The Role of Titanium and Iron Complexes in the Deoxygenation of Aromatic Nitroso-compounds

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Deoxygenation of aromatic nitroso-compounds RNO (R = Ph or biphenyl-2-yl) under very mild conditions by titanium(II) and titanium(III) derivatives such as $[Ti(cp)_2(CO)_2]$, $[\{Ti(cp)_2Cl\}_2]$, $[Ti(cp)Cl_2]$ (cp = η^5-C_5H_5), and $TiCl_3$ led to the formation of oxo-complexes and the corresponding azo- and azoxy-organic compounds. Carbazole was not formed, suggesting a metal-controlled pathway for evolution of the plausible intermediate nitrene. Similar results have been obtained using *N,N'*-ethylenebis(salicylideneiminato)iron(II), [Fe(salen)], which was converted into $[\{Fe(salen)\}_2O]$.

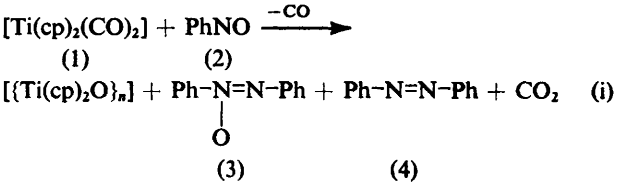
Reduction of organic substrates *via* oxygen abstraction by low-valent early transition metal compounds has been used as a synthetic approach for some important metal-promoted organic transformations.[1-6] This parallels the utilization of phosphorus(III);[7] the metal–oxygen and the phosphorus–oxygen bond energy is the driving force for the reactions. The utilization of chemically ill defined inorganic species [1,3] did not allow the deoxygenation reaction to be interpreted in terms of a special electronic configuration and/or oxidation state of the metal. This prompted us to use well defined complexes [5,6] with organic substrates.

We report here the deoxygenation of aromatic nitroso-compounds by low-valent titanium complexes, namely $[Ti(cp)_2(CO)_2]$,[8] $[\{Ti(cp)_2Cl\}_2]$,[9] $[Ti(cp)Cl_2]$ [10] (cp = η^5-C_5H_5), and $TiCl_3$, related to the so-called McMurry reagents,[1] prepared *in situ* by reduction of titanium(III) and titanium(IV) salts. We also describe the interaction of the same nitroso-compounds with *N,N'*-ethylenebis(salicylideneiminato)iron(II), [Fe(salen)], leading to their deoxygenation.[6] Interaction of the nitroso functional group with iron(II) chelates is a field of recent interest for the simulation of some naturally occurring reactions, and because the nitroso-group displays common features with dioxygen.[11,12] A significant difference between the metallic systems and the classical phosphorus(III) reagents emerges in that the metallic centres seem to affect the electronic properties of intermediate nitrenes.

Results and Discussion

The utilization of low-valent titanium species as deoxygenating agents has received much attention, *e.g.* in the reactions with carbonylic organic functions [1] and epoxides.[2] However, their generation *in situ* prevented any detailed information from being obtained on the reactive metal sites. Well defined complexes of titanium(II) and titanium(III) have now been used for the deoxygenation of organic nitroso-compounds. The experimental conditions and results are summarized in the Table.

A toluene solution of $[Ti(cp)_2(CO)_2]$ reacted with nitrosobenzene to form an oxo-complex and azobenzene as the main product [equation (i)]. Deoxygenation of nitroso-compounds



$$\underset{(1)}{[Ti(cp)_2(CO)_2]} + \underset{(2)}{PhNO} \xrightarrow{-CO}$$

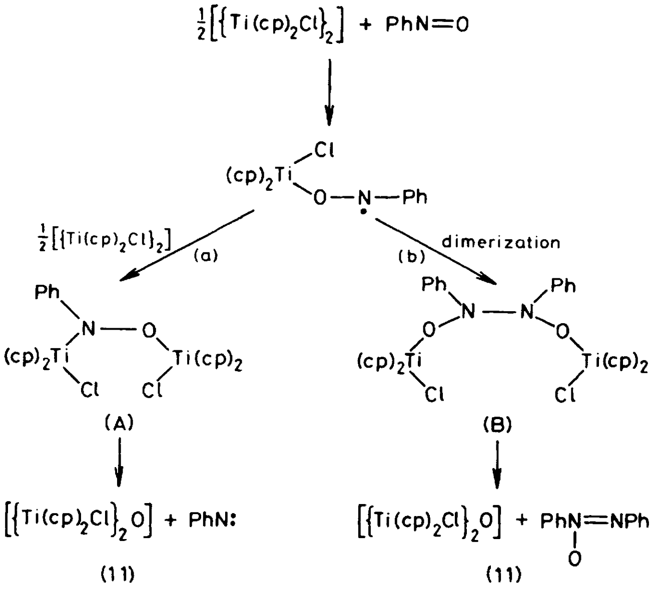
$$[\{Ti(cp)_2O\}_n] + \underset{(3)}{Ph{-}\underset{\displaystyle O}{\underset{|}{N}}{=}N{-}Ph} + \underset{(4)}{Ph{-}N{=}N{-}Ph} + CO_2 \qquad \text{(i)}$$

occurs through both metal oxide formation and, to a lesser extent, *via* the oxidation of CO to CO_2. Deoxygenation by carbon monoxide is a quite common reaction in metal carbonyl chemistry, namely in the synthesis of isocyanates and

