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Azoxy- and Azoferrocenes, and *N*-(Ferrocenylarylmethylene)anilines Formed via Aryliminodimagnesium(IDMg) Procedure. Effect of Ferrocenyl Group on IDMg Reaction and Molecular Structures of Products[1)]

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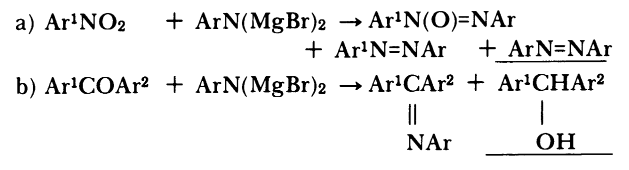
Some unsymmetrical azoxy- and azoferrocenes and *N*-(ferrocenylarylmethylene)anilines were obtained by the reactions of aryliminodimagnesium reagents ($ArN(MgBr)_2$) with nitro- and aroylferrocenes. The types of products were same as those obtained in the similar reactions with nitrobenzenes and benzophenones. The different distribution of products arising from quite mild reactions was understood by the effect of bulky and electron-rich ferrocenyl group which retards the initial coordination and electron transfer processes, in comparison with that of phenyl group. The characteristic molecular structures of the new ferrocene compounds were studied by means of electronic absorption, ^{1}H NMR, and X-ray crystallography. The results were summarized and discussed.

In the electron transfer initiated fifteen reactions of various magnesium reagents with aromatic nitro and carbonyl compounds, the distribution of normal and abnormal (radical) products was recently correlated with the combination of electron-donating and -accepting abilities (EDA and EAA) of reactants,[2)] which represent the efficiency of electron transfer, and was estimated by the difference (ΔE) between the oxidation and reduction potentials of reactants.

Among the fifteen reactions, the deoxygenative condensation of aryliminodimagnesium reagents ($ArN(MgBr)_2$, aryl-IDMg) with substituted nitrobenzenes[3)] and benzophenones[4)] (Schemes 1a and 1b) developed in our laboratory are representative. In the reaction 1a, the ΔE value usually falls into 2.2—2.6, indicating a fairly rapid electron transfer. Since the azoxy product is further deoxygenated to the unsymmetrical azo compound by IDMg in a similar manner,[5)] the formation of azoxy product is favored by the electron-attracting substituents of the reagent and electron-repelling ones of the substrate, whereas that of the two azo products is favored by the reversely substituted reactants. The reaction 1a is "electron transfer controlled."[6)] In the reaction 1b, the larger ΔE value of 2.9—3.1 indicates a mild electron transfer. The electron-repelling substituents of substrate are favorable for σ-complex formation via coordination of carbonyl oxygen to reagent's Mg atom. The reaction 1b is "coordination controlled."[6,7)]

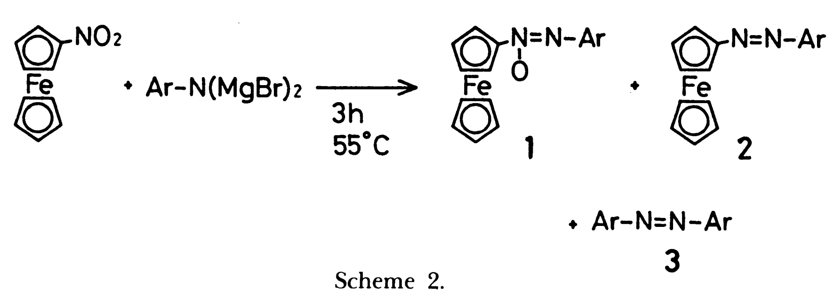


$$\text{a) } Ar^1NO_2 + ArN(MgBr)_2 \rightarrow Ar^1N(O){=}NAr + Ar^1N{=}NAr + \underline{ArN{=}NAr}$$

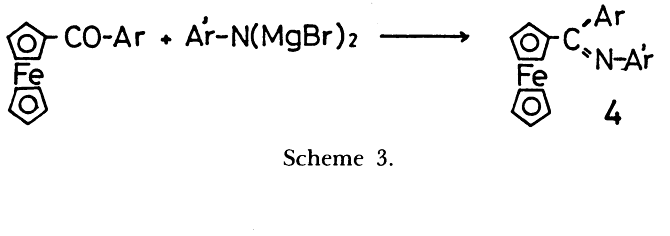
$$\text{b) } Ar^1COAr^2 + ArN(MgBr)_2 \rightarrow \underset{NAr}{\overset{}{Ar^1CAr^2}} + \underline{\underset{OH}{Ar^1CHAr^2}}$$

Scheme 1. (abnormal products underlined)

In the IDMg reactions with nitroferrocene (Scheme



Scheme 2.



Scheme 3.

2) and benzoylferrocenes (Scheme 3), the types of products are same as those in the reactions 1a and 1b. The product distribution in the reactions 2 and 3 is noticeably different reflecting their much milder natures due to the retarding effect of bulky and electron rich ferrocenyl group in comparison with that of phenyl group: Some modification of the EDA-EAA concept is necessary. The azoxy- and azoferrocenes as well as *N*-(ferrocenylarylmethylene)-anilines are new compounds, and the molecular structures were studied by means of ^{1}H NMR, electronic absorption, and X-ray crystallography. The results will be summarized and discussed.

Results and Discussion

The EDA-EAA concept deals with the efficiency of initial processes essential to the reactions, i.e., the σ-complex formation and the subsequent electron transfer.[2] The product distributions in reactions 2 and 3 will be elucidated partly by the simple concept and additionally by modifying it by the effect of ferrocenyl group on the two processes. The phenyl-IDMg reagents used are *p*-MeO-, *p*-Me-, and *p*-Cl-substituted ones: The normalized oxidation peak potentials measured in THF–Bu_4NClO_4 system are 0.912V, 0.941V, and 1.056V, respectively.[8] The large positive value indicates a weak EDA.

