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Meisenheimer−Wheland Complexes between 1,3,5-Tris(*N*,*N*-dialkylamino)benzenes and 4,6-Dinitrotetrazolo[1,5-*a*]pyridine. Evidence of Reversible C−C Coupling in the S_EAr/S_NAr Reaction†

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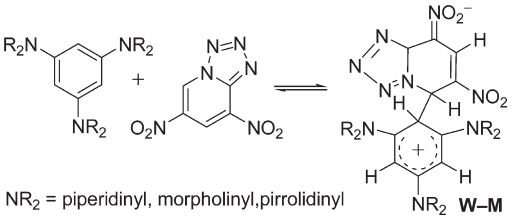

Reactions between a superelectrophilic carbon reagent, 4,6-dinitrotetrazolopyridine, and 1,3,5-tris(*N*,*N*-dialkylamino)benzenes, a supernucleophilic carbon reagent series, afford C−C coupling products which are "double σ-complexes" (**W**−**M**), Wheland-like on the 1,3,5-tris(*N*,*N*-dialkylamino)benzene moiety and Meisenheimer-like on the 4,6-dinitrotetrazolopyridine moiety. These complexes were moderately stable at low temperature, and they were characterized by NMR spectroscopy methods. ^{1}H NMR experiments at variable temperature strongly indicate that the formation of these complexes by a nucleophile/electrophile attack is a reversible process.

Introduction

Searches (including isolation or observation and characterization) about intermediates of the usual ionic reactions on aromatic substrates, such as nucleophilic[1] (S_NAr) or electrophilic[2] (S_EAr) substitution reactions, are of great importance not only to elucidate the proposed mechanism (usually, the so-called "two step" mechanism of both reactions) but also to investigate their reactivity regarding some isolated steps of both S_NAr or S_EAr reactions.

In fact, the major parts of mechanistic studies are measures involving the overall rate of multistep reactions. This fact implies some assumptions and simplifications which, in principle, might be incorrect and dangerous to complete elucidation of the reaction pathway. An instance of that is offered by the reactivity of σ cationic complexes obtained by the reactions between 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and diazonium salts. The generally accepted mechanism for the S_EAr (Scheme 1) indicates the proton departure from the Wheland intermediate (**W**) as a fast step, which is indicated to be the "driving force" of the S_EAr reaction.[3]

Isolation and stability of **W** intermediates, recently reported by us,[4] indicates that this statement is not correct. Our system reveals that the fast step is the attack of the electrophilic reagent to afford the **W** complex while the rate-determining step is that regarding the proton departure from **W**, as clearly indicated also by the observed base catalysis feature from **W** to final product[5] (Scheme 2).

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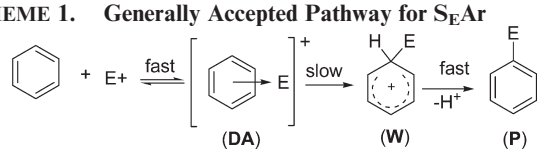
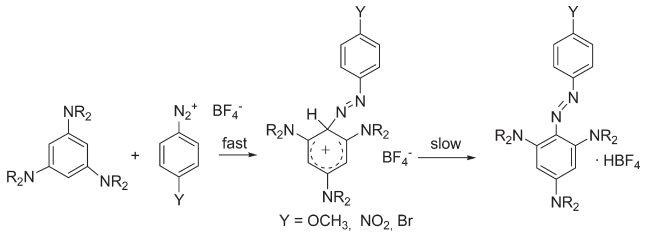
SCHEME 1. Generally Accepted Pathway for S_EAr



SCHEME 2. Reactions between 1,3,5-Tris(*N*,*N*-dialkylamino) benzenes and Diazonium Salts



NR$_2$ = piperidinyl
NR$_2$ = morpholinyl

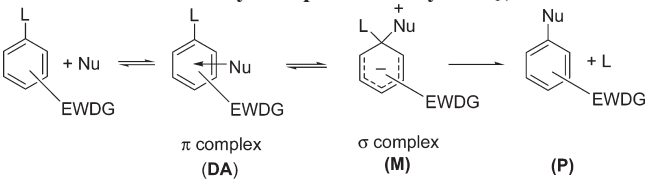
On the other hand, the nucleophilic aromatic substitution pathway[1] (see Scheme 3, where L is the leaving group and EWDG means electron-withdrawing groups) follows a very similar mechanism involving the formation of a donor−acceptor complex, followed by the formation of a σ complex (the Meisenheimer complex, **M**). Finally, the leaving group departure produces rearomatization of the substrate in final products.[6] The π complex formation (donor/acceptor complex) was by us largely investigated in the case of aromatic halo-nitro derivatives and neutral nucleophiles (amines) in poorly polar solvents. In the case of L = H (a hydrogen atom is the leaving group), the departure of the negative charge from the σ complex becomes a difficult process because a hydride ion should be eliminated.

In the case of a simple system, without complications arising from leaving group departure, such as the system formed by 1,3,5-trinitrobenzene and 1,4-diazabicyclo[2.2.2] octane (DABCO), quinuclidine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the formation of the Meisenheimer complex is the only relevant step,[7] together with the possible formation of donor−acceptor (**DA**) complexes.

