Reductive Properties of Low-valent Titanium Reagents. Mechanistic Studies

Marek Malinowski,[*,a] **Łukasz Kaczmarek**[a] **and Franciszek Rozpłoch**[b]
[a] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52 Pl-01-224 Warsaw, Poland*
[b] *Institute of Physics, N. Copernicus University, Grudziądzka 5/7, Pl 87-100 Torun, Poland*

The reduction of nitro compounds and the deoxygenation of *N*-oxides with low-valent titanium reagents were studied. The reaction conditions were optimized. Both the inorganic and the organic part of the reaction are discussed. The reaction mechanism is deduced from stoichiometric studies and EPR measurements. Formation of an intermediate complex of an organic anion-radical with titanium is proposed as the key step in the reduction of nitro compounds and the deoxygenation of *N*-oxides with low-valent titanium. In general, this mechanism is similar to that proposed earlier for the reductive coupling of ketones.

Low-valent titanium compounds, prepared by the action of strong reducing agents on $TiCl_3$ or $TiCl_4$, can reductively couple ketones and aldehydes to give alkenes,[1–5] as well as reduce *N*-oxides to their bases[6,7] and nitro compounds to amines or azo compounds,[8] according to eqns. (1) and (2).

$$TiCl_x + \text{Reducing agent} \xrightarrow[\text{Ar}]{\text{THF}} [M] \qquad (1)$$

$x = 3,4$. Red. agent = K, Mg, $LiAlH_4$

$$[M] + \text{‘S’} \xrightarrow[\text{Ar}]{\text{THF}} [M, O] + \text{‘P’} \qquad (2)$$

‘S’ = ketone, aldehyde, *N*-oxide or nitro compound.
‘P’ = alkene, base, amine or azo compound

The synthetic part of these processes has been explored in recent papers,[5–10] whereas the mechanistic aspects have received far less attention. In this work we will focus our attention on the mechanism of reduction of *N*-oxides and nitro compounds, building on the information obtained by Dams *et al.* in their study of the reductive coupling of ketones.[5,11] The latter authors proposed a model for [M] based on the reaction stoicheiometry, electron microscopy, thermogravimetry, IR and EPR measurements. When Mg or K was used as the reducing agent, [M] was shown to consist of a crystalline carrier ($MgCl_2$ or KCl), upon which active microcrystallites or clusters of titanium(0) are randomly adsorbed.[5] The authors suggested also that [M] prepared by the reduction with $LiAlH_4$ is a cluster of formally Ti^I particles, randomly mixed with LiCl, HCl and Al^O.[5] This is in contrast with the opinion of others, who suggest that Ti^{II} is the result of reduction and is the active agent in the coupling reaction.[2,3]

Since in all cases, *i.e.* the coupling of ketones, the deoxygenation of *N*-oxides, and the reduction of nitro compounds, eqn. (1) is identical, we attempted to obtain more information on the nature of [M] by further experiments.

Results and Discussion

1. *Hydrolysis of* [M].—When we slowly added water to [M] we observed evolution of H_2, which stopped when the molar ratio [Ti]:H_2O reached 1:1. Measurements of the amount of hydrogen evolved (see the Experimental section) led to stoichiometry shown in eqn. (3).

$$[M] + H_2O\,(H_3O^+ \text{ or } OH^-) \longrightarrow [M, O] + \tfrac{3}{2} H_2 \qquad (3)$$

So, three H-atoms are involved per Ti atom: two come from the added water and so the third must already be present in [M]. Dams *et al.*[5] observed in [M] an IR band at 1728 cm^{-1}, which could be interpreted as a Ti–H stretching band. We supposed that the above observation is exclusively a surface phenomenon of the polymeric titanium particles. Since not many strong titanium–ligand bonds are present, the bulk oxidation state is close to zero. The slurry exists in a metastable state and introduction of water or organic reagent breaks down the structure of the titanium particles, causing the evolution of adsorbed/chemisorbed hydrogen. Irrespective of whether K, Mg or $LiAlH_4$ is the reducing agent for $TiCl_3$ and $TiCl_4$ the same results hold. When $LiAlH_4$ is used as the reducing agent it is the source of hydrogen. However, when Mg or K is the reducing agent for $TiCl_3$ or $TiCl_4$, then solvent tetrahydrofuran (THF) seems to be the source of hydrogen, because furan was found in the post-reaction mixture.[5] Hence the complex [M] abstracts hydrogen from THF. Such a process is often observed in organometallic complex chemistry and catalysis.