IDMg Reaction with Nitroferrocene. The product distribution in reaction 2 under fixed conditions is given in Table 1 (Runs 1—5); the two previous results of reaction 1a with *p*-MeO-nitrobenzene[3] are listed for comparison (Runs 6 and 7). The unavoidable formation of symmetrical (*sym*-) azoarene (**3**) indicates involvement with electron transfer.[3,9] The reactivity of azoxyarenes in the IDMg deoxygenation, influencing on the relative yields of azoxy and unsymmetrical azo compounds, was also correlated to EDA and EAA.[5]

For discussing the character of reaction 2, some normalized reduction potentials of nitro and azoxy substrates are given below. The large negative value indicates weak EAA. The ΔE value of 2.6—2.8, estimated from the potential of nitroferrocene, corresponds to the borderline of "electron transfer" and "coordination" controlled reactions.[2] The hybrid character may be one of the reasons of the small effect of EDA indicated by slight variation of yields of azoxy- and azoferrocenes (**1** and **2**) and **3** (Runs 1, 2, 4, and 5). The weaker EAA of nitroferrocene than that of *p*-MeO-nitrobenzene, as shown by remarkably different (185 mV) potentials, seems responsible for the noticeably different yields between Runs 2 and 6 using *p*-MeC_6H_4-IDMg. The small EDA effect, including the almost same yields in Runs 5 and 7 using *p*-ClC_6H_4-IDMg, is understood by the nature of **1** which is resistant to deoxygenation as described below.

(Fc=ferrocenyl)

$FcNO_2$	−1.693V
FcN(O)=NC_6H_4Cl-*p*	−1.604V
p-$MeOC_6H_4NO_2$	−1.508V
p-$MeOC_6H_4N(O)=NC_6H_4Cl$-*p*	−1.563V

Even in Runs 1 and 2 using 5.0 mol of IDMg's having stronger EDA's the yield of **1** is still higher than that of **2**: A larger amount of IDMg is needed for effective deoxygenation (Run 3). The sluggish deoxygenation is in accord with weaker EAA of **1** than that of azoxybenzene (vide supra), but is not in accord with noticeably stronger EAA of **1** than that of nitroferrocene. The neighboring bulky ferrocenyl group of **1** will cause steric repulsion against the attack of anionic IDMg nitrogen on the positive azoxy nitrogen.[5] However, as shown in the final section, the planar molecular structure of **1** is the most reliable reason for the sluggish deoxygenation.

IDMg Reaction with Benzoylferrocenes. The yields of *N*-(ferrocenylarylmethylene)anilines (**4**, anils)[4] and amounts of recovered substrates in reaction 3 are summarized in Table 2 (Runs 1—30). Benzoylferrocenes have weaker EAA than that of benzophenone (reduction potential: −1.989V[2]): their potentials were undetermined, because they are over the potential window of THF–Bu_4NClO_4 system.[2] The ΔE value of reaction 3 is larger than 3.1, suggesting the "coordination controlled" character[2,5] accompanying a much milder electron transfer. This is supported by the almost negligible formation of radical products, ferrocenylarylmethanol and *sym*-azoarene. The

Table 1. Product Distribution in IDMg Reaction with Nitroferrocene and *p*-MeO-nitrobenzene

Run No.	*p*-RC_6H_4-IDMg R	$ArNO_2$ Ar	[IDMg]/[Substr]	Yield/%[a] **1** Azoxy	**2** *unsym*-Azo	**3** *sym*-Azo
1	MeO	Fc[b]	5	53	34	12
2	Me	Fc	5	52	18	8
3	Me	Fc	10	20	50	16
4	H	Fc	5	71	9	4
5	Cl	Fc	5	73	15	3
6	Me	*p*-MeO-Ph[c]	6.2	24	52	4
7	Cl	*p*-MeO-Ph	6.2	73	15	5

a) Yields obtained after heating at 55 °C for 3 h. b) Fc=ferrocenyl. c) Cf. Ref. 1).

former, formed via hydrogen abstraction from the solvent by ketyl radical,[3] was detected by ^{1}H NMR (see Experimental). The formation of the latter will be discussed later. The reaction 3 is clean as shown by high combined amounts of anil and the recovery, and it proceeds very slowly (vide infra). By comparing the relative yields of **4** (Table 2), reflecting the reactivity of reactants, some new type substituent effects depending on the molar ratio were disclosed in the field of Grignard and IDMg reactions.

By use of 1.2 mol of IDMg and unsubstituted benzoylferrocene, the conversion was quite low after treating at 55 °C for 2 h (Runs 1, 6, and 11) and at room temperature (8—12 °C) for 16 h (Runs 16, 21, and 26). In contrast to the reaction 1b giving sufficient conversion at 55 °C for 2 h,[4] reaction 3 is notably sluggish and leads to disclosure of an expected but new type substituent effect of reagent. At both the temperatures, the conversion becomes greater as the substituent changes from MeO via Me and H to Cl. Thus the conversion manner indicates the substituent effect on positive charge of the reagent's Mg atom; the strong charge of Cl reagent is favorable for the σ-complex formation. For estimating the acceleration by temperature elevation, the conversion per 1 h at 55 °C was compared with that at room temperature. A rough estimate, 33-, 13-, and 11-folds for accelerations by MeO, Me, and Cl reagents, respectively, indicates the "coordination controlled" character of reaction 2.

