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Alkylation and acylation of some activated aromatic substrates by organosilicon compounds

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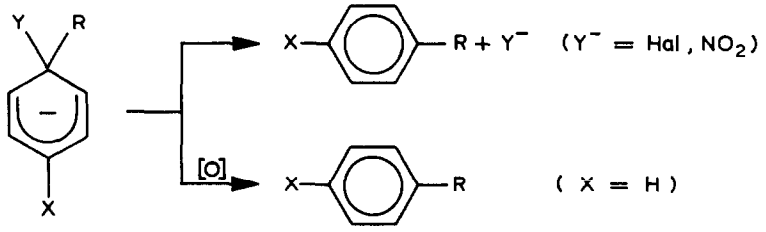
Abstract

A method of alkylation and acylation of trinitrobenzene employing the oxidation of anionic σ-complexes generated from organosilicon reagents in the presence of KF/18-crown-6 ether is described. The method enables the introduction of alkyl and acyl substituents ($R = \overline{CH(CH_2)_4}CO$, CH_2COEt, $CH_2COOMe(Et)$, COMe, COPh, CH_2Ph, $CH_2{=}CHCH_2$ (All), C≡CPh) into 1,3,5-trinitrobenzene. 1,3,5-Tris(trifluoromethylsulfonyl)benzene under the conditions described reacts only with cyclohexanone enol trimethylsilyl ether.

Friedel–Crafts alkylations and acylations which usually provide a facile and straightforward route to the formation of new C–C bonds in the aromatic nucleus fails completely when the aromatic substrates bear strong electron-withdrawing groups. Such substrates are liable to react via the nucleophilic pathway with carbanions. If the intermediate anionic σ-complex lacks good leaving groups, it must be somehow oxidized (by hydride abstraction):



Such a synthetic strategy might be especially advantageous for substrates which form stable σ-complexes, e.g., polynitrobenzenes or tris(trifluoromethylsulfonyl)benzene. Several methods for the generation of σ-complexes with carbon nucleophiles are known, each of them, however, is only suitable for a limited number of substrates [1]. For instance, organolithium and Grignard reagents are the usual choice for alkylations. However, such reactions are successful only with mono-

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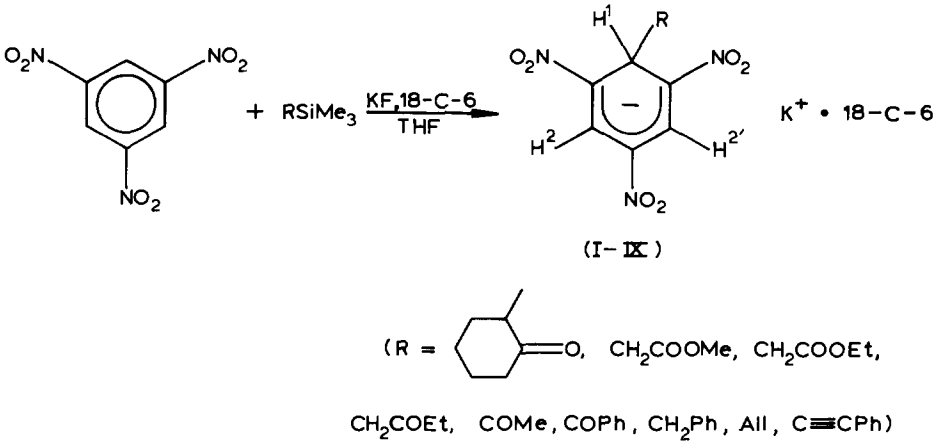
nitrobenzenes [2], since polynitro-derivatives usually give complex mixtures of addition and reduction products [1]. The high basicity of these organometallics restricts their synthetic applicability. So the use of weakly basic organo-tin, -mercuric, -copper and -silver reagents, as well as borates of the series $Alk_4N^+BR_4^-$ enables a variety of radicals R to be introduced into 1,3,5-trinitrobenzene (TNB) [1].

Here we discuss the utility of organosilicon compounds in the formation of a new C–C bond onto an aromatic moiety [3]. It is well known that fluoride anions possess a capability to induce, most likely owing to the formation of penta- or hexacoordinated silicon, the polarization, sometimes the ionization or even the dissociation of carbon–silicon bonds, and thus generate carbanions [4,5]. Organosilicons, $RSiMe_3$, thus have been extensively investigated as a useful source of carbanions, especially in additions to double C = O and C = C bonds [4]. Furthermore, while our investigations were in progress, an article was published dealing with the use of silylated enols in the alkylation of mononitroaromatic compounds [6].

We have examined the behaviour of various $RSiMe_3$, such as benzyl- and allylsilanes, acylsilanes, α-silylated carbonyl compounds and silyl enol ether in the reactions with TNB, promoted by KF and 18-crown-6 ether (18-C-6) to produce anionic σ-complexes I–IX in good to quantitative yields:



The complexes I–IX possess characteristic ^1H NMR and UV spectra [7]. The UV spectra show two bands with λ_{max} in the regions 452–472 and 555–580 nm ($\epsilon_1/\epsilon_2 \approx 2$), each band usually features a short-wavelength shoulder (Fig. 1). In the ^1H NMR spectra, signals of the hydrogens at the tetrahedral carbon appeared at 5.36–4.83 ppm, and those at the sp^2-carbons at 8.40–8.09 ppm (Table 1). All complexes were isolated and their composition ascertained by elemental analysis.

