JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 153–159 (1993)

π-COMPLEXES OF NAPHTHALENE AND ITS DERIVATIVES WITH NITROSONIUM CATION

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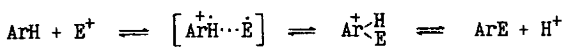
^1H, ^{13}C, and ^{15}N NMR studies, including the use of the ^{13}C NMR deuterium perturbation method, showed that the interaction between naphthalene or its methylated derivatives and the nitrosonium cation result in the formation of π-complexes. The chemical behaviour of these complexes was investigated; in particular, their ability to be converted into binaphthyl derivatives was established.

INTRODUCTION

The nitrosonium cation is a powerful oxidant,[1,2] and its interaction with bi- and polynuclear arenes having low ionization potentials[3] usually leads to radical cation salts or the products of their reactions.[2,4] Thus, naphthalene reacts with nitrosonium salts in trifluoroacetic acid at room temperature to form initially a radical cation monomer, then a dimer and finally a mixture of hydrocarbons, $C_{10}H_7–(C_{10}H_6)_n–C_{10}H_7$.[2,4,5] One can assume that the single electron transfer (SET) between the aromatic substrate and NO^+ is preceded by π-complex formation.[2] However, the ability of bi- and polynuclear arenes to form π-complexes with NO^+ has scarcely been investigated.[6–8] However, data on such complexes are necessary in order to gain deeper insight into the mechanisms of a wide range of electrophilic reactions,[9–12] including the widely discussed SET mechanism[1,12–14] (Scheme 1).



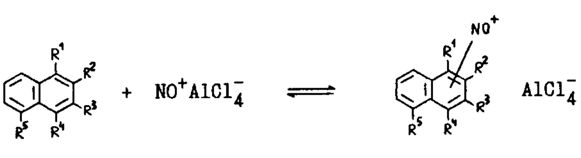
$$ArH + E^+ \rightleftharpoons \left[\overset{+\cdot}{ArH}\cdots\dot{E}\right] \rightleftharpoons \overset{+}{Ar}{<}^{H}_{E} \rightleftharpoons ArE + H^+$$

Scheme 1

In this work, we studied π-complexes of naphthalene and its methylated derivatives with NO^+ as a cationic electrophile.

RESULTS AND DISCUSSION

The complexes **1a–i** were generated by the interaction of $NO^+AlCl_4^-$ with naphthalene and its methyl-substituted derivatives (**2a–i**) in SO_2 at −70 to −80 °C (Scheme 2).



2a–i **1a–i**

(**a**) $R^1 = R^2 = R^3 = R^4 = R^5 = H$
(**b**) $R^1 = CH_3$, $R^2 = R^3 = R^4 = R^5 = H$
(**c**) $R^2 = CH_3$, $R^1 = R^3 = R^4 = R^5 = H$
(**d**) $R^1 = R^2 = CH_3$, $R^3 = R^4 = R^5 = H$
(**e**) $R^1 = R^3 = CH_3$, $R^2 = R^4 = R^5 = H$
(**f**) $R^1 = R^4 = CH_3$, $R^2 = R^3 = R^5 = H$
(**g**) $R^1 = R^5 = CH_3$, $R^2 = R^3 = R^4 = H$
(**h**) $R^4 = R^5 = CH_3$, $R^1 = R^2 = R^3 = H$
(**i**) $R^2 = R^3 = CH_3$, $R^1 = R^4 = R^5 = H$

Scheme 2

The π-complex character of **1a–i** is indicated by their ^1H NMR spectra (Table 1), particularly the relatively small down-field shifts of the signals of methyl and aromatic protons in comparison with the corresponding precursors (**2a–i**). It should be noted that for σ-complexes (naphthalenium ions) the shifts are much larger.[15] The equivalence of CH_3 groups of π-complexes **1f–i** observed in the ^1H NMR spectra may be explained by the fast (on the ^1H NMR time scale) inter- or intramolecular migration of the NO^+ group from

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0894–3230/93/030153–07$08.50