Also, when a nitro compound is reduced to an azo compound we observe evolution of hydrogen from the complex [M] when the starting nitro compound attacks [M] destroying its structure. However, evolution of hydrogen was not observed when water was added to the post-reaction mixture [M, O] that resulted when the nitro compound was reduced to an amine. This fact suggests that the hydrogen bonded to titanium is consumed during the reduction of the nitro compound to the corresponding amine.

The post-reaction mixture when decomposed by water followed by HCl, KOH or aq. ammonia gives a black precipitate (for Mg, K as reducing agents) or a dark blue–violet precipitate (for $LiAlH_4$). A black colour in these titanium compounds is characteristic of valency state +2 or lower, while a dark blue colour is characteristic for +3. If the titanium after reduction, *i.e.* in [M], has formal valency state $(+a)$, it will have valency $(a + 2)$ at the end of the process, *i.e.* in [M, O] (stoichiometrically). The colour of the hydrolysed post-reaction mixture suggests that (a) is $\leqslant +1$. Only if the hydrolysed post-reaction mixture is left for a couple of days is a white precipitate of TiO_2 obtained by slow oxidation of lower-state Ti compounds by air. Recently we have found that the reduction of $TiCl_4$ with $SnCl_2$ (1 mol equiv.) affords a mild and efficient reducing agent for *N*-oxides and nitro compounds.[12,13] In another experiment we observed that titanium prepared by reduction of $TiCl_4$ with $SnCl_2$ does not reduce carbonyl compounds, in contrast to low-valent titanium obtained by reduction of $TiCl_3$ or $TiCl_4$ using

Table 1 Reduction of *p*-nitrobenzonitrile and deoxygenation of pyridine *N*-oxide as a function of the ratio [M]:substrate

	Yield (%)			
Ti:Substrate	$NCC_6H_4NO_2$	$NCC_6H_4NH_2$	Pyridine *N*-oxide	Pyridine
1:2	72	26	52	46
1:1	48	47	0	95
2:1	0	97	0	94

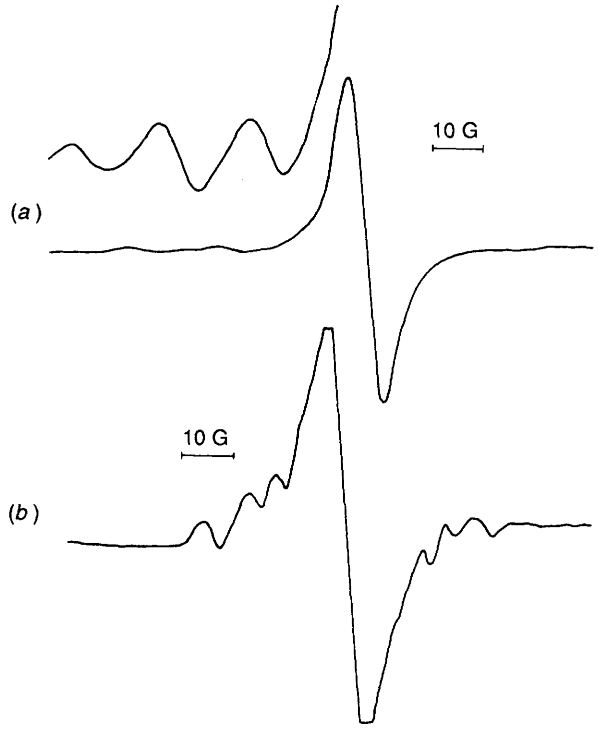


Fig. 1 EPR spectra of the titanium signals ($g < 2$) recorded during: (*a*) the coupling of ketones in the 1:0.5 $TiCl_3$:$LiAlH_4$ system; (*b*) the deoxygenation of phenazine di-*N*-oxide in the 1:2.2 $TiCl_4$:Mg system

$LiAlH_4$, Mg or K. We also found this agent to be EPR inactive. Owing to the above observations and the stoichiometry of the reaction of $TiCl_4$ with one molecular equivalent of $SnCl_2$, the valency state of the resultant titanium is +2 [eqn. (4)].

$$TiCl_4 + SnCl_2 \longrightarrow TiCl_2 + SnCl_4 \qquad (4)$$

The above facts led us to the conclusion that the reductive coupling reaction of ketones and aldehydes requires titanium in a valency state lower than Ti^{II}. On the other hand the facts also suggest that the deoxygenation of *N*-oxides and the reduction of nitro compounds already proceeds at a lower reduction potential than does the reductive coupling reaction of ketones and aldehydes.