It is noteworthy that the UV spectra of the reaction mixtures often give evidence of the formation of some other σ-complex of TNB, probably with fluoride-anion itself. Thus, mixing TNB, $RSiMe_3$, KF and 18-C-6 together results in several concurrent processes:

$$RSiMe_3 + KF \rightleftharpoons [RSiMe_3F]^-K^+ \quad (1)$$

Table 1

Yields and spectra of the anionic σ-complexes $[TNB \cdot R]^- K^+ \cdot 18\text{-C-6}$

σ-complex	R	Yield (%)	UV (λ_{max}(nm))		^{1}H NMR (DMSO-d_6, δ (ppm); J (Hz))		
			λ_{max_1} (lg ε)	λ_{max_2} (lg ε)	H^2 ($H^{2'}$)	H^1	Others [b]
I	$\overline{CH(CH_2)_4CO}$ [a]	93	462	560	8.32 (dd, $J(H^2H^{2'})$ 1.8, $J(H^2H^1)$ 1.1) (8.25, dd, $J(H^{2'}H^2)$ 1.8, $J(H^{2'}H^1)$ 1.1)	5.36 (dd, J(H^1H) 5.1, $J(H^1H^2)$ 1.1)	3.83 (m, 1H) 2.40–1.60 (m, 8H)
II	CH_2COOCH_3	95	462 (4.553)	570 (4.230)	8.26 (s, 2H)	5.01 (t, $J(H^1H)$ 5.2)	3.55 (t, 2H) 3.35 (s, 3H)
III	$CH_2COOC_2H_5$	96	462	570	8.26 (s, 2H)	5.01 (t, $J(H^1H)$ 5.2)	2.56 (q, J 7.0, 2H) 0.93 (t, J 7.0, 3H)
IV	$CH_2COCH_2CH_3$	95	462 (4.556)	565 (4.234)	8.40 (d, $J(H^2H^1)$ 0.8, 2H)	5.13 (tt, $J(H^1H)$ 5.6, $J(H^1H^2)$ 0.8)	2.61 (d, J 5.6, 2 H) 2.52 (q, J 7.3, 2H) 0.96 (t, J 7.3, 3H)
V	COPh	67	464 (4.567)	595 (4.229)	8.33 (s, 2H)	6.43 (s)	8.20–7.20 (m, 5H)
VI	$COCH_3$	72	464 (4.453)	585 (4.107)	8.33 (s, 2H)	5.30 (s)	2.22 (s, 3H)
VIIa	CH_2Ph [c]	70	472 (4.542)	580 (4.174)	8.09 (d, $J(H^2H^1)$ 0.6, 2H)	5.03 (tt, $J(H^1H)$ 4.4; $J(H^1H^2)$ 0.6)	7.30–6.70 (m, 5H) 2.88 (d, J 4.4, 2H)
VIIb	CH_2Ph [d]	85	472	580	8.09 (d, $J(H^2H^1)$ 0.6, 2H)	5.03 (tt, $J(H^1H)$ 4.4; $J(H^1H^2)$ 0.6)	7.30–6.70 (m, 5H) 2.88 (d, J 4.4, 2H)
VIII	$CHCH{=}CH_2$ [c]	62	462 (4.353)	572 (3.972)	8.27 (s, 2H)	4.83 [e]	5.70–5.50 (m, 1H) 5.00–4.85 (m, 2H) 2.43–2.33 (m, 2H)
IX	C≡CPh [c]	41	452 (4.312)	555 (4.037)	8.40 (s, 2H)	5.74 (s)	7.32 (s, 5H)

[a] The spectrum is consistent with that reported in [16]. [b] All ^{1}H NMR spectra show the signal at 3.6 ppm attributed to the 18-C-6 ether protons. [c] The complex contains one extra mole of KF/18-C-6. [d] The complex was isolated after the reaction of TNB with $PhCH_2SnMe_3$. [e] Decoupled from the CH_2 protons at 2.33–2.43 ppm.

$$TNB + KF \rightleftharpoons \underset{(X)}{[TNBF]^-K^+} \quad (2)$$

$$TNB + [RSiMe_3F]^-K^+ \rightleftharpoons \underset{(I\text{–}IX)}{[TNBR]^-K^+} + Me_3SiF \quad (3)$$

For the most reactive of the organosilicons studied, the α-silylated carbonyl compounds and the silyl enol ether, reactions 1 and 3 are rapid (3 h, 25 °C); the product formation step is practically irreversible. Poor solubility of KF in THF is, apparently, the main factor limiting the rate of formation of the σ-complexes, I–IV. We have estimated the solubility of KF in 1 *M* solution of 18-C-6 in THF to be 2.5×10^{-2} *M*. Readily soluble Bu_4NF effected instantaneous formation of σ-complex from cyclohexanone enol trimethylsilyl ether. For less reactive $RSiMe_3$ (R = $PhCH_2$, All, PhCO, MeCO, PhC≡C) reaction 2 competes with reactions 1 and 3. In fact, absorption spectra of the reaction mixtures recorded immediately upon mixing the reagents show bands with λ_{max} at 430 and 512 nm, the same as that observed when equimolar quantities of TNB, KF and 18-C-6, or TNB and Bu_4NF in THF are mixed, this confirmed their assignment to fluoride complex X *. These bands eventually disappeared and instead, bands attributed to the C-bonded σ-complexes (Fig. 1) developed. Thus, we suggest that the formation of the fluoride complex is kinetically controlled, whereas thermodynamics controls the route to the C-bonded complex.

