one CN group) are usually needed for efficient consumption of CN to give sufficient overall yields. However, the data for run 13 indicate that the use of 6 mol of IDMg causes a lowering of the yield. Therefore, a suitable excess of reagent is needed to assist the formation of the normal product,[13] but too large an excess also causes an efficient SET giving the abnormal product (frequently seen in Grignard and IDMg reactions[10, 14]) via a process other than radical dimerization, hydrogen abstraction from solvent or radical substitution on the aromatic ring (cf. **4**$^{\text{fl}}$). Most probably, the abnormal product is an aromatic hydrocarbon formed via removal of an anion (CN^-, X^- or NO_2^-) from the substrate's anion radical (see Wittig reaction) to leave a neutral hydrocarbon radical abstracting hydrogen from the solvent: the lower boiling hydrocarbon is lost on treatment of mixture. The term 'abnormal' means the product coming from one of the pair of substrate and reagent.

Among structural effects of the reagent and substrate, exclusive formation of **8** from the *o*-substrate and the *p*-MeO and *p*-Me IDMg (runs 1 and 2) is notable (see later discussion). The behaviours of the *p*- and *o*-substrates towards *p*-$MeC_6H_4NHMgBr$ (4 mol) are distinct from those towards IDMg. The *p*-substrate gives the double addition product **6** almost quantitatively (99%, with 1% of **5**), implying that ArNHMgBr of stronger EDA is preferable to IDMg.[2a] The *o*-substrate gave **7** and **8** in lower and comparable yields (42% and 46%), implying that, in comparison with IDMg, ArNHMgBr is less favourable for aggregation (and σ-complexation)[13] because of the half equivalent of the Mg atom.

In free anion radicals of benzonitrile and *o*-, *m*- and *p*-dicyanobenzenes, ring carbon atoms have slightly higher spin densities than the CN group.[5] This is not related to the detailed distribution of products, but may represent the weak EAA of the CN group responsible for the notably mild characters of the reactions in Scheme 1[3] and also Scheme 5.

NO_2 and CN groups; effect of added HMPA (Scheme 7)

p-Dinitrobenzene has a small negative E_{red} (− 1·003 V) and gives (via a too efficient SET) unidentifiable black materials in large amounts and the expected bisazoxy and bisazo products in poor yields.[4, 14] However, in spite of the apparently much smaller E_{red} (− 0·886 V), the NO_2 group of *p*-nitrobenzonitrile reacts efficiently to give the expected products in fair yields (probably the CN group is σ-complexed with IDMg, changing the electron distribution of the anion radical): cyanoazoxy (**9**; condensation), cyanoazo (**10**; condensation–deoxygenation), amidinoazoxy (**11**; condensation–addition), 3-anilino (**12**; nuclear substitution) and symmetrical azo (**13**; oxidative coupling[14]) products. Owing to interest in the physical properties of *p*′-alkoxy-*p*-cyanoazoxybenzene,[15] improvement in the synthesis of **9** by using HMPA was examined.

By addition of HMPA (2 mol based on Mg) to IDMg solution in THF, the reaction with nitrobenzenes of strong EAA was modified. Although the coordination of HMPA must cause elevation of the HOMO level of IDMg to make the SET much more efficient, the yield of the normal condensation product was improved.[13] Therefore, it is proposed that, by exchange of two THF ligands on Mg with HMPA, its 3d-orbitals must facilitate an electronic field feasible for the later step succeeding SET, i.e. transfer of radicals. Therefore, the method was applied to the reaction with the *p*-NO_2–CN substrate, the yields in the presence and absence of HMPA being given in Table 6 (runs 1–12). By comparison of the yields in runs 1 and 2 with those in run 4, the yields in run 5 with those in run 7 and the yields in runs 10 and 11 with those in run 12, it is found that, in the presence of HMPA, the yields of **9** and **11** (normal products) are considerably and slightly increased, respectively, and the yields of **10** and **13** are slightly decreased.