Received 25 June 1992
Revised 7 September 1992

Table 1. ^1H NMR data for the complexes **1a–i** and the neutral precursors **2a–i** in SO_2 solution

Compound	Temperature (°C)	Mole ratio, ArH : $NO^+AlCl_4^-$	Chemical shifts (δ, ppm)	
			CH_3[a]	H_{arom}
1a	−70	1 : 1		7·7–8·1 m, 8·2–8·5 m
	−60	1 : 1		7·7–8·1 m, 8·2–8·6 m
	−20	1 : 1		7·7–8·8 m, br
	−70	1 : 2		7·7–8·1 m, 8·1–8·5 m
	−70	1 : 5		7·7–8·1 m, 8·1–8·4 m
2a	−70	–		7·4–7·7 m, 7·8–8·1 m
1b	−60	1 : 1	2·97	7·7–8·7 m
	−40	1 : 1	3·03	7·7–8·7 m
	−20	1 : 1	3·07	7·7–8·8 m, br
2b	−60	–	2·60	7·3–8·2 m
1c	−70	1 : 1	2·66	8·36 d, $H^{4(3)}$; 8·18 s, H^1 7·69 d, $H^{3(4)}$; 7·7–8·2, H^5–H^8
2c	−70	–	2·47	7·62 s, H^1; 7·3–7·9 m, H^3–H^8
1d	−70	1 : 1	2·58, 2·76	7·7–8·5 m
2d	−70	–	2·44, 2·52	7·3–8·1 m
1e	−60	1 : 1	2·59, 2·88	7·66 s, $H^{2(4)}$; 7·8–8·5 m, $H^{4(2)}$, H^5–H^8
	−30	1 : 1	2·67, 2·98 br	7·69 s, br, $H^{2(4)}$; 7·8–8·5 m, br $H^{4(2)}$, H^5–H^8
	−60	1 : 8	2·56, 2·84	7·57 s, $H^{2(4)}$; 7·7–8·4 m, $H^{4(2)}$, H^5–H^8
2e	−60	–	2·36, 2·56	7·22 s, $H^{2(4)}$; 7·4–8·1 m, $H^{4(2)}$, H^5–H^8
1f	−60	1 : 1	3·06	7·65 s, $H^{2,3}$; 7·8–8·3 m, H^5–H^8
2f	−60	–	2·63	7·23 s, $H^{2,3}$; 7·5–8·1 m, H^5–H^8
1g	−60	1 : 1	2·78	7·6–8·6 m
2g	−20	–	2·64	7·3–8·1 m
1h	−60	1 : 1	3·03	7·3–8·2 m
2h	−60	–	2·90	7·2–7·8 m
1i	−60	1 : 1	2·45	8·35 s, $H^{1,4}$; 7·7–8·2 m, H^5–H^8
2i	−40	–	2·34	7·62 s, $H^{1,4}$; 7·3–7·9 m, H^5–H^8

[a] CH_3 group signals are singlets.

one position of the aromatic system to another. When the ArH: $NO^+AlCl_4^-$ ratio and the temperature are varied, the chemical shifts change only slightly, indicating a virtually complete shift of the equilibrium (Scheme 2) towards the π-complexes **1** (c.f. Ref. 7).

In order to obtain additional information regarding the nature of the complexes **1**, we made use of ^{15}N NMR spectroscopy. When 1-methyl-, 1,3-dimethyl- or 1,4-dimethylnaphthalene is added to a solution of the labelled salt $Na^{15}NO_2$ (mole ratio ArH: $Na^{15}NO_2 = 1:1$) in FSO_3H, the ^{15}N NMR spectra no longer show the signal of $^{15}NO^+$ ($\delta_{-70\,°C} = 2·6$ ppm) (c.f. Ref. 16), but contain the signals at 75·8, 76·6 and 144·3 ppm at lower field from external CH_3NO_2, respectively. Since the literature contains no ^{15}N NMR data for π-complexes of NO^+ with unsaturated systems,[17,18] the reliable assignment of these signals to π-complexes is hardly possible. It is important, however, that the ^{15}N chemical shifts found differ greatly from those for the NO group σ-bonded with the carbon atom in RNO compounds (430–600 ppm).[17,18] The difference in ^{15}N chemical shifts for π-complexes **1b**, **e** and **1f** seems to be due to difference in the structure of these complexes, i.e., the absence of one of CH_3 groups in the α-position of complexes **1b**, **e**.