2. *Optimization of Reaction Conditions*.—(a) *Molar ratio of* $TiCl_4$: *reducing agent*. The molar ratio $TiCl_4$:reducing agent is an important parameter in coupling reactions, because the yield of alkene produced in the reduction of carbonyl compounds critically depends upon it.[5] The optimum ratio in the deoxygenation of *N*-oxides and the reduction of nitro compounds proved to be the same as in the case of ketone-coupling reactions, that is $TiCl_4$:$LiAlH_4$ = 1:0.8 and $TiCl_4$:Mg = 1:2.2. This results in the stoichiometries shown in eqns. (5) and (6).

$$5TiCl_4 + 4LiAlH_4 \longrightarrow 5Ti^0 + 4Al^0 + 4LiCl + 16HCl \qquad (5)$$

$$TiCl_4 + 2Mg \longrightarrow Ti^0 + 2MgCl_2 \qquad (6)$$

The slight excess of the reducing agent above the stoichiometric amount is consumed by small amounts of impurities present in $TiCl_4$, $LiAlH_4$ and THF (commercial reagents used without extensive purification).

(b) *Molar ratio of* $TiCl_4$:*substrate* (N-*oxide* or *nitro compound*). At the ratios $TiCl_4$:LiAlH = 1:0.8 and $TiCl_4$:Mg = 1:2.2 we optimized the ratio $TiCl_4$:substrate (*N*-oxide or nitro compound) with respect to the yield of base or amine. The results (Table 1 and refs. 6–9) show that slightly less than one atom of oxygen can be abstracted by one atom of titanium and confirm that the reduction requires two electrons per oxygen atom. This means that the most efficient ratios $TiCl_4$:*N*-oxide and $TiCl_4$:nitro compound are 1:1 and 1:0.5, respectively. At lower ratios some unchanged organic starting material was found in the post-reaction mixture.

3. *EPR Studies*.—The reduction of nitro groups and the deoxygenation of *N*-oxides with low-valent titanium were also investigated using EPR spectroscopy.

Both of the low-valent titanium complexes, prepared from $TiCl_4$:Mg 1:2.2 as well as from $TiCl_4$:$LiAlH_4$ 1:0.8, are EPR inactive. We found (see Table 2) that during the reaction of nitro compounds and *N*-oxides a signal due to Ti^{III} ($g < 2$) starts to grow in the case when [M] is prepared by the reduction of $TiCl_4$ with magnesium. The Ti^{III} signal reaches its highest intensity at the end of the reaction, showing that Ti^{III} is part of the post-reaction complex $[M, O]_{Mg}$. The signal is almost symmetrical, but broadened and not as intense as in the case of the reaction of $[M]_{LiAlH_4}$ with ketones[5] [Fig. 1(*a*)]. This phenomenon, evidently connected with strong complexation of Ti^{III} with the amine/base formed, makes the observation of satellite bands difficult. Nevertheless, we have found broad satellite bands with *A*(Ti) at 17 G [Fig. 1(*b*)]. The lower intensity of the titanium signal is probably connected with the amount of possible different Ti–amine species from which only the monomeric one is EPR active.