One mole of 18-C-6 is bound per mole of σ-complex I–VI to form a solid substance of composition $[TNB \cdot R]^-K^+ \cdot$ 18-C-6. The reaction of TNB with less reactive $RSiMe_3$ (R = $PhCH_2$, All, PhC≡C) gave complexes VII–IX containing one extra equivalent of KF · 18-C-6; thus, their composition was $[TNB \cdot R]^-K^+ \cdot$ 18-C-6 + KF · 18-C-6. Such $RSiMe_3$ are likely to require 2 equivalents of each of KF and 18-C-6, the second mole of KF being bonded with NO_2 for proper activation. The reactions with these $RSiMe_3$ were slower, with yields not exceeding 60–70%, and the remaining $RSiMe_3$ could be recovered as it had not been wasted in side reactions (GLC assayed conversion of $RSiMe_3$ corresponded to the spectrophotometric yield of σ-complex). We have studied the reaction between TNB and $PhCH_2SiMe_3$ under various conditions in order to obtain maximum yields of σ-complex. The results obtained (Table 2) show that the highest yields were achieved in expts. 6, 7. Thus, refluxing an equimolar mixture of TNB and $PhCH_2SiMe_3$ with 2 equivalents of 18-C-6 and an excess of KF for 7 h should be preferred as a route to VIIa.

Meanwhile, the reaction between TNB and benzyltrimethyltin with equimolar quantities of KF and 18-C-6 proceeds faster under milder conditions (4 h, 25 °C), and yields 85% of the corresponding σ-complex VIIb. This result is not unexpected in view of the higher polarity of C–Sn bond as compared with C–Si bond. However, even the organotin reagent was not able to give rise to benzyl anion (neither free,

* We have not been able to prove its formation by ^1H NMR spectroscopy. The spectrum (in DMSO-d_6) of the red solid isolated from the reaction of TNB, KF and 18-C-6 in vacuo showed two broad bands (8.2 and 6.3 ppm) without any traceable spin–spin splitting *J*(FH). It is noteworthy, that ^1H and ^{19}F NMR spectroscopy was used to confirm the formation of the fluoride σ-complex of picryl [8] and cyanuric [9] fluorides. However, for 2,4-dinitrochloro- and fluoro-benzenes which form much less stable σ-complexes, the spectra displayed broadened lines, the splitting pattern of which could not be discerned [10].

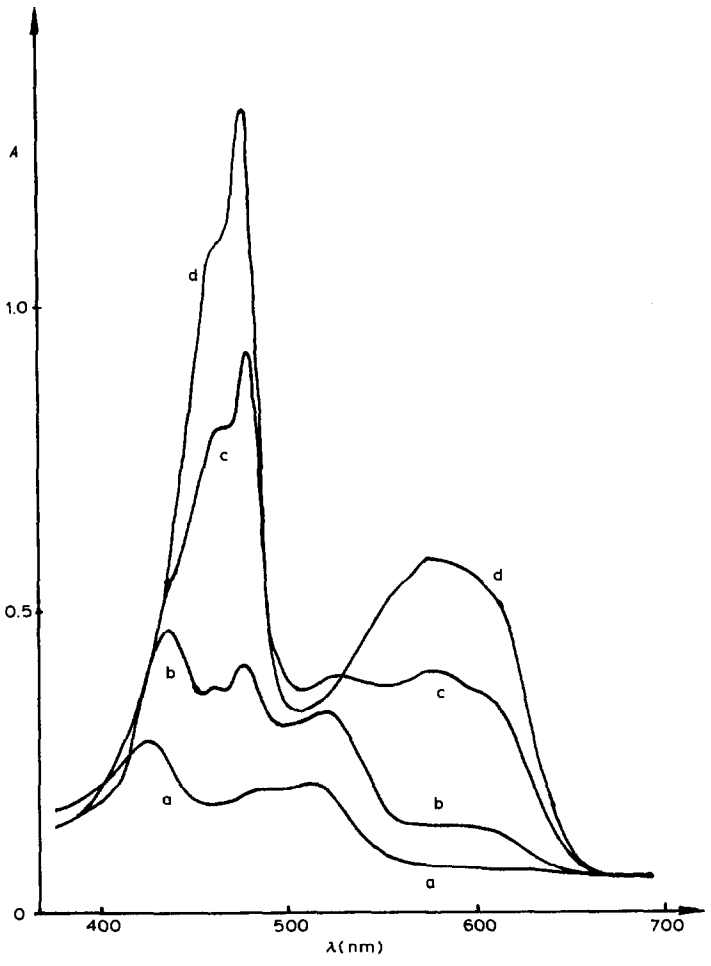


Fig. 1. A change in the absorption spectra of the reaction mixture TNB/$PhCH_2SiMe_3$/KF/18-C-6 with time: (a) 20 min on mixing the reagents; (b) 2 h reflux; (c) 5 h reflux; (d) 7 h reflux. c_{TNB} 5×10^{-5} *M*.