In the reactions with the *o*-substrate ($E_{\text{rerd}} = - 0{\cdot}994$ V), the azoxy compound corresponding to **9** is the major product (32–50% yields) in the absence of HMPA. Even in the presence of HMPA, the yields are only slightly improved (5–8%); the reason for the difference from the case of *p*-substrate is discussed in the next section.

SURVEY OF POSITIONAL EFFECTS

The positional effects of functional groups observed in the reactions in Schemes 2–5 and 7, are surveyed below.

The IDMg reaction in Scheme 2 with the *p*-CO–CN substrate takes place predominantly at the CO group, reflecting its stronger EAA compared with the CN group. In

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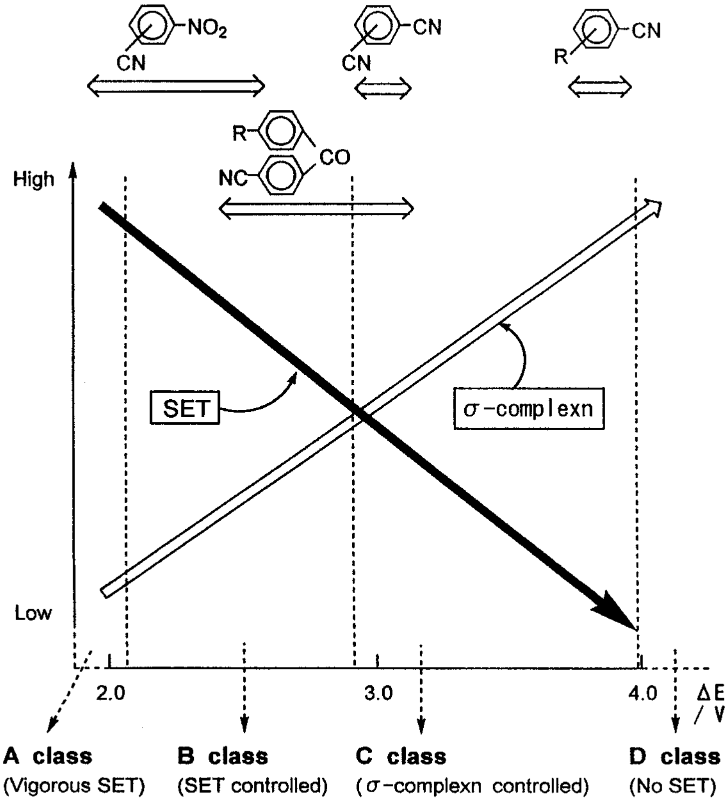

Figure 1. Illustration: relative degree of participation of efficiency of SET and σ-complexation for IDMg and Grignard reactions with monofunctional substrates. Given bifunctional compounds accompanied by short arrows indicate, for comparison, approximate ΔE values for the present IDMg reactions

the reaction in Scheme 3 using ArNHMgBr, part of it condenses with a CO group. The reagent has a stronger EDA than IDMg,[2] and probably disproportionates via SET induction to generate $ArN(MgBr)_2$ and $ArNH_2$ species: the former species is responsible for the formation of **2** and **3**.

In the reaction in Scheme 4 using a sufficient excess of IDMg, in spite of the apparently smaller E_{red} of the 9-CO–1-CN substrate, addition to the 1-CN group is favoured over condensation with the 9-CO group. The reason for the apparent deviation from the order of relative EAA of groups (see Scheme 2) is as follows. With use of the likely oriented lone pairs of electrons, the two groups cooperate to gather IDMg molecules to aggregate and assist σ-complexation with the less crowded CN group. Thus, the σ-complexation must be fairly tight and, accordingly, perturbs the HOMO–LUMO energy levels to make possible the inner-sphere SET. The complexation plays an essential role,[3, 13] i.e. overcomes the weak resonance demand of the CN group (see the small σ_π value[13c]). The energetically less favourable reaction with the CN group (than that with the CO group) becomes predominant.