Additional evidence for the generation of π-complexes was obtained by ^{13}C NMR experiments (Table 2). The signals of carbon atoms C^1–C^{8a} were assigned on the basis of their relative intensities and multiplicities, taking into account that in aromatic systems the spin–spin coupling constants for coupling across three bonds ($^3J_{CH}$) are usually greater than those across two bonds ($^2J_{CH}$)[19,20] (cf. Refs 21 and 22). It is interesting that the spin–spin coupling constant values ($^1J_{CH}$) are close to the value characteristic of the sp^2-hybridized carbon atom,[19,20] and consequently the naphthalene rings of the complexes are planar.

It is well known that the chemical shifts of the same type of carbon atoms in π-electron systems correlate with the π-electron deficiency.[15] The calculated values of the total positive π-charge on atoms C^1–C^{8a}

Table 2. ^{13}C NMR data for complexes **1a–i** in SO_2 at −70 °C

Complex	^{13}C chemical shifts (δ, ppm) and coupling constants ($^{1}J_{CH}$, Hz) CH₃	C¹	C²	C³	C⁴	C⁵	C⁶	C⁷	C⁸	C⁴ᵃ	C⁸ᵃ	$\frac{\Delta\Sigma(\delta C^1-\delta C^4)^a}{\Delta\Sigma(\delta C^5-\delta C^8)}$	$q_\pi^+(C^1\text{–}C^{8a})^a$
1a	–	134·2^{b}	132·2^{b}	132·2^{b}	134·2^{b}	134·2^{b}	132·2^{b}	132·2^{b}	134·2^{b}	134·0	134·0	$\frac{25{\cdot}2}{25{\cdot}2}$	0·34
1b	18·9 (124)	151·5	135·6^{b} (168)	132·5 (169)	138·7^{b} (166)	130·7^{b} (164)	131·7^{c} (165)	132·0^{c} (165)	126·1^{c} (164)	133·7^{d}	133·0^{d}	$\frac{44{\cdot}9}{16{\cdot}2}$	0·40
1c	20·2	138·9^{b}	147·5	134·0^{c}	138·5^{b}	131·9^{c}	130·8^{c}	130·8^{c}	132·0^{c}	132·8^{d}	134·1^{d}	$\frac{40{\cdot}6}{18{\cdot}6}$	0·39
1d	14·4 20·4	153·3^{b}	152·2^{b}	134·9	141·2	130·9	132·4^{c}	133·0^{c}	126·2	134·3^{d}	134·5^{d}	$\frac{60{\cdot}9}{19{\cdot}7}$	0·54
1e	19·4 20·1	153·9^{b}	136·0^{c}	148·6^{b}	141·1^{c}	130·4^{b}	132·1^{b}	132·2^{b}	125·8^{b}	132·6^{d}	134·1^{d}	$\frac{56{\cdot}2}{16{\cdot}9}$	0·47
1f	19·0 (129)	153·7	135·9 (164)	135·9 (164)	153·7	126·4^{b} (164)	132·0^{b} (164)	132·0^{b} (164)	126·4^{b} (164)	132·8	132·8	$\frac{60{\cdot}8}{15{\cdot}6}$	0·49
1g^{e}	18·7 (127)	145·5	134·3^{b} (164)	132·1 (163)	129·9^{b} (163)	145·5	134·3^{b} (164)	132·1 (163)	129·9^{b} (163)	133·5	133·5	$\frac{36{\cdot}2}{36{\cdot}2}$	0·49
1h^{f}	24·9	147·0	137·6^{b}	131·6	135·5^{b}	135·5^{b}	131·6	137·6^{b}	147·0	135·8^{d}	133·3^{d}	$\frac{32{\cdot}7}{32{\cdot}7}$	0·42
1i	18·5	141·4	146·3^{b}	146·3^{b}	141·4	129·3^{c}	131·7^{c}	131·7^{c}	129·3^{c}	133·5^{b}	133·5^{b}	$\frac{47{\cdot}2}{16{\cdot}8}$	0·42

[a] The values were calculated based on comparison of the chemical shifts of C^i atoms of π-complexes **1** and the coresonding precursors **2**. It was taken to be 160 ppm per unit of π-charge.