Table. Experimental conditions and results

Metal complex (mmol dm^{-3})		RNO (mmol dm^{-3})		Solvent	Reaction time	Product (%) [a]		
						Azo-derivative	Azoxy-derivative	Carbazole
(1)	(27.2)	(2)	(27.2)	Toluene	12 h	65 [b]	Absent [b]	—
(1)	(58.4)	(2)	(127.7)	Toluene	10 min	Main products		—
(1)	(48.5)	(5)	(48.5)	Toluene	4 h	Main product [b]	Absent [b]	Absent [b]
(8)	(24.4)	(5)	(28.9)	Toluene	30 min	Main product [b]	Traces [b]	Absent
(9)	(54.7)	(5)	(54.7)	Toluene	45 min	Main product [b]	Traces [b]	Traces [b]
(10)	(84.0) [c]	(5)	(44.0)	thf	3 h	Main product [b]	Traces [b]	Absent [b]
(12)	(55.0) [c]	(5)	(27.5)	CH_2Cl_2	22 h	Main product [b]	Traces [b]	Absent [b]
(12)	(26.3)	(5)	(26.3)	thf	6 h	26.5 [d]	11.2 [d]	Absent [b]
(12)	(25.0)	(5)	(25.0)	thf [e]	12 h	23.7 [d]	14.9 [d]	Absent [b]
(8)	(27.9)	(2)	(24.3)	Toluene	12 h	19.0 [d]	2.6 [d]	—
(12)	(38.0)	(2)	(38.0)	thf [e]	2 h	6.1 [d]	19.4 [d]	—
(12)	(35.2)	(2)	(35.2)	thf	2 h	Traces [b]	90.5 [d]	—

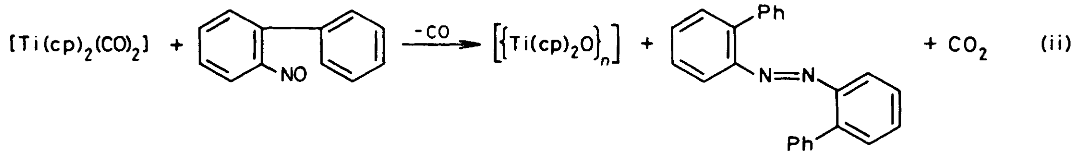
[a] Referred to the reagent in lowest concentration. [b] T.l.c. [c] Solid added to the dissolved RNO. [d] Isolated by column chromatography. [e] Stoicheiometric quantities of $NaBPh_4$ added.



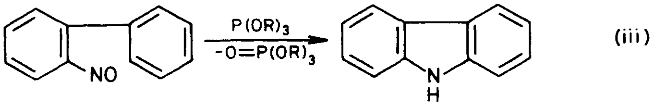
Scheme.

related species [13] from nitro-compounds.[14] No isocyanate is formed in reaction (i) even under a carbon monoxide atmosphere, which takes some part only in the deoxygenation reaction.

Nitrene intermediates have been suggested in many nitro- and nitroso-deoxygenations.[7,15] As a test for these intermediates, 2-nitrosobiphenyl was treated with complex (1), but no carbazole was formed [equation (ii)]. Carbazole, (7), is the only significant product of the deoxygenation of 2-nitrosobiphenyl with $P(OEt)_3$.[7,16] Such a reaction is likely to involve preliminary formation of a 'singlet' nitrene inserting into a C–H bond [17,18] [equation (iii)]; the organometallic species seems therefore to drive the process in a different direction involving either a metal-bonded nitrene, whose chemistry could be different from that of a free nitrene, or promoting the formation of a 'triplet' nitrene which does not insert into a C–H bond.[17,18] Triplet nitrenes would be mainly responsible for the azo- and azoxy-coupling products.