In some cases we observed, in addition, an EPR spectrum of the organic anion-radical (*g* 2.002–2.003), which reached its maximum intensity for some minutes and then decreased, finally to disappear in *ca.* 30–45 min. Owing to the relatively short lifetimes of the anion-radicals in our heterogeneous system, quantitative measurements of the radical concentrations could not be performed. However, the behaviour of the EPR phenomena with time and intensity of the signals clearly suggest that the spectra are a reflection of the bulk of the reaction process.[5] Some of the anion-radical EPR spectra are shown in Fig. 2. For example, the spectrum of 4,4′-bipyridine *N*-oxide anion-radical [Fig. 2(*a*)] consists of 34 lines (theoretically 115 line splittings of nitrogen and hydrogen atoms). The spectra of phenazine di-*N*-oxide [Fig. 2(*b*)] and *p*-nitrotoluene [Fig. 2(*c*)] are less complex (the hyperfine splittings are exclusively of nitrogen). All the anion-radical EPR spectra are very similar to the known spectra

Table 2 EPR *g*-values obtained at room temperature during the reaction of nitro compounds and *N*-oxides with species [M] prepared from $TiCl_4$:Mg 1:2.2

Starting material	Organic ion-radical	Ti^{III}
4,4′-Bipyridine *N*-oxide	2.0023	1.9794
4,4′-Bipyridine di-*N*-oxide	—	1.9843
2,2′-Bipyridine di-*N*-oxide	—	1.9836
Phenazine di-*N*-oxide	2.0024	1.9856
Acridine *N*-oxide	—	1.9800
Nitrobenzene	2.0031	1.9851
2-Chloro-3-nitropyridine	—	1.9856
p-Nitrotoluene	2.0032	1.9831

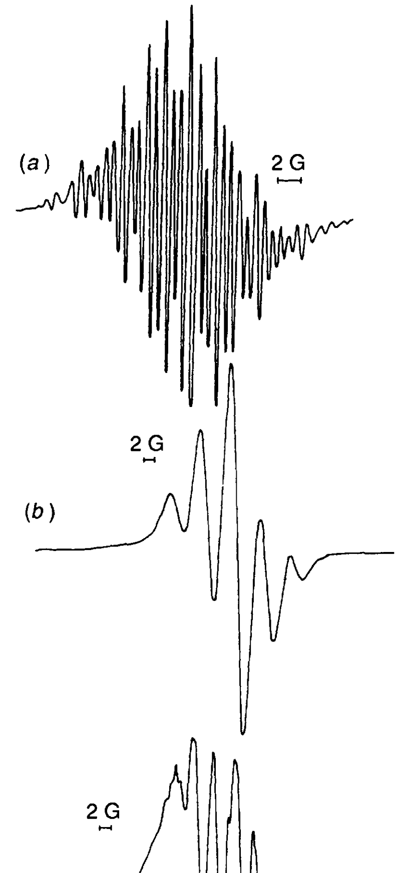
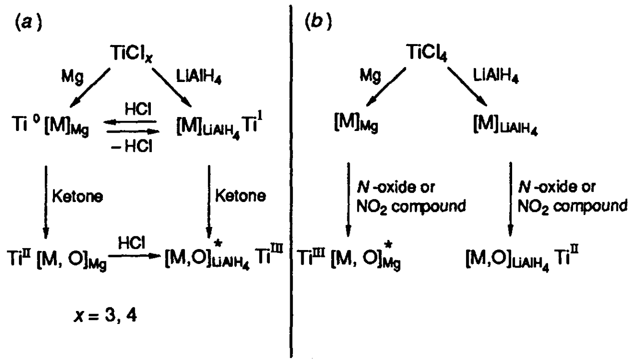


Fig. 2 EPR spectra of the anion-radicals as recorded during the reduction with [M] ($TiCl_4$–Mg system): (*a*) 4,4′-bipyridine *N*-oxide; (*b*) phenazine di-*N*-oxide; (*c*) *p*-nitrotoluene

of the appropriate parents and their hyperfine splitting constants are almost equal to those in the literature.[14,15] For example, 4,4′-bipyridine *N*-oxide anion-radical: a_N 4.13 G (lit.,[14] 4.08 G), $a_{H2,2',6,6'}$ 0.5 G (lit.,[14] 0.56 G), $a_{H3,3',5,5'}$ 2.07 G (lit.,[14] 2.37 G); phenazine di-*N*-oxide: a_N 6.5 G (lit.,[15] 6.5 G); *p*-nitrotoluene: a_N 11.3 G (lit.,[14] 10.4 G).