By use of 2.4 mol of IDMg, the conversion became fairly high, and the substituent effect of reagent was unobservable. These facts suggest a cooperation of two IDMg molecules;[10] the σ-complex is formed by one and electron-donating addition of the other, in which substituent effect may compensate with each other. Instead, the effect of substrate appears in a novel U-shaped manner shown in Fig. 1 by the typical results of Runs 2—5 using MeO-substituted IDMg. The conversion is higher in the cases of MeO and Cl substrates and is lower in the cases of Me and H substrates. The U-shaped variation is common to almost all the runs using fixed substituent of IDMg at both the temperatures (Runs 7—10, 12—15, 17—20, 22—25, and 26—30). The variation is conceivable if

Table 2. Product Distribution in IDMg Reaction with Benzoylferrocenes

Run No.	*p*-R^{1}C$_6$H$_4$COFc R^1	*p*-R^{2}C$_6$H$_4$-IDMg R^2	$\frac{[\text{IDMg}]}{[\text{Substr.}]}$	Reacn. condn.a)	Yield/% Anil	Recov.	*sym*-Azo
1	H	MeO	1.2	A	4	94	Trace
2	H	MeO	2.4	A	32	61	1
3	MeO	MeO	2.4	A	58	37	0
4	Me	MeO	2.4	A	33	65	0
5	Cl	MeO	2.4	A	62	36	0
6	H	Me	1.2	A	16	85	1
7	H	Me	2.4	A	50	49	Trace
8	MeO	Me	2.4	A	59	39	0
9	Me	Me	2.4	A	36	59	0
10	Cl	Me	2.4	A	58	34	0
11	H	Cl	1.2	A	27	67	Trace
12	H	Cl	2.4	A	44	50	Trace
13	MeO	Cl	2.4	A	57	31	0
14	Me	Cl	2.4	A	33	57	0
15	Cl	Cl	2.4	A	58	39	0
16	H	MeO	1.2	B	1	95	2
17	H	MeO	2.4	B	53	42	3
18	MeO	MeO	2.4	B	59	26	Trace
19	Me	MeO	2.4	B	26	69	5
20	Cl	MeO	2.4	B	60	35	0
21	H	Me	1.2	B	10	90	5
22	H	Me	2.4	B	49	44	7
23	MeO	Me	2.4	B	58	38	3
24	Me	Me	2.4	B	38	54	6
25	Cl	Me	2.4	B	46	46	0
26	H	Cl	1.2	B	20	75	3
27	H	Cl	2.4	B	61	31	Trace
28	MeO	Cl	2.4	B	46	50	3
29	Me	Cl	2.4	B	35	59	Trace
30	Cl	Cl	2.4	B	69	28	2

a) The condition A: at 55 °C for 3 h; B: at room temperature for 16 h.

we assume that the σ-complex formed at the most essential process of reaction 3 is a "loose" one due to steric repulsion by the ferrocenyl group with reference to that expected in reaction 1b. As the substituent changes from MeO via Me and H to Cl, the EAA becomes stronger,[2)] while the σ-complex becomes more loose. Thus the high reactivity of the Cl substrate is ascribed to its strong EAA, whereas the reactivity of the MeO substrate is ascribed to formation of a fairly tight σ-complex which assists the substrate in accepting electrons.[7)]

The formation of small amount of *sym*-azoarene, observed also for the first time among IDMg reactions of type 1b, becomes appreciable at lower temperatures. The formation, in spite of the much milder electron transfer, is not unexpected according to the mechanism of two electron oxidation of IDMg molecules proposed recently.[9)] At lower temperatures favorable for accumulating the "loose" σ-complex, a small part of which tends to dissociate, after electron transfer, into ketyl and arylaminyl radicals due to steric repulsion. The latter radicals produced in proximity to each other undergo disproportionation and dimerization affording *sym*-azoarenes.[9)]

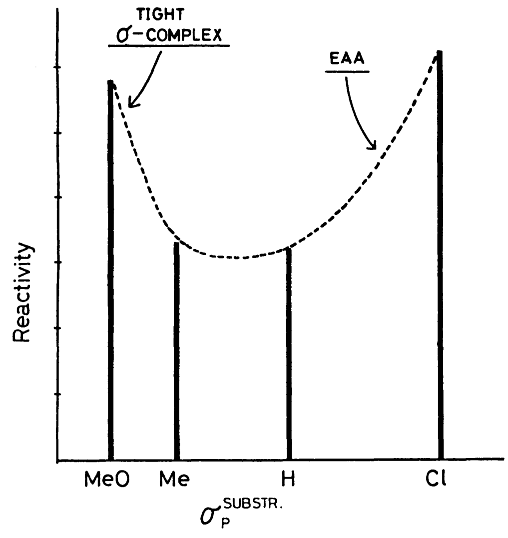


Fig. 1. Schematic diagram for the relative reactivities of *p*-substituted benzoylferrocenes.

Electronic Absorption of Deeply Colored Azoxy- and Azoferrocenes. The azoxy- and azoferrocenes (**1** and **2**) form deep-red crystals. The electronic absorption maxima obtained by measurements in 1,4-dioxane are summarized in Table 3; those of azoxy- and azobenzenes are listed for comparison. The deep color of **1** and **2** is ascribed to the d–d transition[11)] as shown below.

The azoxyferrocenes have two absorption maxima: λ^A in the region of 320—350 nm and λ^B in that of 475—495 nm. As shown in Table 3, λ^A shifts toward red depending on the electron-repelling resonance effect of the substituent in the manner similar to that of λ^C of azoxybenzenes; both λ^A and λ^C are assigned to the π→π* transition. In contrast, λ^B shifts toward blue depending on the inductive effect of the substituent, and is assigned to the d–d transition.