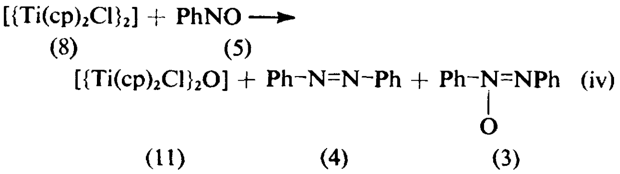


(1) (5) (6)



(5) (7)

Deoxygenation of nitroso-compounds (2) and (5) was carried out also by using free-radical-type reagents related to those resulting in deoxygenation of the organic carbonyl function,[1] namely $[\{Ti(cp)_2Cl\}_2]$ [9] (8), $[Ti(cp)Cl_2]$ [10] (9), and $TiCl_3$ (10). The results are practically independent of the organometallic species in the reaction with (5), which should be sensitive to the deoxygenating agent, as mentioned above. Carbazole was found only in traces when the reaction was carried out with compound (9), azo- and azoxy-coupled products being predominant. These results are exemplified by the reaction of compound (8) with nitrosobenzene [equation (iv)].



$$[\{Ti(cp)_2Cl\}_2] + PhNO \longrightarrow [\{Ti(cp)_2Cl\}_2O] + Ph{-}N{=}N{-}Ph + Ph{-}\underset{\underset{O}{|}}{N}{=}NPh \quad (iv)$$

(8) (5)

(11) (4) (3)

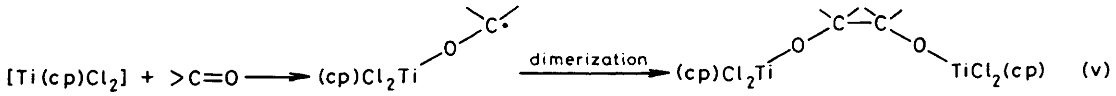
A free-radical-based mechanism (Scheme) can be proposed for reaction (iv) and for the deoxygenation of compound (5) by (8)—(10). This is based on the usual free-radical reactivity of many titanium(III) complexes. Pathways (a) and (b) may be responsible for the formation of azo- and azoxy-benzene, respectively, *via* the extrusion in both cases of the μ-oxo-complex (11) [19] from the proposed intermediates (A) and (B). This is a plausible reaction, because of the high tendency of titanium to form bonds with oxygen.

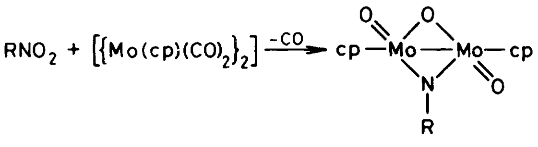
A model reaction exemplifying the first step could be found in the interaction of the free-radical-like $[Co(CN)_5]^{3-}$ with nitro- and nitroso-compounds, producing a nitroxide radical,[20] $[(NC)_5Co{-}NR{-}O^{\bullet}]^{3-}$, although the difference in oxophilicity between titanium and cobalt can induce opposite co-ordination modes of the N–O group. Moreover, a bridge-bonding mode of N–O was found in one of the complexes formed in the reaction between $[Fe_3(CO)_{12}]$ and 2-nitropropane.[21]

Pathway (b) in the Scheme is highly reminiscent of the reductive coupling of ketones promoted by $[\{Ti(cp)Cl_2\}_n]$ [22] [equation (v)].

The absence of carbazole product in the deoxygenation of (5) by compounds (8)—(10) can be ascribed to one of the following facts: (*i*) no nitrene is formed in such a reaction; (*ii*) the metal promotes the selective formation of a triplet nitrene; (*iii*) the metal–nitrene adduct undergoes transformations very different from that of a metal-free nitrene. The existence of a metal–nitrene species in such reactions received recent support from the observation that deoxygenation of nitro-compounds by a molybdenum complex occurred as shown in equation (vi) (R = aryl), with the nitrene remaining complexed by the bimetallic unit [23] in (C). It should be noted that deoxygenation of nitroso-compounds by complexes (1) and (8) is strictly related to the deoxygenation of nitrous oxides by the same compounds.[24]

Deoxygenation Reactions promoted by [Fe(salen)].—Nitro- and nitroso-compounds are capable of oxidizing iron(II) present in naturally occurring systems.[11,12] Such reactions,





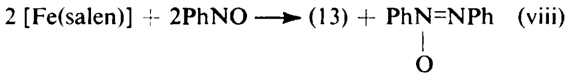
(vi)

(C)

carried out under protic conditions, led to the reduction of the nitro-compound to the corresponding amine.[12] We report here related reactions using nitroso-compounds and [Fe(salen)] (12), which is a high-spin iron(II) complex.[6] The reactions were performed in non-aqueous solvents and the nature of both the organic and inorganic products has been identified. Complex (12) is known to undergo one-electron oxidation by various organic molecules, and to have a rather high oxophilicity.[6,25] Its reaction with molecular oxygen leads to the binuclear μ-oxo-complex,[26] (13) [equation (vii)].