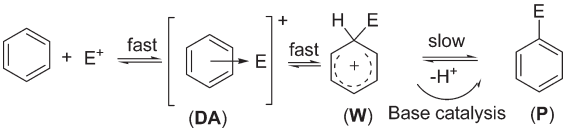
The reactions of very strongly activated electrophilic reagents and/or nucleophilic reagents are of interest because these reagents produce effects which are hardly observed in more usual, less activated systems.

For example, as shown in Scheme 2, our recent data, obtained using 1,3,5-tris(*N*,*N*-dialkylamino)benzene derivatives (which may be considered as supernucleophilic reagents at the neutral carbon atom), corroborate a reaction pathway regarding the electrophilic aromatic substitution different from that reported in Scheme 1. The major difference is the fact that the spontaneous elimination of the proton is the rate-determining step and the attack of the electrophilic reagent occurs in a fast step. Another interesting difference involves the reversibility of the all steps.[8]

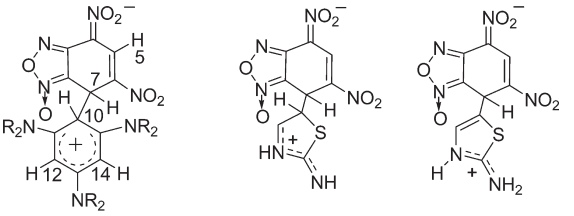
SCHEME 3. Generally Accepted Pathway for S_NAr



SCHEME 4. Plausible Reaction Pathway in S_EAr Reactions



SCHEME 5. First Examples of Detectable and Characterizable Wheland−Meisenheimer Complexes



WM-1a (NR$_2$=piperidinyl)
WM-1b (NR$_2$=morpholinyl)
WM-1c (NR$_2$=pyrrolidinyl)

WM-2 **2**

In Scheme 4, the spontaneous departure of the proton (together with the other steps) may be a reversible process.

Recently,[9] we obtained the first evidence of carbon−carbon Wheland−Meisenheimer (**W**−**M**) complexes (Scheme 5) in the reaction between 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and 4,6-dinitrobenzofuroxan (DNBF), a superelectrophilic reagent at the neutral carbon atom. Zwitterionic adducts **WM**−**1a**−**c** were moderately stable, and their spectroscopic properties were studied mainly by NMR spectroscopy. Adducts **WM**−**1a**−**c** showed, in variable-temperature ^{1}H NMR experiments, an unexpected and interesting behavior. On raising the temperature, the signals related to H-10, H-12, and H-14, well separated at low temperature, became broad until a coalescence situation occurred. This reversible dynamic process was explained hypothesizing the existence, above the coalescence temperature, of a Wheland−Meisenheimer complex in three homomeric structures rapidly exchanging.[9]

Furthermore, we have investigated the system DNBF/2-aminothiazole derivatives[10] which permitted to detect the σ complex **WM**−**2**. However, this complex has proved to be very unstable because it very quickly turns into **2**.

These findings indicate that the C−C coupling between aromatic nucleophilic and electrophilic species can produce zwitterionic **W**−**M** species whose lifetime strongly depends on the combination of the two partners and on their electrophilic and nucleophilic power.

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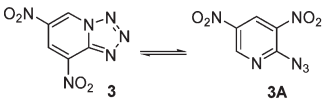
SCHEME 6. Equilibrium between Valence Tautomers 3 and 3A



Relative ratio **3/3A** in different solvents

Solvent	% 3	% 3A
$CDCl_3$	0	100
CD_2Cl_2	10	90
$(CD_3)_2CO$	60	40
CD_3CN	70	30
$(CD_3)_2SO$	94	6

With this consideration in mind, we expected that also the coupling between 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and 4,6-dinitrotetrazolopyridine (**3**) could produce stable **W**−**M** complexes. In fact, within the electrophilic scale developed by Mayr,[11] compound **3** is considerably more powerful electrophile than DNBF.[12] 4,6-Dinitrotetrazolopyridine shows an equilibrium with the azido form **3A**. The position of the ring−chain tautomerism of Scheme 6 strongly depends[13] on the used solvent; however, **3** is a largely better electrophilic reagent than **3A**.

Herein we report about the reactions between some 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and 4,6-dinitrotetrazolopyridine (**3**) that provide evidence of formation of the corresponding carbon−carbon **W**−**M** complexes, giving us not only a further example of these very rarely observed intermediates but also the possibility to deepen and elucidate, through NMR spectroscopy, their behavior observed in VT NMR experiments and to gain precious information on the reversibility of the reaction.

Results and Discussion

Addition of a solution, cooled at −30 °C, of 4,6-dinitrotetrazolopyridine (**3**) in CD_2Cl_2 (or in $CDCl_3$, as well as in CD_3CN) to a solution of an equimolar amount of 1,3,5-tris(*N*,*N*-dialkylamino)benzenes (**4**−**6**), dissolved in the same solvent and precooled at the same temperature, produced an orange solution and the appearance (in the ^{1}H NMR spectrum) of new signals which agree with the **W**−**M** structure of complexes **7**−**9** or of their parents **7A**−**9A**. When the reaction was carried out in acetone at − 30 °C, the zwitterionic complexes were separated, as solid, from the solution.