The azoferrocenes have also two absorption maxima: λ^D in the region of 320—340 nm and λ^E in that of 520—540 nm. As shown in the table, λ^D as well as λ^F of azobenzenes shift in the manner similar to λ^A and λ^C, and is assigned to the π→π* transition. While λ^G of azobenzene in the region of 430—440 nm is assigned to the n→π* transition, λ^E shifts in the manner similar to λ^B and is assigned to the d–d transition. The possibility that the λ^E band overlaps with the n→π* band can, however, not be excluded.

Molecular Structures of Azoxyferrocene (1), Azoferrocene (2), and *N*-(Ferrocenylarylmethylene)aniline (4). An unexpected chemical shift of cyclopentadienyl protons was disclosed from comparison of azoxy- and azoferrocenes (**1** and **2**, Fig. 2). Usually in *p*-substituted azoxybenzenes, both the two doublets of AB-quartet appear at lower magnetic fields compared to those of the corresponding azobenzenes.[3)] In a similar manner, one of the two narrow triplets of cyclopentadienyl protons of **1** appears at a lower field

Table 3. Electronic Absorption Maxima of Azoxy- and Azoferrocenes

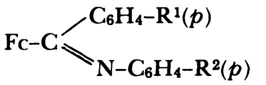
Fc-N(O)=N=C_6H_4-R(*p*)					Fc-N=N-C_6H_4-R(*p*)				
R	λ^A/nm		λ^B/nm		R	λ^D/nm		λ^E/nm	
MeO	347		476		MeO	341		520	
Me	329	$\pi\rightarrow\pi^*$	480	d-d	Me	328	$\pi\rightarrow\pi^*$	522	d-d
H	322		483		H	321		528	($n\rightarrow\pi^*$)
Cl	328		493		Cl	328		539	
(*p*)R-C_6H_4-N(O)=N-C_6H_4-R(*p*)					(*p*)R-C_6H_4-N=N-C_6H_4-R(*p*)				
R	λ^C/nm				R	λ^F/nm		λ^G/nm	
MeO	354		—		MeO	356		430	
Me	329	$\pi\rightarrow\pi^*$	—		Me	328	$\pi\rightarrow\pi^*$	440	$n\rightarrow\pi^*$
H	323		—		H	320		440	
Cl	335		—		Cl	331		440	

(δ 5.21—5.27) compared to that of **2** (δ 4.99—5.11, See Table 4). However, the other triplet of **1** appears at a higher field (δ 4.36—4.40) compared to that of **2** (δ 4.48—4.57). In order to understand the reason for this anomaly, the X-ray structure determination of **1** and **2** was carried out. The single crystals of sufficient size were obtained only in a few cases, and *p*-MeO-substituted azoxyferrocene ($\mathbf{1}^{\mathrm{MeO}}$, 1-ferrocenyl-*ONN*-4-methoxybenzene) and *p*-Cl-substituted azoferrocene ($\mathbf{2}^{\mathrm{Cl}}$, 4-chlorophenylazoferrocene) were submitted to the analyses (Table 4). The structure analysis of an anil ($\mathbf{4}^{\mathrm{MeO}}{}_{\mathrm{H}}$, *N*-(ferrocenylphenylmethylene)-4-methoxy-

Table 4. Analytical Data of Azoxy- and Azoferrocenes

$Fc-N(O)=N-C_6H_4-R(p)$ (**1**)		Found (Calcd)/%			^1H NMR data /δ		
R	Mp θ_m/°C	C	H	N			
MeO	113—113.5	60.82 (60.73)	4.61 (4.80)	8.37 (8.34)	6.94(2H, d), 4.38(2H, t),	8.18(2H, d), 4.23(5H, s),	5.21(2H, d), 3.85(3H, s).
Me	137.5—138.5	63.92 (63.77)	5.09 (5.04)	8.76 (8.75)	8.05(2H, d), 4.40(2H, t),	7.29(2H, d), 4.24(5H, s),	5.27(2H, d), 2.40(3H, s).
H	98.5—99	62.84 (62.77)	4.57 (4.61)	9.27 (9.15)	8.08(2H, m), 4.36(2H, t),	7.44(3H, m), 4.23(5H, s).	5.26(2H, d),
Cl	120.5—121	56.71 (56.42)	3.86 (3.83)	8.24 (8.23)	8.05(2H, d), 4.38(2H, t),	7.40(2H, d), 4.22(5H, s).	5.21(2H, d),
$Fc-N=N-C_6H_4-R(p)$ (**2**)							
MeO	138—138.5	63.86 (63.77)	4.95 (5.04)	8.78 (8.75)	7.76(2H, d), 4.48(2H, t),	6.96(2H, d), 4.19(5H, s),	4.99(2H, d), 3.81(3H, s).
Me	139—140	67.09 (67.12)	5.30 (5.30)	9.25 (9.12)	7.70(2H, d), 4.49(2H, t),	7.25(2H, d), 4.20(5H, s),	5.03(2H, d), 2.36(3H, s).
H	104—104.5	66.58 (66.23)	4.94 (4.86)	9.73 (9.66)	7.82(2H, m), 4.57(2H, t),	7.50(2H, d), 4.23(5H, s).	5.11(2H, d),
Cl	165—165.5	59.24 (59.20)	3.84 (4.04)	8.65 (8.63)	7.72(2H, d), 4.57(2H, t),	7.43(2H, d), 4.23(5H, s).	5.06(2H, d),