[b–d] The values should possibly be reversed.

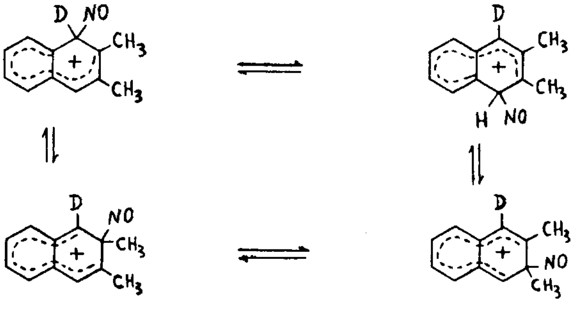
[e] At −75 °C.

[f] At −80 °C.

[$q_\pi^+(C^1\text{–}C^{8a})$] in complexes **1** (Table 2) are essentially smaller than those for naphthalenium ions[15] and depend slightly on the number and positions of methyl groups. A comparison of the total change of chemical shifts of methylated and non-methylated ring carbons of the π-complexes **1b**, **c**, **d**, **e** and **i** indicates that the $\Delta\Sigma(\delta C^1 - \delta C^4)$ values are considerably larger than $\Delta\Sigma(\delta C^5 - \delta C^8)$. This may be explained by preferential bonding of NO^+ with methylated aromatic rings.

We obtained further evidence of π-complex character of ions **1** using the ^{13}C NMR isotopic perturbation method.[23,24] Addition of the salt $NO^+AlCl_4^-$ to a suspension of 1-deuterio-2,3-dimethylnaphthalene in SO_2 resulted in the formation of a complex whose ^{13}C NMR spectrum shows a slight isotopic effect of $C^{1,4}$ signals (δ^{-80} C = 0·35 ppm). This excludes the mechanisms of fast (on the NMR time scale) interconversion of the corresponding σ-complexes, for example, according to Scheme 3.[15]

Thus, the data obtained indicate the π-complex nature of the ions formed in the interaction of naphthalene and its methylated derivatives with nitrosonium cation.



Scheme 3

As mentioned above, at room temperature the NO^+ cation oxidizes naphthalene to the corresponding radical cation.[2,4] In the case of methylated naphthalenes, a similar process might be expected at a lower temperature. Indeed, when the temperature was raised from −60 or −70 °C to −30 or −50 °C, the ^{1}H NMR spectra of complexes **1a–i** showed signal broadening (up to their 'disappearance'), which might be due to the