In the reaction in Scheme 5 of CN–CN substrates, it is notable that the *o*-substrate requires only 2 mol of IDMg (except for the weak *p*-Cl reagent) per CN group for perfect double addition; this is distinct from the reaction with ordinary benzonitrile, requiring 3 mol.[3] The apparently strong EAA seems responsible, but cooperation of neighbouring CN groups similar to the case in Scheme 4 must be more effective. The ArNHMgBr reacts almost perfectly with the *p*-CN–CN substrate but inefficiently with the *o*-CN–CN substrate; a separate dependence on the stronger EDA or on the half equivalent of Mg atoms is noted.

In the IDMg reactions in Scheme 7 with the NO_2–CN substrates, the NO_2 group predominates over the CN group not only at *p*- but also at *o*-positions, i.e. both depend simply on the relative EAA: this arises from the great difference in the EAA of the groups. By comparison with the known effect of added HMPA,[13] the reaction with the *p*-substrate is modified as expected but, unexpectedly, the reaction with the *o*-isomer is poorly modified. The Mg atom of IDMg, reacting with the NO_2 group, is tightly flanked by bulky molecules of HMPA: the 3d-orbitals must be crowded with the *o*-CN group, and may be in an orientation less available for radical transfer.

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Table 7. Melting points and ^{1}H NMR data for products