Table 5. Analytical Data of Aroylferrocene Anils



$$Fc-C\begin{cases}C_6H_4-R^1(p)\\N-C_6H_4-R^2(p)\end{cases}$$

(**4**)

R^1	R^2	Mp θ_m/°C	Found (Calcd)/%			^1H NMR data /δ
			C	H	N	
MeO	MeO	173.5—174	70.82 (70.61)	5.50 (5.45)	3.26 (3.29)	7.38—6.30(8H, m), 4.65(2H, d), 4.35(2H, t), 4.21(5H, s), 3.72(3H, s), 3.68(3H, s).
Me	MeO	129.5—130	73.25 (73.37)	5.72 (5.52)	3.32 (3.65)	7.16—7.06(4H, m), 6.70—6.60(4H, m), 4.70(2H, d), 4.43(2H, t), 4.25(5H, s), 3.65(3H, s), 2.32(3H, s).
H	MeO	176—176.5	72.12 (72.09)	5.38 (5.52)	3.77 (3.65)	7.23—7.20(5H, m), 6.60—6.58(4H, m), 4.53(2H, d), 4.38(2H, t), 4.20(5H, s), 3.63(3H, s).
Cl	MeO	152—153	66.28 (66.13)	4.69 (4.83)	3.20 (3.35)	7.23—7.16(4H, m), 6.66—6.56(4H, m), 4.62(2H, d), 4.20(5H, s), 3.72(3H, s).
MeO	Me	139—140	73.21 (73.37)	5.62 (5.67)	3.40 (3.42)	7.35—6.45(8H, m), 4.69(2H, d), 4.39(2H, t), 4.18(5H, s), 3.73(3H, s), 3.23(3H, s).
Me	Me	96—97	76.21 (76.36)	5.75 (5.90)	3.65 (3.56)	7.14—7.05(4H, m), 6.87(2H, d), 6.52(2H, d), 4.65(2H, d), 4.38(2H, t), 4.21(5H, s), 2.28(3H, s), 2.18(3H, s).
H	Me	139—139.5	75.65 (75.23)	5.62 (5.77)	3.63 (3.81)	7.26—7.20(5H, m), 6.89(2H, d), 6.56(2H, d), 4.65(2H, d), 4.40(2H, t), 4.21(5H, t), 2.19(3H, s).
Cl	Me	129—130	68.89 (68.77)	5.17 (5.02)	3.53 (3.44)	7.25—7.20(4H, m), 6.92(2H, d), 6.55(2H, d), 4.65(2H, d), 4.42(2H, t), 4.22(5H, s), 2.23(3H, s).
MeO	Cl	172.5—173	66.08 (66.13)	4.96 (4.83)	3.42 (3.35)	7.35—6.50(8H, m), 4.70(2H, d), 4.44(2H, t), 4.24(5H, s), 3.83(3H, s).
Me	Cl	151.5—152	68.66 (68.77)	5.00 (5.02)	3.55 (3.49)	7.16—6.96(4H, m), 6.60(2H, d), 4.60(2H, d), 4.44(2H, t), 4.21(5H, s), 2.33(3H, s).
H	Cl	148.5—149	68.29 (68.15)	4.78 (4.68)	3.72 (3.61)	7.36—7.24(5H, m), 7.05(2H, d), 6.54(2H, d) 4.64(2H, d), 4.38(2H, t), 4.18(5H, s).
Cl	Cl	140.5—141	62.67 (62.54)	4.00 (4.06)	3.20 (3.32)	7.20—6.95(6H, m), 6.47(2H, d), 4.62(2H, d), 4.42(2H, t), 4.19(5H, s).

aniline, Table 5) was also carried out.

The structure of the three molecules is shown in Fig. 3; the numbering schemes of atoms and the definition of planar groups are given in the figure. The structures are viewed from the direction perpendicular to the plane passing through C(1), N(1), and N(2) atoms in **1**$^{\mathrm{MeO}}$ and **2**$^{\mathrm{Cl}}$, whereas C(1), C(41), and N atoms in **4**$^{\mathrm{MeO}}_{\mathrm{H}}$. The dihedral angles between the planar groups are shown in Table 6. Crystal data, selected bond lengths and angles are summarized in Tables 7—9. Tables of atomic coordinates, thermal parameters, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8767.