In $CDCl_3$ the azido form **3A** is reported[13] to be a largely more populated form (about 100%) with respect to the tetrazole form **3**, which may be considered present in a very low percent. In order to discriminate between forms **7**−**9** and **7A**−**9A** we analyzed the complexes by IR spectrophotometry.

FT-IR spectral data of **W**−**M** complexes were in accordance with the ring-closed form. In fact, no absorption bands in the FT-IR spectrum of the azido group (in the 2100−2170 cm^{-1} region) were detectable in spectra recorded in different solvents. Structures **7**−**9** are more populated forms (the only detectable forms) with respect to **7A**−**9A**.

Regarding the formation of complexes **7**−**9**, there are two main possibilities: (1) The azido form **3A** is the reactive specie and the ring closure occurs (by a ring−chain tautomeric equilibrium) after the coupling of the reagents by a carbon−carbon bond formation. (2) The less populated tetrazolic isomer **3** reacts and remains in **W**−**M** complexes **7**−**9** in the ring closed form.

Owing to the electronic effect of the azido group, the second possibility represents the more probable reaction pathway. In fact, the electron-withdrawing effect of the azido group in **3A** is moderate,[14] as expressed by σ_{meta} value (0.27) of the azido substituent, while the resonance electronic effect is an electron donating effect, as expressed by σ_R value (−0.35).

This is a case which concerns a less populated form (the tetrazolo form) as the more reactive form.

Dynamic Behavior of Complexes 7−**9.** Investigation on compounds **7**−**9** regarding the effect of the change of the temperature by NMR spectroscopy reveals some interesting features.

^{1}H NMR spectra, recorded at low temperature (below − 30 °C), of compounds **7**−**9** showed four signals in the region between δ = 4.33 ppm and 6.56 ppm (see Table 1). Three of these signals belong to the dialkylaminobenzene moiety, while the last is due to the H-7 proton of the dinitrotetrazolopyridine moiety that presents the other signal (H-5) at low field, in the characteristic region of aromatic protons. Direct proton to carbon correlation experiments (gHSQC sequence), performed at the same temperature, confirmed the structure of complexes **7**−**9** (see Figure 1 and Figure SI-2, Supporting Information). In the case of complex **7** in CD_2Cl_2, chosen as an example, the correlation experiment shows that the proton signals at 5.01 and 5.35 ppm are connected to the two carbon atoms indicated as C-12 and C-14, whose ^{13}C signals fall at 91.5 ppm, in a range typical of the sp^2 carbon signals of 1,3,5-tris(*N*,*N*-dialkylamino) benzene. The two remaining proton signals at 6.47 and 4.76 ppm show direct correlation with carbon signals at 63.38 and 41.63 ppm, respectively, providing clear evidence for the sp^3 hybridization of these carbon atoms of the two partners.

The apparent incongruence of two anisochronous hydrogens (and carbons) for the two CH signals C-12 and C-14 of the complexes **7**−**9** can be easily explained because of the presence of an asymmetric carbon center (C-7) and a "C_2-centre" (C-10):[15] under these conditions, the two CH are diastereotopic, so displaying anisochronous signal both in ^{1}H and ^{13}C spectra. The same effect can be observed on the aromatic quaternary carbons that show three separated signals, as well as on the piperidinyl, morpholinyl, and pyrrolidinyl rings (see Tables 1 and 2).

On raising the temperature, ^{1}H NMR spectra of compounds **7**−**9** in CD_2Cl_2 showed a gradual line broadening of

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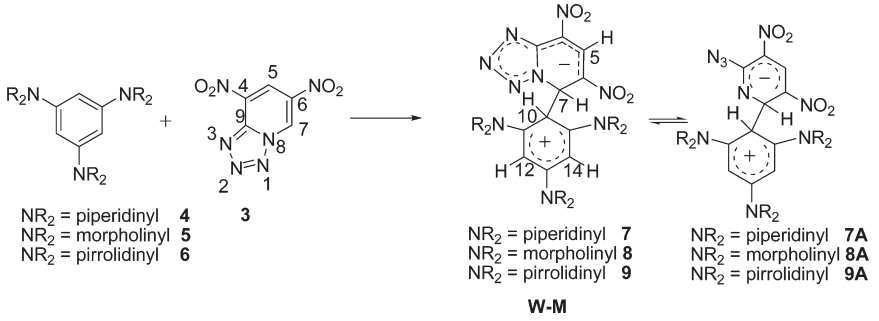
TABLE 1. ^{1}H NMR Spectral Data of Starting Reagents and of W−M Complexes 7−9 in CD_2Cl_2