Product No.[a]	M.p. (°C)	δ (ppm) in CDCl$_3$
$\mathbf{1}^{\mathrm{MeO}}_{\mathrm{MeO}}$	177·0–178·9	7·89–7·62 (4H, m, ArH), 7·20 (1H, d, ArH), 7·01–6·60 (7H, m, ArH), 4·65 (2H, s), 3·89 (6H, d)
$\mathbf{1}^{\mathrm{MeO}}_{\mathrm{Me}}$	150·0–151·8	8·01–7·80 (6H, M, ArH), 7·20 (2H, d, ArH), 6·99–6·89 (4H, M, ArH), 4·90 (2H, s), 3·90 (3H, s), 2·35 (3H, s)
$\mathbf{1}^{\mathrm{MeO}}_{\mathrm{Cl}}$	190·0–193·0	7·95, 7·35 (4H, ABq,*J*=8·79 Hz), 7·85 (4H, d, ArH), 7·01–6·94 (4H, m, ArH), 4·91 (2H, s), 3·90 (3H, s)
$\mathbf{1}^{\mathrm{Me}}_{\mathrm{MeO}}$	Oil	8·11 (2H, s), 7·76–7·63 (3H, m, ArH), 7·54 (1H, d, ArH), 7·28–6·60 (8H, m, ArH), 3·76 (3H, s), 2·44 (3H, s)
$\mathbf{1}^{\mathrm{Me}}_{\mathrm{Me}}$	150·0–151·8	7·96–7·68 (6H, m, ArH), 7·29–7·15 (4H, m, ArH), 6·87 (2H, d, ArH), 4·98 (2H, s), 2·44 (3H, s)
$\mathbf{1}^{\mathrm{Me}}_{\mathrm{Cl}}$	190·0–193·0	7·95–7·82 (4H, m, ArH), 7·70 (2H, d, ArH), 7·31 (4H, m, ArH), 6·95 (2H, d, ArH), 3·66 (2H, s), 2·45 (3H, s)
$\mathbf{1}^{\mathrm{Cl}}_{\mathrm{Me}}$	155·0–156·9	8·00 (2H, m, ArH), 7·82–7·74 (4H, m, ArH), 7·50 (2H, m, ArH), 7·18 (2H, m, ArH), 6·92 (2H, d, ArH), 4·91 (2H, s), 2·35 (3H, s)
$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{MeO}}$	128·5–130·0	7·84–7·56 (4H, m, ArH), 7·25 (1H, d, ArH), 7·03–6·57 (7H, m, ArH), 3·85 (6H, q)
$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{Me}}$	164·0–165·0	7·84–7·54 (4H, m, ArH), 7·25–6·53 (8H, m, ArH), 3·90 (3H, t), 2·20 (3H, d)
$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{Cl}}$	124·8–126·5	7·85–7·64 (4H, m, ArH), 7·23–6·56 (8H, m, ArH), 3·80 (3H, d)
$\mathbf{2}^{\mathrm{Me}}_{\mathrm{MeO}}$	146·0–147·3	7·85–6·56 (8H, m, ArH), 6·71–6·60 (4H, m, ArH), 3·75 (3H, d), 2·41 (3H, d)
$\mathbf{2}^{\mathrm{Me}}_{\mathrm{Me}}$	164·0–165·0	7·84–7·54 (3H, m, ArH), 7·27–6·89 (6H, m, ArH), 6·62 (3H, m, ArH), 2·41 (6H, d)
$\mathbf{2}^{\mathrm{Me}}_{\mathrm{Cl}}$	124·8–126·5	7·58–7·54 (4H, m, ArH), 7·25–7·10 (5H, m, ArH), 7·96 (1H, d, ArH), 6·60 (2H, m, ArH), 2·34 (3H, d)
$\mathbf{2}^{\mathrm{Cl}}_{\mathrm{Meo}}$	167·0–169·0	7·87–7·22 (8H, m, ArH), 7·06 (1H, d, ArH), 6·75–6·58 (3H, m, ArH), 3·76 (3H, d)
$\mathbf{2}^{\mathrm{Cl}}_{\mathrm{Cl}}$	177·0–178·3	7·84–7·02 (12H, m, ArH)
$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{MeO}}$	Oil	7·84–7·64 (4H, m, ArH), 7·20 (2H, d, ArH), 7·05 (1H, d, ArH), 6·91–6·88 (5H, m, ArH), 6·78 (1H, d, ArH), 6·71 (1H, s, ArH), 6·67 (2H, s, ArH), 3·80 (9H, q)