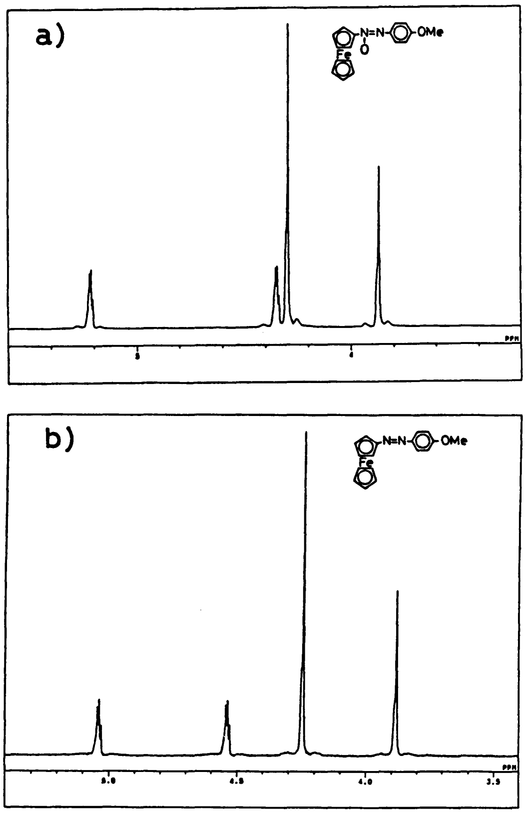
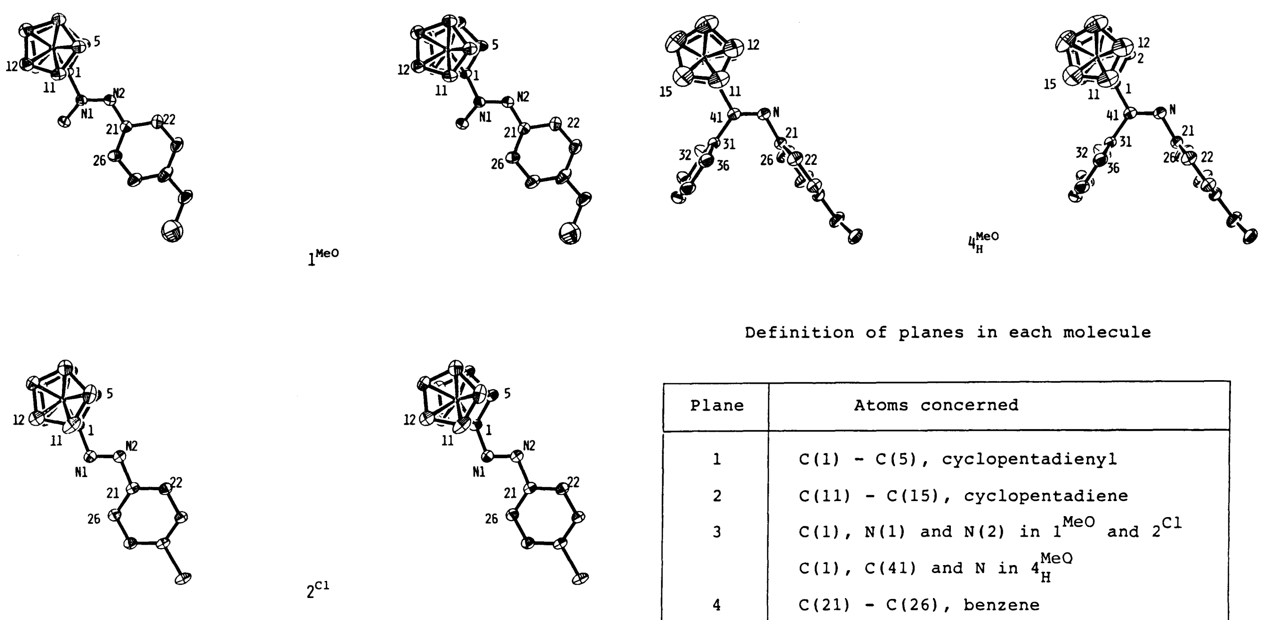


Fig. 2. Cyclopentadienyl proton chemical shift of azoxy- and azoferrocenes.

A common structural feature of the three molecules is that cyclopentadiene and -dienyl rings in ferrocenyl moiety are in an eclipsed conformation, which was reported previously in the case of ferrocenecarboxylic acid.[12] The presence of oxygen atom attached to diazo group in **1**$^{\mathrm{MeO}}$ seems to have a little effect on the overall conformation of molecule (vide infra), judging from the tabulated values of molecular dimensions. The effective delocalization of π-electrons of diazo and phenyl groups in **1**$^{\mathrm{MeO}}$ and **2**$^{\mathrm{Cl}}$ is shown by the

Table 6. Dihedral Angles between Planes Defined in Each Molecule

	1$^{\mathrm{MeO}}$	**2**$^{\mathrm{Cl}}$	**4**$^{\mathrm{MeO}}_{\mathrm{H}}$
1-2	1.4	1.1	3.3
1-3	6.1	6.2	1.7
1-4	6.2	3.5	86.5
2-3	6.3	6.5	3.3
2-4	6.4	4.1	88.6
3-4	0.3	9.3	88.0
3-5			85.5
4-5			69.7



Definition of planes in each molecule

Plane	Atoms concerned
1	C(1) - C(5), cyclopentadienyl
2	C(11) - C(15), cyclopentadiene
3	C(1), N(1) and N(2) in 1^{MeO} and 2^{Cl}
	C(1), C(41) and N in $4^{\mathrm{MeO}}_{\mathrm{H}}$
4	C(21) - C(26), benzene
5	C(31) - C(36), benzene only in $4^{\mathrm{MeO}}_{\mathrm{H}}$

Fig. 3. Molecular structures of azoxyferrocene, azoferrocene, and benzoylferrocene anil.

tabulated values of bond length.

The structure of $\mathbf{4}^{MeO}_{H}$ is quite different from those of $\mathbf{1}^{MeO}$ and $\mathbf{2}^{Cl}$, mainly because of the steric repulsion between the two phenyl rings. These rings are perpendicular to C(1), C(41), and N planes. No delocalization of π-electrons is indicated by the

Table 7. Crystal Data and Experimental Conditions

	$\mathbf{1}^{MeO}$	$\mathbf{2}^{Cl}$	$\mathbf{4}^{MeO}_{H}$
Formula	$C_{17}H_{17}FeN_2O_2$	$C_{16}H_{13}ClFeN_2$	$C_{24}H_{21}FeNO$
Mol. wt.	337.2	314.6	395.3
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	16.952(9)	12.239(3)	8.486(2)
b/Å	7.652(4)	10.681(2)	17.630(4)
c/Å	11.710(4)	11.605(2)	13.347(3)
β/°	98.26(4)	115.41(2)	106.66(2)
D_c/g cm^{-3}	1.49	1.53	1.37
Z	4	4	4
Abs. coeff./cm^{-1} (Mo $K\alpha$)	10.4	14.0	8.2
Crystal size/mm^3	0.5×0.4×0.05	0.3×0.3×0.2	0.3×0.2×0.2
No. of reflections	2476	2922	3145
R	0.078	0.063	0.051