compd	T (°C)	δ_{H5}	δ_{H7}	δ_{H10}	δ_{H12}[a]	δ_{H14}[a]	δ_{NCH2}	$\delta_{otherCH2}$
3	+25	10.16 (d, J = 1.9 Hz)	9.37 (d, J = 1.9 Hz)					
3A	+25	9.09 (d, J = 2.4 Hz, H_4)	9.35 (d, J = 2.4 Hz, H_6)					
4	+25			6.00			3.00−3.10 (m, 12 H)	1.46−1.57 (m, 6 H), 1.58−1.72 (m, 12 H)
5	+25			6.00			3.05−3.12 (m, 12 H)	3.65−3.90 (m, 12 H)
6	+25			5.18			3.19−3.27 (m, 12 H)	1.85−2.09 (m, 12 H)
7	−35	8.80	6.47	4.76	5.35	5.01	2.87−4.23 (m, 12 H)	1.33−2.03 (m, 18 H)
7	+25	8.81	6.52	5.08	5.08	5.08	3.20−3.75 (m,12 H)	1.51−1.80 (m,18 H)
8	−40	8.87	6.55	4.74	5.40	5.02	2.85−3.38 (m, 12 H)	3.38−4.42 (m, 12H)
8	0	8.88	6.70	5.53	5.53	5.53	2.87−3.53 (m, 12 H)	3.60−4.05 (m, 12 H)
9	−30	8.69	6.56	4.39	4.33	4.69	2.77−3.55 (m,10 H), 3.67−3.74 (m, 1 H), 4.14−4.24 (m, 1 H)	1.73−2.22 (m, 12 H)
9	+25	8.70	6.62	4.48	4.48	4.48	2.78−3.92 (m,12 H)	1.83−2.26 (m, 12 H)

[a]Interchangeable assignements.

SCHEME 7. Reactions between Compound 3 and Supernucleophilic Carbon Reagents 4−6



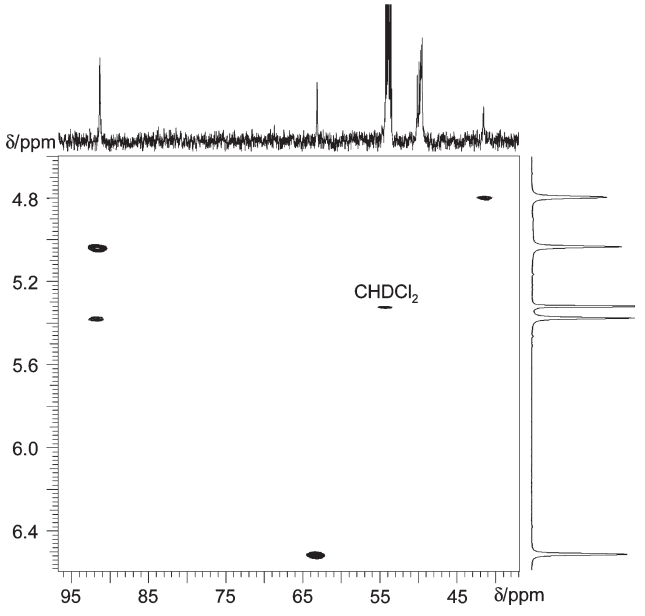


FIGURE 1. gHSQC spectrum of **W−M** complex **7** in CD_2Cl_2 at −40 °C.

the three signals ascribed to the hydrogen atoms of the trisaminobenzene moiety, until the coalescence was reached (at +15, −20, and +25 °C for compounds **7**, **8**, and **9**, respectively). A further increas of the temperature caused a dynamically averaged signal. The same dynamic process was observed also in the ^{13}C spectra. Both in the ^{1}H NMR and in the ^{13}C NMR spectra, the fourth signal, belonging to the H-7 (or C-7) of the dinitrotetrazolopyridine ring, was always sharp on varying the temperature. The VT experiment carried out in acetonitrile for compound **7** showed the same behavior.

It is interesting to observe that the spectra, recorded at −40 °C, of compounds **7**−**9** prepared by addition of the reagents at this temperature are identical to those obtained after mixing the reagents at room temperature (+25 °C) and cooling the mixture at −40 °C. A gradual heating of this mixture again caused the coalescence described above, and the "heat-up/cooling off" cycle was repeated many times, always giving the same behavior.

This observed phenomenon indicates a reversible process, probably arising from a dynamic process similar to that already reported for **WM−1a−c**, that can be explained assuming the existence, above the coalescence temperature, of a Wheland−Meisenheimer complex in three homomeric structures $\mathbf{W-M_{A-C}}$ (see Scheme 8) with bonds C-7/C-10, C-7/C-12, and C-7/C-14 rapidly exchanging into each other.