$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{Me}}$	153·0–154·5	7·93–7·64 (4H, m, ArH), 7·21–6·58 (12H, m, ArH), 4·84 (2H, s), 3·89 (3H, d), 2·30 (6H, t)
$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{Cl}}$	176·0–177·3	7·85–7·64 (3H, m, ArH), 7·33–6·61 (9H, m, ArH), 4·87 (2H, s), 3·38 (3H, d)
$\mathbf{3}^{\mathrm{Me}}_{\mathrm{MeO}}$	149·8–151·6	7·83–7·56 (12H, m, ArH), 7·18–6·65 (4H, m, ArH), 4·92 (2H, s), 3·76 (6H, t), 2·38 (3H, d)
$\mathbf{3}^{\mathrm{Me}}_{\mathrm{Me}}$	153·0–154·5	7·91–7·76 (3H, m, ArH), 7·61 (1H, d, ArH), 7·21–6·85 (10H, m, ArH), 6·63 (2H, m, ArH), 4·89 (2H, s), 2·33 (9H, t)
$\mathbf{3}^{\mathrm{Me}}_{\mathrm{Cl}}$	176·0–177·3	7·90–7·70 (3H, m, ArH), 7·60 (1H, d, ArH), 7·34–6·87 (10H, m, ArH), 6·65 (2H, m, ArH), 4·90 (2H, s), 2·40 (3H, d)
$\mathbf{3}^{\mathrm{Cl}}_{\mathrm{MeO}}$	159·8–160·4	7·88–7·64 (4H, m, ArH), 7·38–6·91 (8H, m, ArH), 6·74–6·65 (4H, m, ArH), 4·85 (2H, s), 3·80 (6H, q)
$\mathbf{3}^{\mathrm{Cl}}_{\mathrm{Me}}$	151·0–152·0	7·98–6·84 (14H, m, ArH), 6·62 (2H, d, ArH), 4·83 (2H, s), 2·30 (6H, t)
$\mathbf{3}^{\mathrm{Cl}}_{\mathrm{Cl}}$	181·0–183·5	7·92–7·65 (4H, m, ArH), 7·39–6·89 (10H, m, ArH), 6·63 (2H, d, ArH), 4·84 (2H, s)
$\mathbf{1}^{\mathrm{fl}}_{\mathrm{MeO}}$	182·0–184·1	8·26 (1H, s, ArH), 7·67–7·53 (3H, m, ArH), 7·35–7·26 (5H, m, ArH), 6·95 (2H, s, ArH), 6·46 (2H, s), 3·82 (3H, s)
$\mathbf{1}^{\mathrm{fl}}_{\mathrm{MeO}}$	169·0–169·5	8·30 (1H, s, ArH), 7·67–7·52 (5H, m, ArH), 7·34–7·24 (1H, m, ArH), 7·20 (2H, d, ArH), 6·92 (2H, d, ArH), 6·46 (2H, s), 2·34 (3H, s)
$\mathbf{1}^{\mathrm{fl}}_{\mathrm{Cl}}$	Oil	8·20 (1H, s, ArH), 7·67–7·53 (4H, m, ArH), 7·34–7·30 (4H, m, ArH), 6·95 (2H, d, ArH)
$\mathbf{2}^{\mathrm{fl}}_{\mathrm{MeO}}$	Oil	8·24 (1H, d, ArH), 7·78–7·28 (6H, m, ArH), 7·08–6·93 (4H, m, ArH), 3·81 (3H, d)
$\mathbf{2}^{\mathrm{fl}}_{\mathrm{Me}}$	187·0–189·3	7·81 (1H, d, ArH), 7·66–7·21 (4H, m, ArH), 7·07 & 6·85 (4H, Abq,*J*=7·8 Hz), 6·93 (1H, d, ArH), 2·42 (3H, d)
$\mathbf{2}^{\mathrm{fl}}_{\mathrm{Cl}}$	225·0–227·8	7·82 (1H, d, ArH), 7·67–7·51 (3H, m, ArH), 7·44–7·37 (3H, m, ArH), 7·10–6·95 (3H, m, ArH), 6·81 (1H, d, ArH)
$\mathbf{3}^{\mathrm{fl}}_{\mathrm{MeO}}$	186·0–187·8	8·06 (1H, s, ArH), 7·67–7·31 (4H, m, ArH), 6·97–6·83 (8H, m, ArH), 6·70 (2H, d, ArH), 3·86 (3H, s), 3·76 (3H, s)