On the other hand, when the reaction of nitro compounds or *N*-oxides was carried out with [M] prepared by the reduction of $TiCl_4$ with $LiAlH_4$, no signals were observed in the EPR spectrum of the post-reaction mixture $[M, O]_{LiAlH_4}$ [Scheme 1(*b*)]. In contrast, the post-reaction mixtures in the coupling of ketones with low-valent titanium show a Ti^{III} signal in the EPR spectrum if starting reagent [M] is prepared with $LiAlH_4$.[5] Dams *et al.* interpreted[5] their observations of the ketone coupling by the scheme given in Scheme 1(*a*).



Scheme 1 Proposed scheme of the reaction pathways for: (*a*) the coupling of ketones with [M]; (*b*) reduction of *N*-oxides and nitro compounds with [M]. * EPR active species.

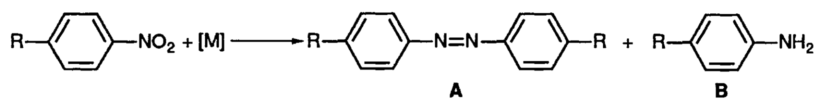
In their studies on the nature of [M] these authors found that the formal oxidation state of Ti depends upon whether H_2 or HCl was adsorbed/chemisorbed. Hydrogen ligands are characteristic of the Mg system, and HCl ligands of the $LiAlH_4$ system. As a consequence of this, when Mg is used as the reducing agent the bulk oxidation state is zero. With $LiAlH_4$ much HCl is formed and chemisorbed, resulting in an average bulk valency state of +1. Since, however, no monomeric Ti species are present in [M], it is EPR inactive regardless of the method of preparation.[5] An important consequence of the described model is that $[M] \longrightarrow [M, O]$ change in the $LiAlH_4$ system means a $Ti^I \longrightarrow Ti^{I+n}$ change, whereas in the Mg system it means a $Ti^O \longrightarrow Ti^{O+n}$ change.

4. *Reduction of Substituted Nitrobenzenes.*—In our investigations into the reduction of substituted nitrobenzenes with low-valent titanium species [M] we have found that the course of the reaction depends on the Hammett constant σ_P of the substituent.[8] Namely, if $|\sigma_p| < 0.3$, the reduction yielded a mixture of the azo compound (often the major component) and the amine, whereas for $|\sigma_p| > 0.3$ only amines were obtained. It should be noted that these results[8] apply to reactions performed at room temperature and with [M] prepared from $TiCl_4$:$LiAlH_4$ 1:0.8 (Table 3, entries 1–14). To gain insight into the underlying reasons for the substituent dependency we have performed experiments by varying the reaction conditions (reaction temperature, type of reducing agent and molar ratio $TiCl_4$:reducing agent), as shown in Table 3, entries 15–20.

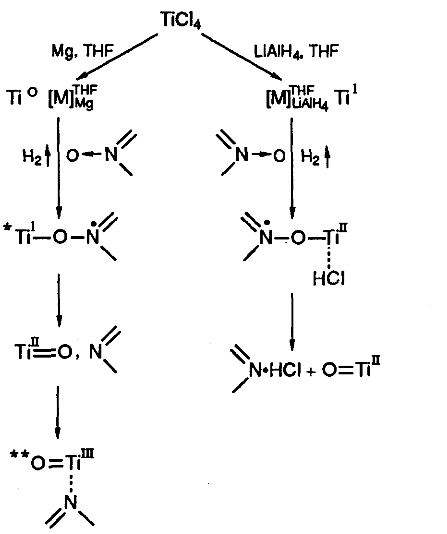
5. *Discussion of Reaction Mechanism.*—Now we propose a reaction mechanism which is consistent with all available experimental and literature data. However, this proposition is based also on some speculations and simplifications and the mechanism could be more complex.

For *N*-oxides the reaction mechanism is shown in Scheme 2. In the first step the *N*-oxide becomes attached to [M] and one electron is transferred from the titanium to the *N*-oxide, yielding the organic anion-radical. When [M] is prepared by the reduction of $TiCl_4$ with Mg, the anion-radical is stable enough to be observed by EPR spectroscopy. The titanium then withdraws an oxygen atom producing Ti^{II}=O, which transfers one electron to the remainder of the organic *N*-oxide to form an EPR active complex of Ti^{III}. On the other hand, [M] prepared from $TiCl_4$ and $LiAlH_4$ contains chemisorbed HCl,[5] which instantly reacts with the anion-radical–Ti^{II}