Line shape simulation treatment of the proton spectra of **7**−**9** was performed at various temperatures (Figures SI-1 and SI-3, Supporting Information), and by means of the Eyring equation[16] the thermodynamic activation parameters were derived. These parameters are collected in Table 3, together with those obtained for **WM-1a−c** complexes.[9] As already observed for **WM-1a−c**, compounds

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TABLE 2. ^{13}C NMR Spectral Data of Starting Reagents and of W−M Complexes 7−9 in CD_2Cl_2

compd	T (°C)	$\delta_{C4,C6,C9}$[a]	δ_{C5}	δ_{C7}	δ_{C10}[a]	$\delta_{C12,C14}$[a]	$\delta_{C11,C13,C15}$[a]	δ_{NCH2}	$\delta_{otherCH2}$
3[b]	+25	148.27 (C_9), 144.36 (C_6), 138.42 (C_4), 131.83 (C_7), 125.88 (C_5)							
3A	+25	154.10 (C_2), 148.68 (C_6), 140.10 (C_5), 134.23 (C_3), 131.60 (C_4)							
4	+25				99.32	99.32, 99.32	154.80	52.15	25.29, 26.94
5	+25				97.64	97.64, 97.64	154.06	50.72	67.69
6	+25				86.67	86.67, 86.67	150.67	48.46	26.12
7	−35	112.49, 116.97, 148.79	133.87	63.38	41.63	91.49 (2 sig overl.)	158.85, 159.83, 160.84	49.54, 49.74, 49.88, 50.12 (2 sig. overl.), 50.31	24.10, 24.48, 24.56, 24.79, 25.54, 26.43, 26.62, 26.93, 27.53
7	+25	113.44, 117.53, 148.79	133.76	64.55		92.35[c]	160.73	50.39	24.72, 26.69
8	−40	112.62, 116.07, 148.87	133.78	64.32	41.16	92.39 (2 sig. overl.)	159.96, 161.21, 161.15	47.84, 48.23, 48.46 (2 sig. overl.), 48.83, 49.18	65.26 (2 sig. overl.), 66.09, 66.48 (2 sig. overl.), 66.91
9	−30	112.86, 116.45, 149.73	132.87	61.31	47.01	89.05, 90.28	154.65, 155.54, 158.69	49.26, 49.39, 49.49, 49.63, 49.66, 49.92	25.16, 25.20, 25.32 (2 sig. overl.), 26.23, 26.48
9	+25	113.47, 116.61, 150.23	133.16	62.07		90.88[c]	158.80	50.00	25.88

[a]Interchangeable assignements. [b]In acetone-d_6. [c]Broad signal.

SCHEME 8. Dinamic Process between Homomeric Forms of W−M Complex

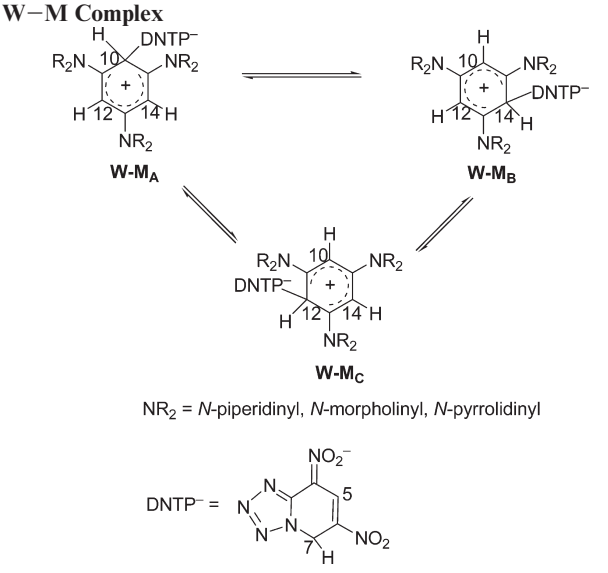


TABLE 3. Thermodynamic Activation Parameters for the Process Shown in Scheme 8

entry	W−M complex[a]	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)
1	**WM-1a**[b]	17.6 ± 0.2	18 ± 6
2	**WM-1b**[b]	10.4 ± 0.3	10 ± 6
3	**WM-1c**[b]	22.7 ± 0.2	32 ± 5
4	**7**	18.4 ± 0.2	17 ± 6
5	**8**	14.7 ± 0.3	10 ± 6
6	**9**	19.3 ± 0.2	17 ± 6
7	**7**[c]	16.0 ± 0.4	6 ± 3

[a]In CD_2Cl_2. [b]Data from ref 9. [c]In CD_3CN.

7−**9** show a positive $\Delta S^{\ddagger}$, suggesting a mechanism in which the C-7/C-10 bond of the **W**−**M** complex is broken in an important step.

In agreement with that, complexes involving morpholine derivatives (entries 2 and 5) show thermodynamic activation parameters lower than those of piperidine derivative, according to the lower basicity of nitrogen in morpholine with respect to the basicities of the other considered amines ($pK_{a\ piperidine}$ = 18.92, $pK_{a\ morpholine}$ = 16.61 and $pK_{a\ pyrrolidine}$ = 19.58, in CH_3CN[17]) which enhance the ability of **WM**−**1b** and **8** to break the C-7/C-10 bond in the leaving group departure. In other words, the difference observed in VT NMR experiments between the two cases reflects the different electron-releasing abilities of the nitrogen atoms in piperidine with respect to those in morpholine.

The trend reported in Table 3, regarding the three triamino derivatives, is similar for both electrophilic substrates DNBF and **3**. In addition, CD_3CN (which is a more polar solvent than CD_2Cl_2) shows a less relevant importance of the bond-breaking step toward separated partners which, probably, are interacting in a π complex; see below.