Table 2

Spectrophotometric and GLC assayed yields of the complex VIIa from the reaction of TNB with $PhCH_2SiMe_3$ under different conditions

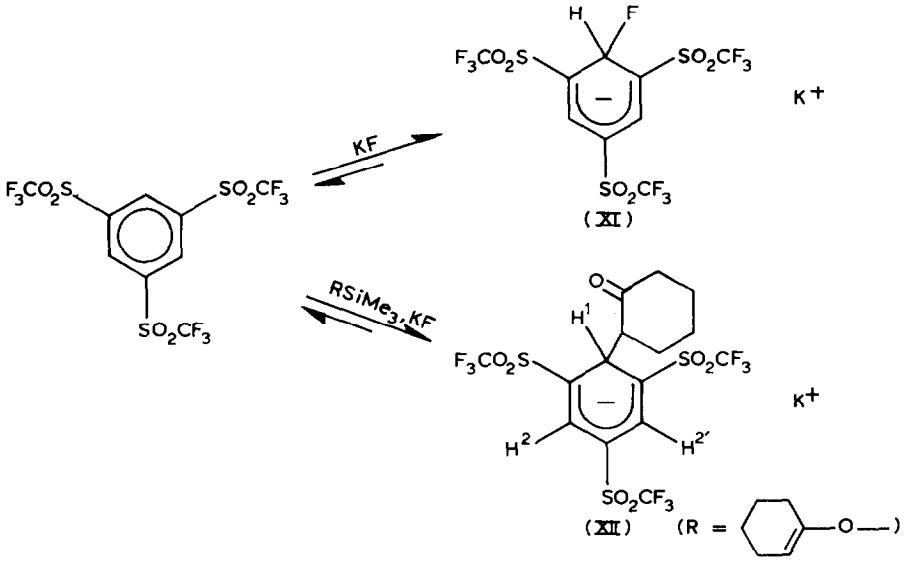
No.	Molar ratio [a]		*T* (°C)	Time (h)	Yield (%)
	KF	18-C-6			
1	1	1	25	20	45
2	1	1	60	7	16
3	2	2	25	48	45
4	3	2	25	50	60(55 [b])
5	3	3	25	16	63
6	4	4	25	7	75
7	3	2	60	7	75(70 [b])
8	1 TBAF	–	25	100	70

[a] Per mole of TNB and $PhCH_2SiMe_3$. [b] Preparative yield.

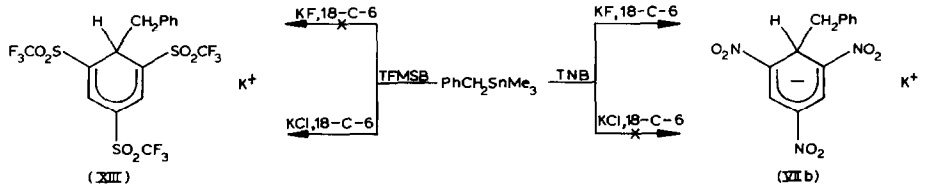
nor ion-paired), since a mixture of $PhCH_2SnMe_3$ and KF/18-C-6 after a prolonged period gave a solution, the UV spectrum of which lacked a benzyl anion absorption band.

All attempts to obtain the vinyl complex of TNB failed. Prolonged heating of a mixture of $Ph_3SiCH{=}CH_2$, TNB and TBAF in DMSO/THF (v/v 1/1) gave no traces of the C-bonded σ-complex as could be ascertained from the UV spectra.

Another aromatic substrate under study has been 1,3,5-tris(trifluoromethylsulfonyl)benzene (TFMSB), which is known to form much more stable σ-complexes than TNB [11], that, however, unexpectedly turned into a disadvantage. TFMSB appeared to form the expected σ-complex only with the most reactive cyclohexanone enol trimethylsilyl ether. In all other cases this substrate effectively scavenged fluoride-anion to form the fluoride σ-complex XI.



Even $PhCH_2SnMe_3$, which reacts smoothly with TNB (complex VIIb), did not form the C-bonded σ-complex with TFMSB in the presence of F^- anion. Nevertheless, benzylic σ-complex of TFMSB could be obtained in the presence of chloride ions instead of F^-; the former may have formed σ-complex with this substrate, though, obviously, of much lesser stability. It should be noted here, that Cl^- was unable to induce the formation of the corresponding σ-complex from TNB and $PhCH_2SnMe_3$.