$$\underset{(12)}{2\,[\mathrm{Fe(salen)}]} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \underset{(13)}{[(\mathrm{salen})\mathrm{Fe{-}O{-}Fe(salen)}]} \qquad \text{(vii)}$$

Compound (13) is easily formed when a tetrahydrofuran (thf) solution of nitrosobenzene is treated with (12) [equation (viii)]. Azoxybenzene is the only significant product along



$$2\,[\mathrm{Fe(salen)}] + 2\mathrm{PhNO} \longrightarrow (13) + \mathrm{PhN{=}}\underset{\substack{|\\ \mathrm{O}}}{\mathrm{N}}\mathrm{Ph} \qquad \text{(viii)}$$

with traces of azobenzene. The reaction path we propose is very similar to that suggested for titanium(III) complexes.

Co-ordination of nitroso-compounds to iron(II) has been found to occur in iron(II) complexes, mainly in the low-spin state.[21,27] Interaction through the oxygen or nitrogen atom is possible, although only the latter has been structurally identified in chelate-type complexes.[11] Co-ordination of a nitroso-group to an iron(II) centre resembles the co-ordination of molecular oxygen,[11] which occurs *via* preliminary formation of a superoxo-complex. Moreover, [Fe(salen)] showed a free-radical-like behaviour in promoting the dehalogenation of alkyl and aryl halides.[6] Reaction of complex (12) with 2-nitrosobiphenyl, as in the case of titanium complexes and uranocenes,[28] did not produce carbazole. When nitrene-type species are produced, a metal centre seems to be able to select pathways different from those followed by the same species in the absence of the metal.

Recently, we observed similar free-radical-like chemistry when a cobalt(II)–Schiff base complex reacted with elemental sulphur upon introducing an alkali-metal cation into the reaction medium.[29] Therefore, deoxygenation of compounds (2) and (5) was carried out either in the presence or in the absence of $NaBPh_4$ in thf solution (Table). The corresponding azo- and azoxy-derivatives were obtained from (5), without traces of carbazole, as in the absence of the alkali-metal cation, but the ratio of the azo- to azoxy-compounds formed from (2) was significantly different. Thus, the alkali-metal cation seems to exert some influence, even if this is quite difficult to rationalize at the moment.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were purified and dried by standard methods. 2-Nitrosobiphenyl,[7] [Fe(salen)],[26] [Ti(cp)$_2$(CO)$_2$],[8] [{Ti(cp)$_2$Cl}$_2$],[9] and [Ti(cp)Cl$_2$] [10] were synthesized as reported in the literature. Infrared spectra were recorded using a 283 Perkin-Elmer spectrophotometer. All the reactions, except where otherwise stated, were carried out with a deficit of the nitroso-compounds, by dropwise addition of their solutions to stirred solutions of the metal complexes. The reaction temperatures never exceeded 25 °C. After the reported reaction time, the mixtures were exposed to air. T.l.c. and column chromatography were performed by using standard methods and materials. The formation of CO_2 in reactions (i) and (ii) was detected by g.c. The organic derivatives were characterized by comparison with authentic samples. The reaction conditions and products are summarized in the Table. Only two examples are described.

Reaction between Nitrosobenzene (2) *and* [{Ti(cp)$_2$Cl}$_2$].—To a solution of complex (8) (0.827 g, 3.9 mmol) in toluene (90 cm^3) was added compound (2) (0.368 g, 3.4 mmol) dissolved in toluene (50 cm^3). A yellow solid precipitated (Found: C, 54.5; H, 4.40; Cl, 16.05. Calc. for $C_{20}H_{20}Cl_2OTi_2$: C, 54.25; H, 4.50; Cl, 16.05%). The organic products were investigated in air by chromatography (silica gel, benzene): both azo- (0.059 g, 0.32 mmol; 19%) and azoxy-benzene (0.009 g, 0.045 mmol; 2.6%) were isolated.

Reaction between [Fe(salen)] (12) *and Nitrosobenzene* (2) *in the Presence of* $NaBPh_4$.—To a filtered solution obtained from complex (12) (1.217 g, 3.8 mmol), $NaBPh_4$ (0.8 g, 2.3 mmol), and thf (50 cm^3) was added compound (2) (0.404 g, 3.8 mmol) dissolved in thf (50 cm^3) in 40 min. After stirring for 2 h the mixture was filtered in air and [{Fe(salen)}$_2$O] (1.23 g, 98.5%) was recovered. By chromatography (silica gel, heptane–benzene in decreasing ratio) two organic products were isolated: azoxybenzene (0.073 g, 19.4%) and azobenzene (0.021 g, 6.1%).

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