Reversibility of Formation of Complexes 7−9. Evidence of the reversibility of the formation of complexes **7**−**9** is provided by the experimental finding reported in the following sections.

(17) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005–5010.

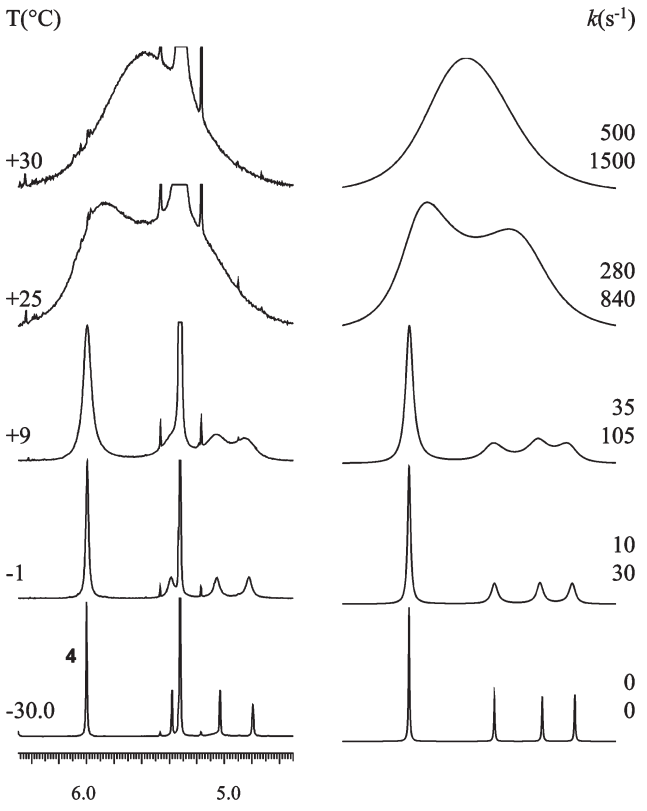


FIGURE 2. (Left) experimental variable-temperature ^{1}H NMR spectra in CD_2Cl_2 of compound **7** in the presence of an excess of **4**. (Right) line-shape simulation obtained with the rate constant indicated.

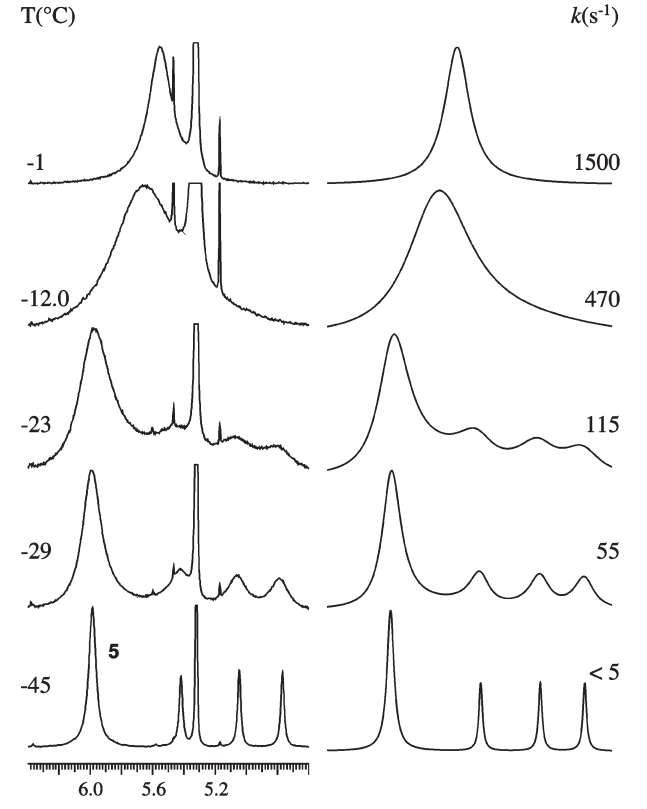
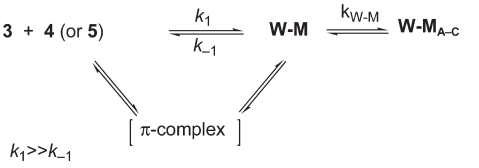
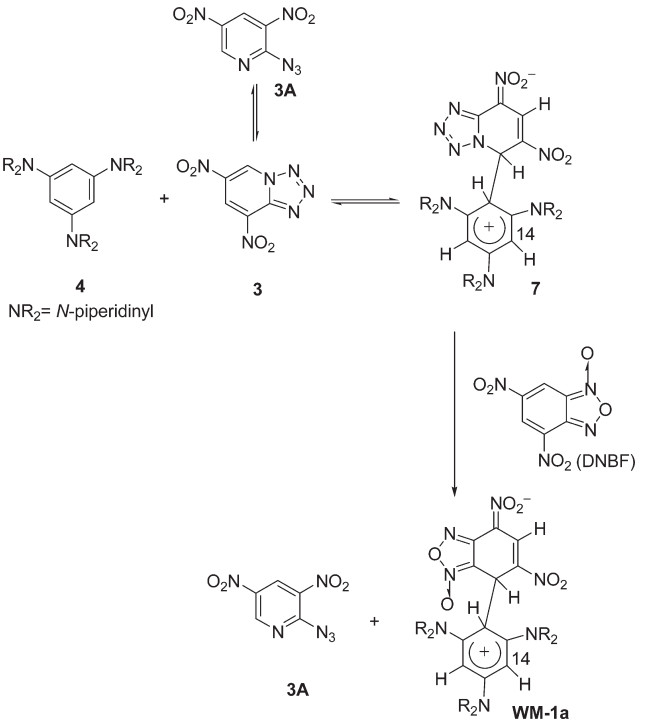