UV spectra of σ-complexes XII and XIII show the following characteristic bands (λ in nm): λ_{max_1} 230 ($lg\epsilon = 4.423$), λ_{max_2} 272 ($lg\epsilon = 4.498$), λ_{max_3} 385 ($lg\epsilon = 3.879$) and

Table 3

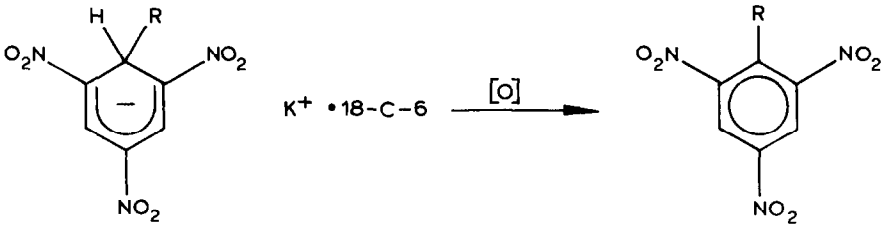
Yields of the substitution products and the reaction conditions for the oxidation of TNB σ-complexes

σ-Complex	R of σ-complex	Oxidant	Yield (%)
I	$\dot{C}H(CH_2)_4\dot{C}O$	NBS	81
I	$\dot{C}H(CH_2)_4\dot{C}O$	$(NH_4)_2Ce(NO_3)_6$	85
II	CH_2COOMe	NBS (2 equiv.)	60 [a]
III	CH_2COOEt	$(NH_4)_2Ce(NO_3)_6$	80
IV	CH_2COEt	$(NH_4)_2Ce(NO_3)_6$	82
V	COPh	NBS	67
VI	COMe	NBS	72
VIIa	CH_2Ph	NBS (3 equiv.)	65
VIIa	CH_2Ph	Br_2/H_2O	77
VIIa	CH_2Ph	Cl_2O/CCl_4	71
VIIa	CH_2Ph	(1) H_2SO_4 (2) chloranil	0
VIIb	CH_2Ph	NBS (1 equiv.)	80
VIII	$CH_2CH{=}CH_2$	Cl_2O/CCl_4	71
IX	$C{\equiv}CPh$	Cl_2O/CCl_4	45

[a] Yield of methyl bromo-(2,4,6-trinitrophenyl)-acetate.

λ_{max_1} 231 nm (lgε = 4.501), λ_{max_2} 275 (lgε = 4.429), λ_{max_3} 390 (lgε = 3.880), respectively. ^{1}H NMR spectra of XII in DMSO-d_6 (δ, ppm): 7.38 (s, H^2), 7.30 (s, $H^{2'}$), 4.53 (d, *J* 5.0 Hz, H′), 2.40–1.60 (m, 8H), and of XIII: 7.33 (s, $2H^2$), 7.15–7.00 (m, 5H), 4.04 (t, *J* 4.8 Hz, H′), 2.82 (d, *J* 4.8 Hz, 2H), agree fairly well with the reported spectra of other σ-complexes of TFMSB with carbanions [12,13].

The σ-complexes I–IX obtained were oxidized to yield substitution products (Table 3).



Many oxidants are capable of hydride abstraction from such σ-complexes [14], but none has proved to be a good all-purpose reagent.

N-Bromosuccinimide (NBS) was successfully used to oxidize σ-complexes of TNB with cycloaliphatic ketones [15]. We have found that NBS readily oxidized the complexes I, V and VI to yield the corresponding substitution products (Table 3). The oxidation of the complex II required two equivalents of NBS to give methyl bromo-(2,4,6-trinitrophenyl)-acetate (R=CH(Br)COOMe) in 60% yield. Benzylic complexes VIIb were also oxidized by NBS, complex VIIa required a three-fold excess of the reagent. In this case the use of bromine water or Cl_2O solution gave better results. Oxidation by chloranil of reaction mixtures acidified with diluted H_2SO_4 resulted only in the recovery of TNB. Some complexes (I–IV) were conveniently oxidized by cerium(IV) ammonium nitrate, while others (V–IX) gave mixtures

containing TNB and substitution products. Dichlorine monoxide Cl_2O was selective in the oxidation of allylic and phenylacetylenic complexes of TNB (VIII and IX). Other oxidants failed, and gave complex mixtures of products along with recovered TNB.

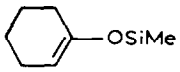
Thus, organosilicon reagents are useful in the preparation of various anionic σ-complexes, which can be further oxidized to otherwise inaccessible alkyl- (All, $PhCH_2$, CH_2CO_2R) and acyl- (COMe, COPh) substituted trinitrobenzenes. For instance, starting from α-silylated ketones, this method enables selective introduction of trinitrophenyl moiety into ketones, whereas the routine base-catalysed condensation of TNB with unsymmetrical ketones produces isomeric products. In some cases, e.g. I and IX [16,17], the use of $RSiMe_3$ is more convenient, and gives better results.

Experimental

^1H NMR spectra were recorded on Tesla BS-467 (60 MHz) and Bruker WM250 instruments, with Me_4Si as an internal standard. UV-VIS spectra were recorded on a Hitachi-124 instrument. IR spectra were recorded in KBr pellets on a Zeiss UR-20 spectrometer. GLC analyses were run on an LHM-8MD gas chromatograph, carrier gas: N_2, flow rate 30 ml/min, FID, stainless steel column 3×3000 mm, packed with 5% SE-30 on Chromaton N-AW. Concentration of fluoride was monitored by a fluoride-selective electrode supplied by Radelkis (Hungary), interfaced with an EV-74 ion-meter. A saturated solution of KF in 1 *M* solution of 18-C-6 in THF contains 2.5×10^{-2} *M* of fluoride. Reactions were controlled by either TLC chromatography (Silufol UV-254) by disappearance of the starting $RSiMe_3$ or spectrophotometrically by disappearance of the band ascribed to the fluoride σ-complex of TNB (see text).