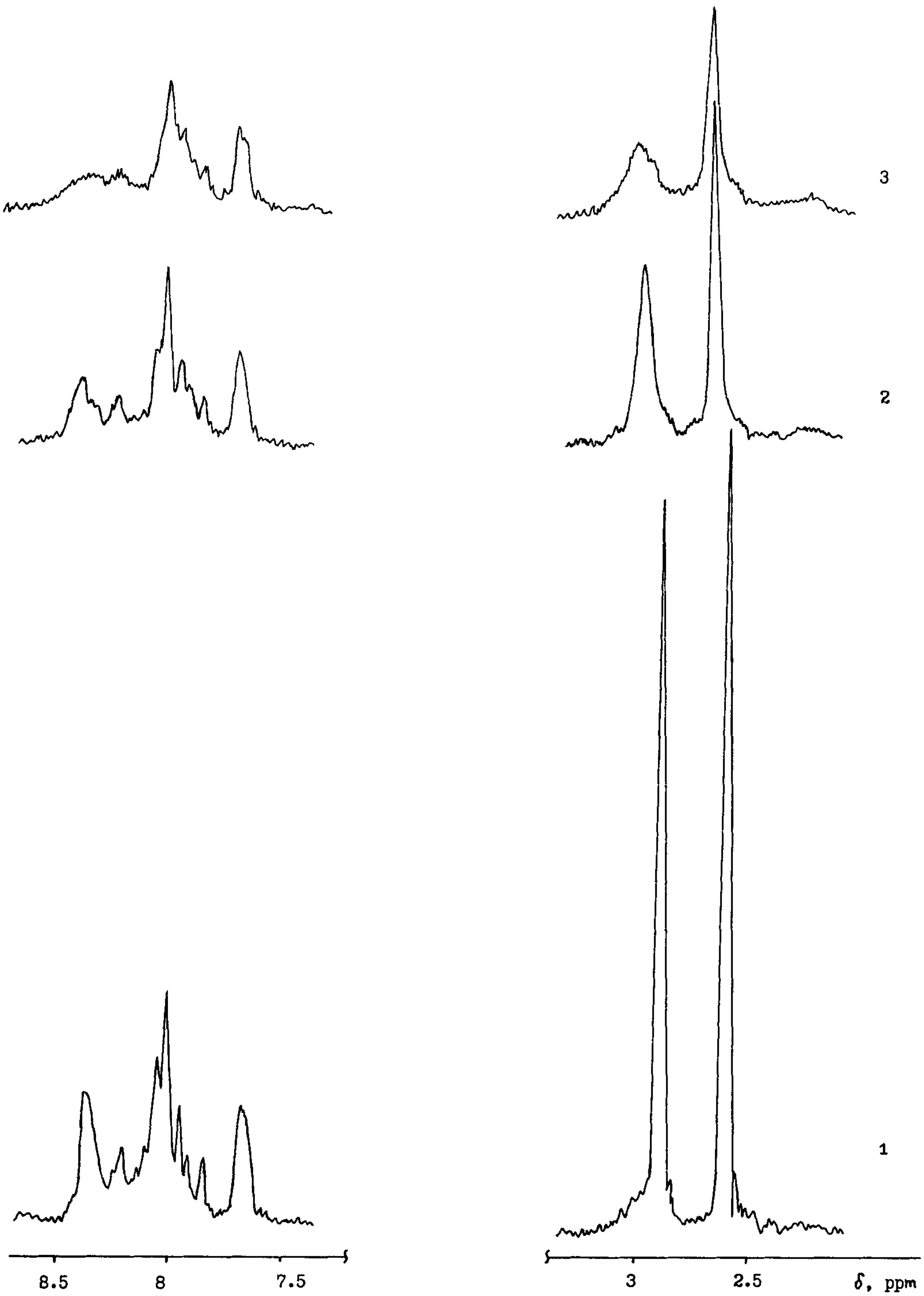
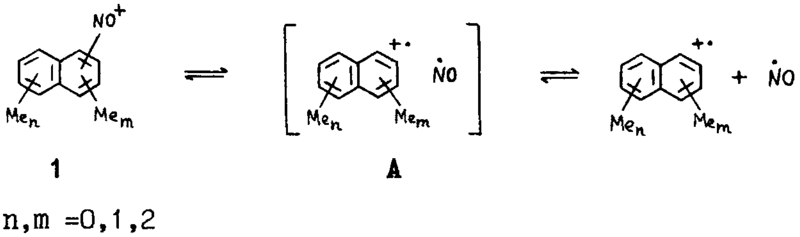


Figure 1. ^{1}H NMR spectra of the π-complex **1e** in SO_2 solution at different temperatures: (1) −70; (2) −30; (3) −20 °C



Scheme 4

single electron transfer between the aromatic moiety of complexes and the NO group (Scheme 4).