Table 3 Results of reaction of nitro compounds with low-valent titanium



Entry	R	σ_p	[M] (mol ratio Ti : reducing agent)	Reaction temp. (T/°C)	Yield of product (%) A	B
1	Me_2N	−0.83	$LiAlH_4$ 1:0.8	20	—	98
2	H_2N	−0.66	$LiAlH_4$ 1:0.8	20	—	96
3	HO	−0.37	$LiAlH_4$ 1:0.8	20	—	95
4	MeO	−0.27	$LiAlH_4$ 1:0.8	20	41	48
5	Me	−0.17	$LiAlH_4$ 1:0.8	20	45	45
6	H	0	$LiAlH_4$ 1:0.8	20	98	—
7	F	+0.06	$LiAlH_4$ 1:0.8	20	97	—
8	Cl	+0.23	$LiAlH_4$ 1:0.8	20	71	27
9	$PhSO_2CH_2$	+0.30	$LiAlH_4$ 1:0.8	20	—	96
10	EtO_2C	+0.45	$LiAlH_4$ 1:0.8	20	—	96
11	Ac	+0.50	$LiAlH_4$ 1:0.8	20	—	97
12	CF_3	+0.54	$LiAlH_4$ 1:0.8	20	—	95
13	NC	+0.66	$LiAlH_4$ 1:0.8	20	—	98
14	$MeSO_2$	+0.72	$LiAlH_4$ 1:0.8	20	—	97
15	Me	−0.17	Mg 1:2.2	20	—	98
16	Me	−0.17	$LiAlH_4$ 1:1.6	20	—	97
17	Me	−0.17	$LiAlH_4$ 1:0.8	80	—	98
18	H	0	Mg 1:2.2	20	—	98
19	H	0	$LiAlH_4$ 1:1.6	20	—	97
20	H	0	$LiAlH_4$ 1:0.8	80	—	98



Scheme 2 Proposed reaction mechanism for *N*-oxide deoxygenation. * EPR active anion-radicals. ** EPR active titanium.

complex to give the organic base hydrochloride and EPR inactive Ti^{II}=O.

In the case of nitro compounds, the reaction mechanism is more complex. Sobota *et al.*[16] proposed that the reduction of nitrobenzene by low-valent titanium proceeds *via* a nitrene intermediate. The nitrene then reacts with hydrogen to form aniline or recombines to yield azobenzene. In this mechanism the type of reducing agent used to form [M] should have little effect on the product composition, because the formation of all organic products proceeds *via* the common nitrene intermediate. Our results described in the preceding section 4 are difficult to reconcile with the mechanism proposed by Sobota *et al.*, but are consistent with the conclusions drawn from EPR studies.

In our view, the intermediate complexes of the organic anion-radical with titanium are different depending on whether the reaction starts from $[M]_{Mg}$ or $[M]_{LiAlH_4}$ (Scheme 2). If the reduction of nitrobenzene is mediated by $[M]_{Mg}$ the intermediate is relatively stable, which is confirmed by EPR spectroscopy [see Fig. 2(*c*)]. The stability prevents it from recombining to form azobenzenes, it can only react with hydrogen to give aniline. On the other hand, if nitrobenzene is reduced using $[M]_{LiAlH_4}$, the organic anion-radical–titanium complex is very unstable. This complex is believed to react with hydrogen (to give aniline) as well as to recombine (to give azobenzene).

Earlier investigations[5] have shown that any excess of $LiAlH_4$ used in the reduction of $TiCl_4$ reacts with the originally formed HCl. If sufficient $LiAlH_4$ is present (Ti : $LiAlH_4$ 1 : 1.6, see Table 3, entries 16 and 19) the resulting low-valent titanium is similar to that prepared with magnesium. Another way to remove HCl from the reaction medium is to raise the temperature, and this results in a low-valent titanium species similar to $[M]_{Mg}$ (Table 3, entries 17 and 20). Furthermore, the distribution of the reaction products (amine *versus* azo compound) depends on the delocalization of the electron in the intermediate anion-radical, and this phenomenon explains the σ_p-dependence of the reaction composition. To reject the occurrence of nitrenes as an intermediate we tried to trap hypothetical nitrenes with cyclohexene.[17] Despite considerable effort, we found no evidence of the expected 1,2-cycloaddition of the nitrene to cyclohexene in the reduction of nitro compounds with low-valent titanium. Hence it seems from our observations that the intermediate in the reduction of nitrobenzene with low-valent titanium is an anion-radical rather than a nitrene as Sobota[16] supposed. The presence of traces of nitrosobenzenes in the post-reaction mixtures also indicates that the reaction proceeds *via* an anion-radical rather than a nitrene intermediate.[17]

Additionally we found that azo compounds also react with low-valent titanium to give the corresponding amines, but this seems to be a simple hydrogenation of the N=N bond.