$\mathbf{3}^{\mathrm{fl}}_{\mathrm{Me}}$	Oil	8·17 (1H, s, ArH), 7·70–7·50 (3H, m, ArH), 7·37–7·23 (3H, m, ArH), 7·20 (2H, d, ArH), 7·11 (2H, d, ArH), 6·97–6·84 (2H, m, ArH), 6·65 (2H, d, ArH), 2·41 (3H, s), 2·30 (3H, s)
$\mathbf{3}^{\mathrm{fl}}_{\mathrm{Cl}}$	196·0–197·5	7·87 (1H, s, ArH), 7·69–7·49 (3H, m, ArH), 7·41–7·21 (5H, m, ArH), 7·10–6·87 (5H, m, ArH), 6·65 (1H, d, ArH)
$\mathbf{4}^{\mathrm{fl}}_{\mathrm{MeO}}$	129·0–130·0	7·84–7·36 (6H, m, ArH), 7·06–6·93 (4H, m, ArH), 3·87 (3H, s)
$\mathbf{4}^{\mathrm{fl}}_{\mathrm{Me}}$	162·5–163·8	7·84 (1H, d, ArH), 7·68 (1H, d, ArH), 7·57 (1H, d, ArH), 7·24 (1H, d, ArH), 7·10 (1H, d, ArH), 6·95 (1H, m, ArH), 6·63 & 6·53 (4H, Abq,*J*=8·3 Hz), 2·33 (3H, q)
$\mathbf{5}^{m\text{-}}_{\mathrm{MeO}}$	Oil	8·18 (1H, s, ArH), 8·09 (1H, d, ArH), 7·74 (1H, d, ArH), 7·55 (1H, t, ArH), 6·91 (4H, s, ArH), 4·94 (2H, b), 3·81 (3H, s)
$\mathbf{5}^{m\text{-}}_{\mathrm{Me}}$	Oil	8·19 (1H, s, ArH), 8·10 (1H, d, ArH), 7·73 (1H, d, ArH), 7·55 (1H, t, ArH), 7·18, 6·86 (4H, Abq,*J*=8·3 Hz), 4·92 (2H, b), 2·34 (3H, s)
$\mathbf{5}^{m\text{-}}_{\mathrm{Cl}}$	Oil	8·16 (1H, s, ArH), 8·08 (1H, d, ArH), 7·74 (1H, d, ArH), 7·54 (1H, t, ArH), 7·32, 6·89 (4H, Abq,*J*=8·3 Hz), 5·05 (2H, s)
$\mathbf{5}^{p\text{-}}_{\mathrm{MeO}}$	151·5–152·0	8·00, 7·74 (4H, ABq,*J*=8·3 Hz), 6·92 (4H, s, ArH), 4·92 (2H, b), 3·81 (3H, s)
$\mathbf{5}^{p\text{-}}_{\mathrm{Me}}$	144·0–145·5	8·01, 7·75 (4H, ABq,*J*=8·79 Hz), 7·19 & 6·87 (4H, ABq,*J*=8·3 Hz), 4·87 (2H, b), 2·34 (3H, s)
$\mathbf{5}^{p\text{-}}_{\mathrm{Cl}}$	159·0–160·0	7·99, 7·76 (4H, ABq,*J*=8·3 Hz), 7·35 & 6·91 (4H, ABq,*J*=8·79 Hz), 4·89 (2H, b)
$\mathbf{6}^{m\text{-}}_{\mathrm{MeO}}$[b]	175·0–176·5	8·67 (1H, s, ArH), 8·21 (2H, d, ArH), 7·75 (1H, t, ArH), 7·25 & 7·02 (8H, ABq,*J*=8·79 Hz), 3·84 (6H, s), 4·76–2·54 (4H, b)
$\mathbf{6}^{m\text{-}}_{\mathrm{Me}}$	92·0–94·0	8·36 (1H, s, ArH), 7·95 (2H, d, ArH), 7·45 (1H, t, ArH), 7·17, 6·90 (8H, ABq,*J*=8·3 Hz), 5·49–4·51 (4H, b), 2·34 (6H, s)
$\mathbf{6}^{m\text{-}}_{\mathrm{Cl}}$[b]	243·5–244·5	8·39 (1H, s, ArH), 8·04 (2H, d, ArH), 7·53 (1H, t, ArH), 7·34, 6·94 (8H, ABq,*J*=8·3 Hz), 5·33 (4H, b)
$\mathbf{6}^{p}_{\mathrm{MeO}}$[b]	223·0–224·5	8·00 (4H, s, ArH), 6·92 (8H, s, ArH), 6·68–6·14 (4H, b), 3·57 (6H, s)