FIGURE 3. (Left) experimental variable-temperature ^{1}H NMR spectra in CD_2Cl_2 of compound **8** in the presence of an excess of **5**. (Right) line-shape simulation obtained with the rate constant indicated.

SCHEME 9. Equilibria Involving W−M Complexes



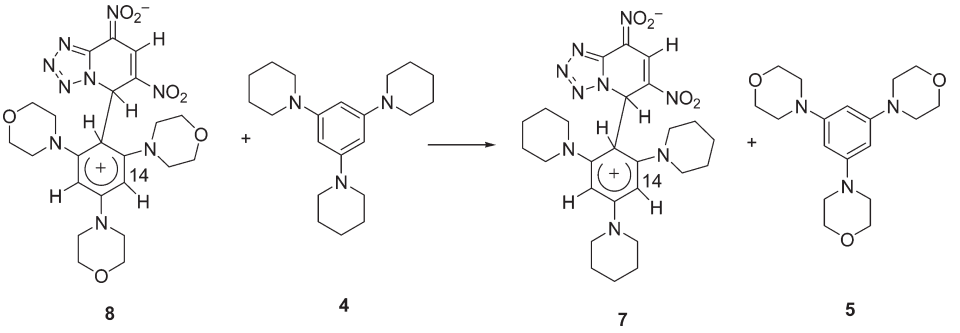
SCHEME 10. Exchange of the Electrophilic Partner



1. Variable-Temperature ^{1}H NMR Experiments in the Presence of Excess of Nucleophilic Reagent. In order to achieve more information about the exchange process, an excess of triaminobenzene derivative was employed in the preparation, directly in the NMR tube, of new samples of **7** and **8** in CD_2Cl_2. The ^{1}H NMR spectrum of the obtained solutions, prepared and cooled to −30 and −45 °C, respectively, was identical to that already observed in the equimolar case, with the obvious exception of the presence of the signal corresponding to the excess of base (see the lowest trace of Figures 2 and 3 in the case of **7** and **8**, respectively).

On raising the temperature, the dynamic process involved four signals, the three signals of the hydrogen atoms of the trisaminobenzene moiety of the **W−M** complex and the signal of the aromatic hydrogen atoms of the base, until a single averaged signal was observed (see the upper traces of Figures 2 and 3), and this indicated that the neutral base (1,3,5-tris(*N*-piperidinyl)benzene (**4**) in **7** and 1,3,5-tris(*N*-morpholinyl)benzene (**5**) in **8** was involved somehow in the exchange process. Line shape simulation (Figures 2 and 3) of the proton spectra of **7** and **8** was performed at various temperatures. A different behavior was experimentally observed. In the case of **7**, a satisfactory simulation of the spin system was achievable only when two different constants were used: the three lines

SCHEME 11. Exchange of the Nucleophilic Partner



corresponding to the complex **7** exchanged into each other with k_{W-M} rate constants that were identical, within the experimental errors, to that determined in absence of the base excess. The line of the free base exchanged with the three signals with a different rate constant. Line shape simulation of the behavior of **8** in the presence of free 1,3,5-tris(*N*-morpholinyl)benzene was obtained using only one rate constant,[18] corresponding to the exchange of the signal of the free base with each of the three lines of the complex **8**.

The observed behavior may be elucidated on the basis of two main processes involving the neutral starting materials, the **W**−**M** complex, and a further complex (not fully detected and characterized)[19] such as a noncovalent, π-like complex. Scheme 9 is a tentative picture of the whole interactions.

The dynamic process involving the covalent **W**−**M** complex present, above the coalescence temperature, in its homomeric forms represented as $\mathbf{W-M_{A-C}}$ regards an internal motion relative to two partners, as shown in Scheme 8.

The exchange process observed (in the chemical shift range from 4.0 to 7.0 ppm) between the signals of the **W**−**M** complex, already involved in its own internal equilibrium, and that of the free nucleophile, suggests the existence of one or more equilibria between **W**−**M** and **4** (or **5**). This phenomenon, evident when the nucleophile is present in excess, may be conceived to come through noncovalent π-like complexes.[19] In any case, the NMR data led us to exclude the possibility of radical incursions.[20]

2. Exchange of the Electrophilic Partner. Further evidence of the reversibility of the process of formation of compounds **7**−**9** was obtained by adding an equimolar amount of 4,6-dinitrobenzofuroxane to a solution containing the complex **7** in CD_2Cl_2 (Scheme 10).