On cooling the solutions of π-complexes **1** the starting spectra are almost completely restored. Figure 1 shows as an example the ^{1}H NMR spectra of the π-complex **1e** at different temperatures. As can be seen, the exchange broadening of the signals of the 1- and 3-CH_3 groups is different, being larger for the 1-CH_3 signal. This may be explained as follows. It is known that signal broadening in NMR spectra for SET processes forming radical ion species is described by the following equation:[25]

$$\frac{\Delta T_2^{(2)}}{\Delta T_2^{(1)}} = \frac{\dfrac{a_n^{(1)}}{2[D]} + k\left(\dfrac{a_n^{(1)}}{a_n^{(2)}}\right)^2}{1 + \dfrac{a_n^{(1)}}{2[D]}}$$

where k is the rate constant of electron transfer, $a_n^{(1)}$ and $a_n^{(2)}$ are the hyperfine splitting (HFS) constants for nuclei of two types (1 and 2), $1/T_2^{(1)}$ and $1/T_2^{(2)}$ are the exchange broadenings of signals in the ^{1}H NMR spectra of these nuclei and [D] is the concentration of a diamagnetic compound. Unfortunately, the literature contains no HFS constants for the 1,3-dimethylnaphthalene radical cation. It is known, however, that the constants for α-CH_3 groups are generally higher in absolute values than those for β-CH_3 groups of methylnaphthalene radical cations.[26] This accounts for the larger broadening of 1-CH_3 signal compared with 3-CH_3 signal in the ^{1}H NMR spectrum of the π-complex **1e**. A similar picture is observed for the π-complex **1d**. The partially reversible exchange broadening in the ^{1}H NMR spectra might be considered to be due to partial exit of the radical cation from cell **A** and its further transformations. One of the possible routes of transformation is dimerization of radical cations according to Scheme 5 (c.f. Ref. 27).

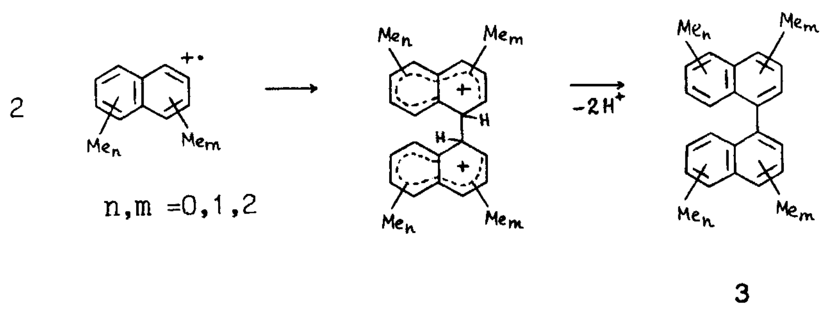
Indeed, after the solutions of complexes **1b**, **d**, **e** and **h** had been kept for 1–2 h at −20 to −30 °C and subsequently treated with water, the reaction mixtures contained the starting hydrocarbons together with their dimers in *ca* 20% yield, viz. 4,4′-dimethylbinaphthyl, 3,3′,4,4′-tetramethylbinaphthyl, 2,2′,4,4′tetramethylbinaphthyl and 4,4′,5,5′-tetramethylbinaphthyl, respectively.

CONCLUSION

The results of this work suggest π-complexes of type **1** to be prospective models for investigating the mechanism of electrophilic aromatic substitution involving single electron transfer from an aromatic molecule to an electrophilic agent (Scheme 1).

EXPERIMENTAL

Spectral measurements. The NMR spectra were recorded on Varian A56/60A (^{1}H) and Bruker WP-200-SY (^{1}H, ^{13}C, ^{15}N) spectrometers. As internal standards,



Scheme 5

hexamethyldisiloxane (^{1}H, δ 0·04 ppm), CH_2Cl_2 (^{1}H, δ 5·33 ppm) and CD_2Cl_2 (^{13}C, δ 52·9 ppm) were used. For ^{15}N NMR chemical shifts, 1 : 1 (v/v) CH_3NO_2–CD_2Cl_2 solution (δ 0·0 ppm) was used as an external standard.

Materials. Analytical-grade naphthalene and 1-methyl- and 1,4-dimethylnaphthalene (pure grade) were distilled. 1,2-Dimethyl- and 1,5-dimethylnaphthalene (pract. and pure grade, respectively) (Fluka), 1,3-dimethyl- and 2,3-dimethylnaphthalene (pure grade) (Loba Chemie) and 1,8-dimethylnaphthalene (pure grade) (Merck) were used as received. $AlCl_3$ (for synthesis) (Merck) was sublimed. Technical FSO_3H was distilled twice. $NaNO_2$ was of pure grade. $Na^{15}NO_2$ had a ^{15}N content of 96·8 at.% and concentrated deuteriochloric acid had a ^{2}H content of 99 at.%.