Table 8. Selected Bond Lengths with Estimated Standard Deviations in Parentheses

Bond		$\mathbf{1}^{MeO}$	$\mathbf{2}^{Cl}$	$\mathbf{4}^{MeO}_{H}$
C(1)	- C(2)	1.418(11)	1.443(8)	1.433(6)
C(2)	- C(3)	1.443(12)	1.430(8)	1.426(6)
C(3)	- C(4)	1.451(11)	1.448(8)	1.418(6)
C(4)	- C(5)	1.432(11)	1.442(8)	1.426(6)
C(5)	- C(1)	1.447(11)	1.458(8)	1.428(5)
C(1—5)	- Fe av.	2.049(8)	2.053(6)	2.040(4)
C(11)	- C(12)	1.432(10)	1.439(9)	1.418(9)
C(12)	- C(13)	1.434(11)	1.424(9)	1.431(10)
C(13)	- C(14)	1.440(11)	1.436(9)	1.399(9)
C(14)	- C(15)	1.434(11)	1.433(11)	1.437(9)
C(15)	- C(11)	1.447(10)	1.438(11)	1.424(8)
C(11—15)	- Fe av.	2.053(8)	2.058(6)	2.039(4)
C(1)	- N(1)	1.449(10)	1.428(7)	
C(1)	- C(41)			1.470(5)
N(1)	- O(1)	1.258(8)		
N(1)	- N(2)	1.267(8)	1.247(6)	
C(41)	- N			1.272(5)
C(41)	- C(31)			1.495(5)
N(2)	- C(21)	1.409(9)	1.456(7)	
N	- C(21)			1.436(6)
C(21)	- C(22)	1.410(11)	1.387(8)	1.367(6)
C(22)	- C(23)	1.371(12)	1.397(8)	1.403(6)
C(23)	- C(24)	1.410(14)	1.397(8)	1.360(6)
C(24)	- C(25)	1.399(14)	1.391(8)	1.369(8)
C(25)	- C(26)	1.395(12)	1.411(8)	1.383(9)
C(26)	- C(21)	1.406(11)	1.402(8)	1.365(8)
C(24)	- O(2)	1.377(12)		
C(24)	- O			1.386(6)
C(24)	- Cl		1.744(5)	
O(2)	- Me	1.651(18)		
O	- Me			1.430(7)
C(31)	- C(32)			1.369(7)
C(32)	- C(33)			1.390(9)
C(33)	- C(34)			1.374(9)
C(34)	- C(35)			1.364(9)
C(35)	- C(36)			1.391(8)
C(36)	- C(31)			1.386(6)

Table 9. Selected Bond Angles with Estimated Standard Deviations in Parentheses

Bond angle	$\mathbf{1}^{\mathrm{MeO}}$	$\mathbf{2}^{\mathrm{Cl}}$	$\mathbf{4}^{\mathrm{MeO}}_{\mathrm{H}}$
C(1) -N(1) -N(2)	115.7(6)	111.1(5)	
C(1) -C(41)-N			118.0(4)
C(1) -N(1) -O(1)	116.5(6)		
C(1) -C(41)-C(31)			117.5(4)
N(2) -N(1) -O(1)	127.8(6)		
N -C(41)-C(31)			124.4(4)
N(1) -N(2) -C(21)	121.2(6)	112.4(5)	
C(41)-N -C(21)			120.6(4)

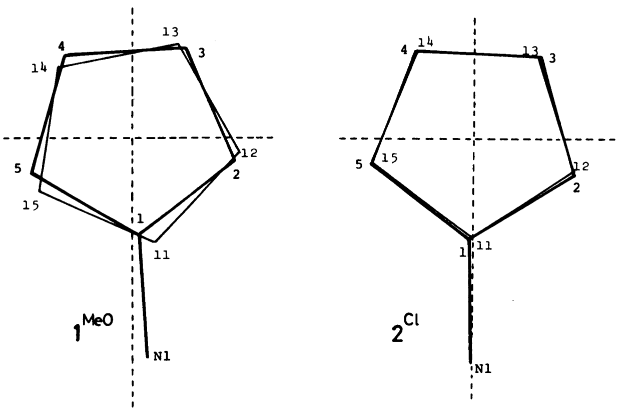


Fig. 4. Projection of plane 2 on plane 1.

C(41)-N bond length of 1.272(5) Å which is comparable to the value of the pure C=N bond.

The projection of diene plane(2) on dienyl plane(1) of $\mathbf{1}^{\mathrm{MeO}}$ and $\mathbf{2}^{\mathrm{Cl}}$ is shown in Fig. 4. In contrast to almost completely eclipsed conformation of $\mathbf{2}^{\mathrm{Cl}}$, the plane 2 in $\mathbf{1}^{\mathrm{MeO}}$ is slightly twisted from the plane 1 seemingly due to steric repulsion with the negative azoxy oxygen caused by planarity. The twist, however, does not provide any clue to elucidation of the abnormal chemical shift of 3- and 4-protons of dienyl ring observed in solution (vide supra), because the singlet signal of the diene protons (δ 4.22—4.24, Fig. 2 and Table 4) indicates the free rotation. The low barrier to internal rotation of diene planes in ferrocene was reported.[13] It is significant that both the pairs of narrow triplets of $\mathbf{1}^{\mathrm{R}}$ and $\mathbf{2}^{\mathrm{R}}$ have almost the same centers at δ 4.73—4.84, and that the splitting by ca. 0.43 ppm from the center of $\mathbf{1}^{\mathrm{R}}$ is notably larger than that by ca. 0.26 ppm of $\mathbf{2}^{\mathrm{R}}$. The large splitting suggests a participation of polarized resonance structure of the dienyl ring of $\mathbf{1}^{\mathrm{R}}$ caused by positive azoxy nitrogen. The polarization may be the true reason causing the ^{1}H NMR anomaly (Fig. 2) as well as the twist (Fig. 4).