THF, Et_2O, hexane, CCl_4 were purified by standard methods. THF was stored over $LiAlH_4$ or benzophenone ketyl.

Commercially available TNB was recrystallized twice from ethanol. KF was dried for 2 h at 200 °C in vacuum (1 Torr) and stored over P_2O_5. 18-C-6 ether was distilled from the commercial acetonitrile complex at 165 °C/1 Torr. Bu_4NF, obtained as described in [18], was dried prior to use at 30–40 °C/0.1 Torr for 24 h. NBS was twice recrystallized from water. Commercial cerium(IV) ammonium nitrate was dried for 2 h at 70 °C/1 Torr. A solution of Cl_2O in CCl_4 was made by a published procedure [19]. Organosilicon reagents were prepared by standard methods: $PhCH_2SiMe_3$ [20], $AllSiMe_3$ [21], $EtCOCH_2SiMe_3$ [22], Me_3SiCH_2COOMe [23], Me_3SiCH_2COOEt [24], $PhCOSiMe_3$ [25], $PhC{\equiv}CSiMe_3$ [26],



[27], $CH_2{=}CHSiPh_3$ [28].

Acetyltriphenylsilane was obtained by reaction of Ph_3SiLi with MeCOCl in the presence of CuI [29]. A solution of Ph_3SiLi (from Ph_6Si_2 (20 g, 40 mmol) and Li (4 g)) in THF (170 ml) at −30 °C was added to a suspension of CuI (1.5 g, 8 mmol) in THF (20 ml). On cooling to −50 °C a solution of MeCOCl (5.6 ml, 80 mmol) in THF (30 ml) was added dropwise. The reaction mixture was warmed to −10 °C, kept at this temperature for 1 h, then allowed to warm to room temperature and

filtered through a layer of SiO_2 (40/100). After the THF had been removed by vacuum distillation the residue was extracted with benzene. After the solvent had been evaporated off in vacuum, a solid remained, which was washed twice with hexane and recrystallized from ethanol to give white crystals, yield 20 g (83%), m.p. 125–126 °C (lit. 126–127 °C [30]). ^{1}H NMR spectrum (CD_2Cl_2), δ (ppm): 7.80–7.30 (m, 15H), 2.43 (s, 3H). IR 1648 (ν(C=O)) cm^{-1}.

Preparation of the anionic σ-complexes

A solution of TNB (0.21 g, 1 mmol), organosilicon reagent (1 mmol), 18-C-6 (0.26 g, 1 mmol) and KF (0.06 g, 1 mmol) in THF (5 ml) was stirred for 3 h (unless otherwise indicated) at 25 °C under dry Ar. The reaction mixture was filtered, and added dropwise to an Et_2O/hexane mixture (v/v 1/1, 50 ml). The crystalline precipitate which separated was filtered off and dried in vacuum.

I. From cyclohexanone enol trimethylsilyl ether (0.17 g). Yield 0.57 g (93%), m.p. 127–129 °C.

II. From Me_3SiCH_2COOMe (0.15 g). Yield 0.57 g (95%), m.p. 125–127 °C. Anal. Found: C, 42.34; H, 5.74; N, 7.16. $C_{21}H_{32}N_3O_{14}K$ calc: C, 42.78; H, 5.43; N, 7.13%.

III. From Me_3SiCH_2COOEt (0.16 g). Yield 0.58 g (95%), m.p. 125–127 °C.

IV. From Me_3SiCH_2COEt (0.14 g). Yield 0.56 g (95%), m.p. 126–128 °C. Anal. Found: C, 44.97; H, 5.71; N, 7.35. $C_{22}H_{34}N_3O_{13}K$ calc: C, 44.97; H, 5.79, N, 7.16%.

V. From $PhCOSiMe_3$ (0.18 g), stirring for 10 h. Yield 0.42 g (67%), m.p. 155–157 °C. Anal. Found: C, 48.07; H, 4.82; N, 7.12. $C_{25}H_{32}N_3O_{13}K$ calc: C, 48.31; H, 5.15; N, 6.76%.

VI. From $CH_3COSiPh_3$ (0.3 g), stirring for 5 h. Yield 0.4 g (72%), m.p. 124–126 °C. Anal. Found: C, 43.77; H, 5.28; N, 7.54. $C_{20}H_{30}N_3O_{13}K$ calc: C, 42.93; H, 5.37; N, 7.51%.

Reaction of TNB with benzyltrimethylsilane (σ-complex VIIa)

A mixture of TNB (0.21 g, 1 mmol), $PhCH_2SiMe_3$ (0.16 g, 1 mmol), 18-C-6 (0.53 g, 2 mmol) and KF (0.18 g, 3 mmol) was refluxed in THF for 7 h. The isolation procedure is described above. Yield 0.65 g (70%), m.p. 107–109 °C. Anal. Found: C, 48.07; H, 6.30; N, 5.61; F, 2.71. $C_{37}H_{58}N_3O_{18}FK_2$ calc: C, 47.79; H, 6.24; N, 4.52; F, 2.05%.