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Table 7. Continued

Product No.[a]	M.p. (°C)	δ (ppm) in $\mathrm{CDCl_3}$
$\mathbf{6}^{p\text{-}}_{\mathrm{Me}}$	266·0–268·0	7·95 (4H, s, ArH), 7·18 & 6·90 (8H, Abq,J=8·3 Hz), 4·88 (4H, b), 2·34 (6H, s)
$\mathbf{6}^{p\text{-}\,\mathrm{b}}_{\mathrm{Cl}}$	269·0–270·0	7·36 (4H, s, ArH), 7·32, 6·95 (8H, ABq,J=8·3 Hz), 5·40 (4H, b)
$\mathbf{7}^{o\text{-}\,\mathrm{b}}_{\mathrm{Me}}$	181·0–186·0	8·40 (1H, s), 7·85 (1H, d, ArH), 7·78 (1H, d, ArH), 7·55 (2H, t, ArH), 7·22, 7·09 (4H, ABq,J=8·3 Hz), 2·29 (3H, s)
$\mathbf{7}^{o\text{-}}_{\mathrm{Cl}}$	—[c]	7·97 (1H, m, ArH), 7·62 (2H, t, ArH), 7·50 (1H, d, ArH), 7·36 (1H, s), 7·38, 7·02 (4H, ABq,J=8·79 Hz)
$\mathbf{8}^{o\text{-}}_{\mathrm{MeO}}$	80·0–81·5	8·03, 7·67 (4H, ABq,J=8·79 Hz), 6·93 (8H, m, ArH), 3·83 (6H, t)
$\mathbf{8}^{o\text{-}}_{\mathrm{Me}}$	141·1–141·5	8·03 (2H, d, ArH), 7·68 (2H, d, ArH), 7·14, 6·91 (8H, ABq,J=8·3 Hz), 2·36 (6H, s)
$\mathbf{8}^{o\text{-}}_{\mathrm{CL}}$	159·0–160·0	7·99 (2H, t, ArH), 7·63 (2H, m, ArH), 7·37, 7·03 (8H, ABq,J=8·3 Hz)
$\mathbf{9}_{\mathrm{MeO}}$	203·0–204·0	8·34, 7·83 (4H, Abq,J=9·28 Hz), 8·42, 7·02 (4H, ABq,J=8·79 Hz), 3·90 (3H, s)
$\mathbf{9}_{\mathrm{Me}}$	154·0–154·5	8·43, 7·85 (4H, Abq,J=9·28 Hz), 8·17, 7·33 (4H, ABq,J=8·3 Hz), 2·44 (3H, s)
$\mathbf{9}_{\mathrm{Cl}}$	168·0–169·0	8·21, 7·86 (4H, Abq,J=9·27 Hz), 8·43, 7·46 (4H, Abq,J=8·79 Hz)
$\mathbf{10}_{\mathrm{MeO}}$	—[c]	7·93, 7·81 (4H, Abq,J=8·79 Hz), 7·93, 7·01 (4H, Abq,J=8·79 Hz), 3·91 (3H, s)
$\mathbf{11}_{\mathrm{MeO}}$	170·5–171·0	8·39 (4H, d, ArH), 8·04 (2H, d, ArH), 6·99 (2H, d, ArH), 6·95 (4H, s, ArH), 4·92 (2H, b), 3·90 (3H, s), 3·82 (3H, s)
$\mathbf{11}_{\mathrm{Me}}$	167·0–168·0	8·37 (2H, d, ArH), 8·17 (2H, d, ArH), 8·05 (2H, d, ArH), 7·19 (2H, d, ArH), 7·32, 6·92 (4H, Abq,J=8·3 Hz), 4·89 (2H, b), 2·43 (3H, s), 2·35 (3H, s)
$\mathbf{11}_{\mathrm{Cl}}$	185·0–186·0	8·37 (2H, d, ArH), 8·04 (2H, d, ArH), 7·49 (2H, d, ArH), 7·36 (2H, d, ArH), 8·20, 6·96 (4H, ABq,J=8·79 Hz), 4·92 (2H, b)
$\mathbf{12}_{\mathrm{Cl}}$	168·5–169·5	9·41 (1H, s), 8·29 (1H, d, ArH), 7·38 (1H, s, ArH), 7·45, 7·26 (4H, ABq,J=8·79 Hz), 7·03 (1H, d, ArH)

[a] Superscripts indicate substrate; fl = 1-cyano-9-fluorenone, *o*-, *m*-, *p*- = *o*-dicyano-, *m*-dicyano, *p*-dicyanobenzene. Subscripts indicate IDMg and anilinomagnesium (Ar-NHMgBr).

[b] in DMSO-d_6.

[c] Undetermined.

GENERAL DISCUSSION AND CONCLUSION

The $\mathrm{Mg^{2+}}$ ion has a small ionic radius, and thus has a very strong polarizing ability. This is reflected in the relative EDA of magnesium reagents (CMg > NMg > OMg)[2] according to the electronegativities, the known donative effects of lone pair electrons of N and O atoms (combined with carbon atoms) being eliminated. This specific nature of magnesium reagents is responsible for the SET-governed features of reactions in general, i.e. the product distribution depends principally on the combination of EDA and EAA (relative value of ΔE). Moreover, the polarized $\mathrm{N^{-}}$—$\mathrm{Mg^{+}}$ bond allows lone pair electrons of functional groups to coordinate with the Mg atom (i.e. σ-complexation). Participation of this factor causes modification of the reaction.[1]

The concept of relative participation of SET and σ-complexation applied to reactions of IDMg and Grignard reagents with monofunctional substrates (concerning the classification into B and C[1]) is illustrated in Figure 1. As a reference, the apparent ΔE values for bifunctional cases [estimated from E_{ox} and E_{red} (of the whole molecule)] are indicated by short and broad arrows. However, the role of the relative EAA of individual groups of the substrates used is of great significance (see below).