Immediately, the ^{1}H NMR spectrum of the resulting mixture showed a disappearance of the signals of **7** and concomitant appearance of signals of complex **WM**−**1a** together with those of the azido form **3A**. This finding clearly indicates that complex **7** undergoes exchange of the electrophile (**3** displaced by the DNBF).

3. Exchange of the Nucleophilic Partner. When the nucleophilic power of the partner is moderate, such as in the case of morpholine derivative **5**, the reaction carried out in hexadeuteroacetone at room temperature (by using **3** and **5** in equimolar ratio) produced an orange solid (powdery) which was collected by filtration and divided in two parts; one of these was dissolved in CD_2Cl_2 and the other in $CDCl_3$. Both solutions were analyzed through ^{1}H NMR at low temperature (−30 °C). In CD_2Cl_2, the spectrum revealed the presence of a relevant amount of complex **8**, while, probably because of different solvation energies of complex **8** and related starting materials, in chloroform the only signals recorded by ^{1}H NMR spectroscopy were related to the starting electrophile, present in 95% in its form **3A**[13] and to the starting nucleophile **5**, together with a small amount of **8**. The fact that, when dissolved in $CDCl_3$, the complex **8** dissociates into starting reagents constitutes a further indication of the reversibility of the coupling reaction.[19] When an equimolar amount of **4** was added to this solution, kept at −20 °C, the signals related to **8** disappeared and those of **7**, arising from **4**, appeared. The exchange of the nucleophilic partner was observed also in the CD_2Cl_2 solution. In both cases, the chemical shifts and the coalescence temperature of the complex obtained after the addition of **4** were in agreement with those of **7**. These findings are a further indication of the presence of an equilibrium between the two partners (Scheme 11).

Conclusions

The following conclusions can be reached. The present work reports further evidence of the formation of C−C zwitterionic complexes (called **W**−**M** by us). Formation of such as **W**−**M** complexes reduces the importance of tassonomic classification of reactions (is the present reaction in the field of the electrophilic aromatic substitution or in the field of the nucleophilic aromatic substitution reactions?) which, obviously, is a conventional classification. Exchange of the nucleophilic and the electrophilic parts of the **W**−**M** complexes strongly indicates that this reaction is a reversible reaction. In agreement with the reversibility of the **W**−**M** formation, the dynamic behavior of the complexes clearly

(18) This is probably due to the different solubility and, consequently, concentration of the partners in solution.

(19) Evidence of a possible $\pi-\pi$ charge-transfer complex was obtained in the case of compound **WM-1b**. On gradual warming of a CD_2Cl_2 solution of this compound, we observed, above the coalescence temperature (−40 °C), a spectrum corresponding to its homomeric forms.[9] When the solution was warmed at about 25 °C, spectral data are different from those registered above the coalescence temperature and are in agreement with a $\pi-\pi$ charge-transfer complex between DNBF and 1,3,5-tris(*N*-morpholinyl)benzene. This hypothesis is supported by the fact that, on cooling the solution to −50 °C again, a complete reversibility toward the formation of **WM-1b**, passing through the coalescence situation, was observed. In addition, when the spectrum of a $CDCl_3$ solution of **WM-1b** was recorded at 50 °C, the signals of a mixture of DNBF and compound **5**, the original starting materials, were observed.

(20) The presence of even a very small amount of radical species would render the NMR lines very broad due to fast relaxation.

indicates the shift of the electrophilic moiety from one carbon to another (as a 1−3 shift). This shift probably occurs via a π complex which may be (owing the experimental behavior and the nature of involved reagents) a simple donor/acceptor complex.

Experimental Section

Preparation of Compounds 7−9. General Procedure. To a solution of 4,6-dinitrotetrazolopyridine (**3**, 0.015 g, 0.071 mmol) in acetone (2.0 mL), cooled at −30 °C, was added 0.071 mmol of 1,3,5-tris(*N*,*N*-dialkylamino)benzene derivative (**4**, **5**, or **6**). Immediately a red-brick color solid precipitated. The solid, isolated by filtration, when heated in a melting point apparatus, gradually darkened (from 158 to 177 °C, from 122 to 166 °C, and from 162 to 192 °C for compounds **7**, **8**, and **9**, respectively) and then decomposed. However, their ^{1}H and ^{13}C NMR spectra are identical to those obtained for compounds **7**−**9**, directly formed in the NMR tube, recorded at 25 °C. In all cases, the yield of the complex recovered by filtration was about 50%, and the ^{1}H NMR analysis of the remaining solution revealed the presence of the same complex. The IR spectra (KBr) of solids **7**−**9** do not show typical bands of the azido group in the 2100−2170 cm^{-1} region (see the Supporting Information). The NMR spectral data of compounds **7**−**9** in various solvents and at different temperatures are collected in Tables 1 and 2 and Table SI-1 (Supporting Information).

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Supporting Information Available: General experimental details, additional spectroscopic data, and copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.