σ-complex VIII was obtained from $AllSiMe_3$ similarly (0.11 g, 1 mmol). Yield 0.55 g (62%), m.p. 123–125 °C. Anal. Found: C, 44.65; H, 5.88; N, 6.34; F, 2.19. $C_{33}H_{56}N_3O_{18}FK_2$ calc: C, 45.05; H, 6.37; N, 4.78; F, 2.16%.

Reaction of TNB with trimethylsilylphenylacetylene (σ-complex IX)

A mixture of TNB (0.21 g, 1 mmol), $PhC{\equiv}CSiMe_3$ (0.17 g, 1 mmol), 18-C-6 (0.26 g, 1 mmol) and KF (0.06 g, 1 mmol) in 5 ml THF was stirred for 20 h and worked up as described for the other σ-complexes. Yield 0.38 g (41%), m.p. 88–90 °C. Anal. Found: C, 48.51; H, 5.68; N, 4.40; F, 1.67. $C_{38}H_{56}N_3O_{18}FK_2$ calc: C, 48.56; H, 5.96; N, 4.47; F, 2.02%.

Reaction of TNB with $PhCH_2SnMe_3$ (σ-complex VIIb)

An equimolar mixture (1 mmol) of the reagents in 5 ml THF was stirred for 4 h at 25 °C. Yield 0.52 g (85%), m.p. 139–141 °C.

Reaction of TFMSB with cyclohexanone enol trimethylsilyl ether (σ-complex XII)

A mixture of the sulfone (0.047 g, 0.1 mmol), silyl enol ether (0.017 g, 0.1 mmol), 18-C-6 (0.026 g, 0.1 mmol) and KF (0.006 g, 0.1 mmol) in 2 ml of THF was stirred at 25 °C for 3 h. The reaction mixture was filtered, THF removed nearly to dryness, then the residue was treated with dry ether to give a crystalline solid, which was filtered off and dried in vacuum. Yield 0.078 g (90%), m.p. 145–147 °C. Anal. Found: C, 37.55; H, 4.28. $C_{27}H_{36}S_3O_{13}F_9K$ calc: C, 37.08; H, 4.12%.

Reaction of TFMSB with $PhCH_2SnMe_3$ (σ-complex XIII)

A mixture of sulfone (0.047 g, 0.1 mmol), $PhCH_2SnMe_3$ (0.026 g, 0.1 mmol), 18-C-6 (0.026 g, 0.1 mmol) and KCl (0.075 g, 0.1 mmol) in 2 ml THF was stirred for 3 h. The work-up is similar to that for the previous reaction. Yield 0.082 g (95%), m.p. 154–156 °C. Anal. Found: C, 37.86; H, 4.16. $C_{28}H_{34}S_3O_{12}F_3K$ calc: C, 38.71; H, 3.92%.

Oxidation of the σ-complexes

Method A. Oxidation by NBS

α-(2,4,6-Trinitrophenyl)cyclohexanone. To a solution of the complex I (0.59 g, 1 mmol) in 5 ml THF, was added NBS (0.18 g, 1 mmol). The mixture was stirred for 30 min, filtered, and the filtrate acidified with 5 ml 0.1 *M* HCl and then extracted with benzene. The organic layer was separated, washed with water and dried over $MgSO_4$. The benzene was removed, and the residue was chromatographed on a column packed with SiO_2 (40/100, eluent: benzene). Yield 0.25 g (81%), m.p. 143–144 °C (lit.: m.p. 86 °C [15]). ^1H NMR ($CDCl_3$, δ, ppm): 8.77 (s, 2H), 3.83 (m, 1H), 2.70–1.40 (m, 8H).

2,4,6-Trinitrophenyl(phenyl)methane was obtained from the σ-complex VIIa (0.93 g, 1 mmol) and NBS (0.54 g, 3 mmol) similarly. Yield 0.2 g (65%), m.p. 101–102 °C. ^1H NMR ($(CD_3)_2CO$, δ, ppm): 9.05 (2, 2H), 8.00–7.20 (m, 5H), 4.55 (s, 2H). IR (ν, cm^{-1}): 3100, 1610, 1550, 1350. Anal. Found: C, 51.49; H, 2.97; N, 13.86. $C_{13}H_9N_3O_6$ calc: C, 51.61; H, 3.30; N, 13.55%.

2,4,6-Trinitrophenyl(phenyl)methane. By reaction of σ-complex VIIb (0.61 g, 1 mmol) with NBS (0.18 g, 1 mmol). Yield 0.24 g (80%).

Methyl-bromo-(2,4,6-trinitrophenyl)-acetate. By reaction of σ-complex II (0.59 g, 1 mmol) and NBS (0.36 g, 2 mmol). Yield 0.22 g (60%), m.p. 109–110 °C. ^1H NMR ($(CD_3)_2CO$, δ, ppm): 9.08 (s, 2H), 6.38 (s, 1H), 3.75 (s, 3H). IR (ν, cm^{-1}): 3100, 1750, 1610, 1550, 1350. Anal. Found: C, 29.97; H, 1.70; N, 11.02; Br, 21.71. $C_9H_6N_3O_8Br$ calc: C, 29.67; H, 1.65; N, 11.54; Br, 21.98%.