Data of ^{1}H NMR summarized in Tables 4 and 5 are similar to each other. Thus it may be concluded that all the products, $\mathbf{1}^{\mathrm{R}}$, $\mathbf{2}^{\mathrm{R}}$, and $\mathbf{4}^{\mathrm{R^1}}{}_{\mathrm{R^2}}$, have the molecular structures same as those described above.

General Discussion. The simple EDA-EAA concept, useful for understanding the reactions of magnesium reagents with noncrowded benzene derivatives,[2] seems unsuitable for extending directly to the IDMg reactions with somewhat bulky and electron rich ferrocene derivatives. However, new type substituent effects were disclosed and elucidated, in line with the previous discussion,[2] by modifying the concept based on the effect of ferrocenyl group retarding two initial processes of the reactions.

The elucidation of the results of reactions is compatible with the structure analyses of products. The coplanar structure of $\mathbf{1}^{\mathrm{R}}$ is distinct from twisted ones of azoxybenzenes; an example of the latter having the dihedral angle of ca. 23 degree between the two phenyl rings was reported.[14] The planarity and effective π-electron delocalization of $\mathbf{1}^{\mathrm{R}}$ lead to reduction of the positive charge on azoxy nitrogen making it unfavorable to the attack of anionic IDMg nitrogen (vide supra).[9] Thus the quite sluggish deoxygenation of $\mathbf{1}^{\mathrm{R}}$ in reaction 2 is most plausibly ascribed to its planar structure involving the electron rich ferrocenyl group. The perpendicular twist between ferrocenyl and phenyl planes in $\mathbf{4}^{\mathrm{R^1}}{}_{\mathrm{R^2}}$ reflects the steric repulsion responsible for the sluggishness of reaction 3.

The synthetic aspect of formation of **1**, **2** (reaction 2), and **4** (reaction 3) should be noted, though the optimum conditions for preparing them were undetermined. Azo-substituted ferrocene is so far difficult to access because of the instability of ferrocene ring under diazotization conditions. The symmetrical diferrocenyl diazene is known,[15] and only one phenylazo derivative was prepared in a low yield by treating an equimolar mixture of phenylazo- and unsubstituted cyclopentadienyllithiums with iron(II) chloride.[16] Neither symmetrical nor unsymmetrical azoxyferrocene has been reported. Thus the IDMg procedure will provide a convenient route for preparing unsymmetrical azoxy- and azoferrocenes if the method for preparing nitroferrocene (See Experimental) is improved. Concerning the condensation of diaryl ketones with anilines, a Lewis acid catalyst (e.g., BF_3) gives sufficient yields of anils only when the carbonyl component is a strong electrophile, e.g., fluorenone and its nitro derivatives.³⁾ In contrast, the IDMg procedure applied to the moderate electrophiles such as benzophenones can be extended to the extremely weak electrophile, i.e., benzoylferrocenes.

Experimental

Materials and Reaction Procedures. Nitroferrocene was obtained in yields lower than 20% by lithiation of ferrocene with BuLi followed by nitration with N_2O_4.¹⁷⁾ Benzoylferrocenes were prepared in good yields by Fridel-Crafts method using appropriate aroyl chlorides.¹⁸⁾ The IDMg reactions were carried out by adding the substrate (1.3 mmol) dissolved in THF (10 ml) to a solution of reagent in THF (35 ml) at 0 °C, and the resulting mixture was stirred at 55 °C or at room temperature (8—12 °C); the reaction times are given in Tables 1 and 2. The products were separated by column chromatography on silica gel (Wako Gel C-200 and C-300). The melting points, the elemental analysis results, and ^{1}H NMR data are summarized in Tables 4 and 5. The melting points are uncorrected. The trace amount of ferrocenylarylmethanols in reaction 3 was confirmed by ^{1}H NMR signal of benzylic proton appearing at δ 4.05—4.25.

Crystallographic Analyses. The three dimensional structures of $\mathbf{1}^{\mathrm{MeO}}$, $\mathbf{2}^{\mathrm{Cl}}$, and $\mathbf{4}^{\mathrm{MeO}}{}_{\mathrm{H}}$ were established by X-ray diffraction. The intensity data were collected on an automated single-crystal diffractometer by use of graphite-monochromated Mo $K\alpha$ radiation. The structure was solved by combined use of the direct method with MULTAN 78 and heavy atom method, and then refined by the block-diagonal least-squares procedure. Anisotropic temparature factors are assigned for non-hydrogen atoms except for methyl carbon atom in $\mathbf{1}^{\mathrm{MeO}}$. Hydrogen atoms were not considered in structure factor calculation for $\mathbf{1}^{\mathrm{MeO}}$ and $\mathbf{2}^{\mathrm{Cl}}$, whereas they could be located in the difference map for $\mathbf{4}^{\mathrm{MeO}}{}_{\mathrm{H}}$ and were included in the least-squares computations. Absorption correction was not applied; it may limit the accuracy of the present structure analyses. Crystal data and some indices concerning the results of structure determination were listed in Tables 7—9.

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