The consistency in the positions of highest spin density with the most reactive site implies that the SET process is involved in the IDMg reaction with bifunctional nitriles. Owing to the mild natures of the CN group and IDMg reagent (in spite of the apparently strong EAA of the whole molecule of bifunctional nitriles), positional effects are observed and categorized into competition and cooperation of functional groups. Scheme numbers are given in square brackets below.

The category of *competition* represents the ordinary contribution of the EAA of individual groups and the EDA of reagents when the groups are located apart from each other. The category includes the reported case of the p-$\mathrm{NO_2}$–CO substrate[4] and the present cases of p-CO–CN [2] and p-$\mathrm{NO_2}$–CN substrates [7]. The EAA–EDA dependence of the behaviour of the p-CO–CN substrate [3] causing suggested disproportionation of ArNHMgBr is an example of the same category. Also included is the behaviour of the p-CN–CN substrate [5] reflecting the EDAs of two reagents,[2] i.e. reacting sluggishly with IDMg and efficiently with ArNHMgBr.

The category of *cooperation* implies an extraordinary participation of σ-complexation, overwhelming the effect of the difference (not so great) in the EAA of two groups located as neighbours. This category, caused by access of reagent, includes the reported case of an α-CO–CO substrate,[7] and the present case of the 9-CO–1-CN substrate [4]. In contrast to the p-CN–CN substrate, the o-isomer [5] is converted easily by IDMg but sluggishly with ArNHMgBr, the behaviour depending on the number of Mg atoms as the accepting site of σ-complexation is of the same category. The behaviour of the o-$\mathrm{NO_2}$–CN substrate [7] is outside this category owing to the too great difference in EAA. This o-substrate undergoes a novel type of steric hindrance causing depression of the HMPA effect.

In conclusion, the concept of the relative participation of SET and σ-complexation[1] can be reasonably applied, with a small modification, to cases of bifunctional substrates. It is

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worthwhile using this concept as a general guiding principle for the study of reactions of magnesium reagents.

EXPERIMENTAL

Materials. *p*-Cyanobenzophenones were prepared by Friedel–Crafts reaction of *p*-cyanobenzoyl chloride and substituted benzenes and/or reaction of *p*-bromobenzophenones with copper cyanide in pyridine. 1-Cyano-9-fluorenone was prepared by Sandmeyer reaction of 1-amino-9-fluorenone[18] using copper cyanide or dehydration of the 1-NH_2CO derivative. Other substituted (*p*-MeO, *p*-Me, *p*-Cl; *o*-, *m*-, *p*-CN; *o*-, *m*-, *p*-NO_2) benzonitriles were commercially available.

Procedures. The preparation of aryl-IDMg[2a] and the reaction with various substrates were carried out in THF according to the reported method. The molar concentrations of IDMg and the molar ratios with substrates are given under Tables 1–6. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with diethyl ether and/or dichloromethane, dried over $MgSO_4$, rotoevaporated and separated by flash chromatography on silica gel (Wako Gel FC-40).

Products. During the course of the chromatographic separation of products of the reactions in Scheme 1, two types of amidines are isolated: a highly soluble one having a lower melting point and simple ^{1}H NMR spectrum, and a poorly soluble one having a higher melting point and more complex spectrum. The latter amidine is completely converted into the former on the treatment with water, and is assigned to a hydrogen-bonded dimeric compound consisting of the (amine-type) amidine and its (imine-type) tautomer. In Table 7, summarizing the melting points and ^{1}H NMR data for amidines, those for the dimeric compounds are omitted.

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