2,4,6-Trinitrobenzophenone. By reaction of σ-complex V (0.62 g, 1 mmol) with NBS (0.18 g, 1 mmol). Yield 0.21 g (67%), m.p. 178–179 °C. ^1H NMR ($(CD_3)_2CO$, δ, ppm): 9.35 (s, 2H), 8.05–7.20 (m, 5H). IR (∂, cm^{-1}): 3100, 1680, 1610, 1555, 1350. Anal. Found: C, 48.74; H, 2.28; N, 13.34. $C_{13}H_7N_3O_7$ calc: C, 49.21; H, 2.48; N, 13.25%.

2,4,6-Trinitroacetophenone. By reaction of σ-complex VI (0.56 g, 1 mmol) with NBS (0.18 g, 1 mmol). Yield 0.18 g (72%), m.p. 133–134 °C. ^1H NMR ($(CD_3)_2CO$, δ, ppm): 9.08 (s, 2H), 2.78 (s, 3H). IR (∂, cm^{-1}): 3100, 1725, 1610, 1550, 1350. Anal. Found: C, 38.12; H, 2.17; N, 16.45. $C_8H_5N_3O_7$ calc: C, 37.65; H, 1.96; N, 16.47%.

Method B. Oxidation by cerium(IV) ammonium nitrate

α-(2,4,6-Trinitrophenyl)cyclohexanone. To a solution of σ-complex I (0.59 g, 1 mmol) in THF (5 ml) cerium ammonium nitrate (0.54 g, 1 mmol) was added. After 1 h stirring the solution was filtered and THF removed under reduced pressure. The residue was chromatographed on a column packed with SiO_2 (40/100, benzene). Yield 0.26 g (85%).

Ethyl 2,4,6-trinitrophenylacetate was obtained similarly from σ-complex III (1.2 g, 2 mmol) and $(NH_4)_2Ce(NO_3)_6$ (1.03 g, 2 mmol). Oil, yield 0.48 g (80%). ^1H NMR ($(CD_3)_2CO$, δ (ppm)): 9.05 (s, 2H), 4.35 (s, 2H), 4.15 (q, *J* 7.0 Hz, 2H), 1.25 (t, *J* 7.0 Hz, 3H). IR (ν, cm^{-1}): 3100, 1735, 1610, 1550, 1350. Anal. Found: C, 42.80; H, 3.39; N, 13.90. $C_{10}H_9N_3O_8$ calc: C, 43.14; H, 3.01; N, 14.05%.

2,4,6-Trinitrobenzylethylketone was obtained similarly from σ-complex IV (0.59 g, 1 mmol) and $(NH_4)_2Ce(NO_3)_6$ (0.54 g, 1 mmol). Yield 0.23 g (82%), m.p. 61–62°C. ^1H NMR ($(CD_3)_2CO$, δ (ppm)): 9.13 (s, 2H), 4.60 (s, 2H), 2.56 (q, *J* 7.3 Hz, 2H), 0.93 (t, *J* 7.3 Hz, 3H). IR (ν, cm^{-1}): 3100, 1710, 1610, 1540, 1350. Anal. Found: C, 42.43; H, 3.10; N, 14.76. $C_{10}H_9N_3O_7$ calc: C, 42.40; H, 3.18; N, 14.84%.

Method C. Oxidation by Cl_2O

2,4,6-Trinitrophenyl(phenyl)methane. To a solution of VIIa (0.939 g, 1 mmol) in THF (7 ml) a solution of Cl_2O in CCl_4 (2.5 ml, 0.2 *M*) was added dropwise. After filtration and evaporation of the solvent the residue was passed through a column SiO_2 (40/100, eluent: benzene). Yield 0.22 g (71%).

2,4,6-Trinitrophenyl(vinyl)methane was obtained similarly from σ-complex VIII (0.88 g, 1 mmol) and Cl_2O in CCl_4 (2.5 ml, 0.2 *M*). Oil, yield 0.18 g (71%). ^1H NMR (CCl_4, δ (ppm)): 8.77 (s, 2H), 6.15–5.49 (m, 1H), 5.23–4.73 (m, 2H), 3.90–3.83 (m, 2H). IR (∂, cm^{-1}): 3100, 1610, 1550, 1350. Anal. Found: C, 42.22; H, 2.85; N, 16.26. $C_9H_7N_3O_6$ calc: C, 42.69; H, 2.77; N, 16.60%.

2,4,6-Trinitrophenyl(phenyl)acetylene was obtained similarly from σ-complex IX (0.95 g, 1 mmol) and Cl_2O in CCl_4 (2.5 ml, 0.2 *M*). Yield 0.14 g (45%), m.p. 204–205°C (lit.: m.p. 204–205°C [31]). ^1H NMR ($(CD_3)_2CO$, δ (ppm)): 9.16 (s, 2H), 7.60 (s, 5H). IR (∂, cm^{-1}): 3100, 2207, 1610, 1540, 1340.

Oxidation of σ-complex VIIa by bromine water

To a solution of σ-complex VIIa (0.93 g, 1 mmol) in THF (7 ml) was added dropwise bromine water until the colour of σ-complex disappeared. The reaction mixture was extracted with benzene, the extract dried over $MgSO_4$ and solvent removed under reduced pressure. The residue was chromatographed on SiO_2 (40/100). Yield 0.23 g (77%).

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