SO_2 was prepared by a literature procedure[28] and purified by passage through concentrated H_2SO_4. The salt $NO^+AlCl_4^-$[29] and 1-bromo-2,3-dimethylnaphthalene[30] were obtained according to literature procedures.

1-Deuterio-2,3-dimethylnaphthalene. Deuteriochloric acid (1 ml) was added dropwise to a solution of 2,3-dimethyl-1-naphthyllithium prepared from 5·9 g of 1-bromo-2,3-dimethylnaphthalene and 0·38 g of lithium in 30 ml of absolute diethyl ether.[31] The reaction mixture was poured into 100 ml of water and extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$. After the solvent had been distilled off, the product was crystallized from methanol and sublimed in vacuum; yield 35%, m.p. 103–105 °C. The ^{1}H NMR spectrum of 1-deuterio-2,3-dimethylnaphthalene is identical with that of compound **2i** but the intensity of its $H^{1,4}$ signal is half that of the latter.

Solutions. Solutions of complexes **1a–i** for recording the ^{1}H NMR spectra were obtained by adding the powder of the respective precursor (**2a–i**) to an SO_2 solution of the salt $NO^+AlCl_4^-$ at −70 °C. The solution concentrations were 0·5–0·8 mol l^{-1}. Mole ratios of ArH : $NO^+AlCl_4^-$ are given in Table 1.

A solution of complex **1f** for recording the ^{13}C NMR spectra was obtained by adding $NO^+AlCl_4^-$ powder to an SO_2–CD_2Cl_2 solution (7 : 1, v/v) of the precursor (**2f**) at −70 °C. The solution concentration was 0·4 mol l^{-1}.

Solutions of complexes **1a–e** and **g–i** for recording the ^{13}C NMR spectra were obtained by adding a solution of the corresponding precursor (**2a–e** and **g–i**) in 0·2 ml of CD_2Cl_2 to an SO_2 solution of $NO^+AlCl_4^-$ at −70 to −80 °C. The CD_2Cl_2 : SO_2 ratio was 1 : 6 or 1 : 9 (v/v). The solution concentrations were 0·4–0·7 mol l^{-1}. The mole ratio ArH : $NO^+AlCl_4^-$ was 1 : 1.

Solutions of complexes **1b**, **e** and **f** for recording the ^{15}N NMR spectra were obtained by adding the powder of the corresponding precursor (**2b**, **e** and **f**) to an FSO_3H–SO_2–CD_2Cl_2 solution (3 : 14 : 2, v/v) of $Na^{15}NO_2$ at −80 °C. The mole ratio ArH : $Na^{15}NO_2$: FSO_3H was 1 : 1·2 : 6. The solution concentrations were 0·4–0·5 mol l^{-1}.

Synthesis of 1,1-binaphthyl derivatives. The salt $NO^+AlCl_4^-$ in an equimolar amount with respect to ArH was added to an SO_2 solution of **2b**, **d**, **e** or **h** (*ca.* 1–2 mol l^{-1}) at −30 °C. The mixture was stirred at −30 to −20 °C for 1–2 h and poured dropwise into ice–water, then extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$. After the ether had been distilled off, the resulting oil was purified by thin-layer chromatography on alumina with hexane as eluent to give the starting hydrocarbons (**2b**, **d**, **e** and **h**) (16, 36, 45 and 40%, respectively) and their dimers, which were crystallized from the EtOH–$CHCl_3$ mixture. The yields of the dimers, 4,4′-dimethylbinaphthyl,[32] 3,3′,4,4′-tetramethylbinaphthyl,[32] 2,2′-4,4′-tetramethylbinaphthyl[33] and 4,4′,5,5′-tetramethylbinaphthyl,[34] were 13, 24, 22 and 23%, respectively.

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