Conclusions

The formation of an anion-radical (Scheme 2) is the key step in the reduction of nitro compounds and the deoxygenation of *N*-oxides with low-valent titanium. In the case of *N*-oxides the generated base forms a relatively stable complex with the post-reaction titanium. The complex is ultimately destroyed in the work-up procedure. On the other hand, the reduction of nitro compounds leads to intermediate anion-radicals, which can react with hydrogen to produce amines, or recombine to give azo compounds. The actual reaction course depends on the stability of the intermediate radical, which is connected with its ability to form a complex with titanium, as well as on electron delocalization (the influence of substituents). The supposition that the reduction of nitro compounds proceeds *via* an anion-radical is supported by the EPR spectra of the reaction mixture and by the lack of by-products, which would be present if the reaction had an alternative nitrene mechanism.[17]

In general, the organic aspects of the mechanism of the reduction of nitro compounds and the deoxygenation of *N*-oxides with low-valent titanium seems to be similar to that proposed for the coupling of ketones.[5] However, the presence of a nitrogen atom connected to oxygen causes the reaction to be more complex. One of the most important factors is the formation of stable complexes of nitrogen-containing compounds with titanium. This factor is probably the reason for the failure of all attempts at titanium-mediated nitrogen fixation:[18] it seems that the process stops when the titanium : nitrogen ratio is 1:1.

Experimental

Instrumentation.—For the EPR measurements we used a Bruker PHYSIK B-ER 4185 Q-band apparatus.

Materials.—Solvents (Aldrich) were thoroughly dried over sodium wire and $LiAlH_4$ (when appropriate) and redistilled under N_2 prior to use.

Preparation of [M].—*With* Mg. Titanium tetrachloride (6.7 cm^3, 0.06 mol) was slowly added to stirred, dry THF (150 cm^3) at 0 °C. To the immediately formed yellow suspension was added Grignard magnesium (3.2 g, 0.133 mol) and the mixture was refluxed for 3 h to give a black slurry of the titanium(0) reagent.

With $LiAlH_4$. Lithium aluminium hydride (1.55 g, 0.044 mol) was added portionwise to a stirred, yellow suspension obtained by addition of titanium tetrachloride (6.7 cm^3, 0.06 mol) to dry THF (150 cm^3) and the black slurry was stirred at room temperature for 15 min.

Hydrolysis of [M].—The slurry of low-valent titanium complex in THF [M] was introduced into a two-necked flask equipped with a reflux condenser connected to a volumeter, magnetic stirrer and a dropping funnel containing water. Water was added dropwise, during which the mixture was stirred and cooled in a water-bath and the volume of evolved gas was measured. Hydrogen was detected using a HWD-gas chromatograph. The same procedure was applied for the post-reaction mixture after reduction of the corresponding nitro compound (2-chloro-3-nitropyridine or nitrobenzene) with low-valent titanium.

EPR Measurements.—An aliquot of the reaction mixture was transferred with the help of a syringe into an EPR tube, which had been flushed previously with argon and was carefully closed immediately after being filled. The reduction of *N*-oxides/nitro compounds was studied by starting with a species [M], generated under optimal conditions, which showed no EPR activity. Then, again under a vigorous argon stream, the *N*-oxide/nitro compound was added in one portion. After evolution of hydrogen the tubes were closed and EPR signals were followed with respect to time at room temperature. The EPR tubes, solvents and reagents were checked to be inactive in the EPR spectrometer.

All other apparatus and chemical procedures have been described previously.[5–9,12]

Acknowledgements

We express our sincerest gratitude to Professor H. J. Geise for his critical remarks and stimulating discussions. We thank also Dr. J. Herbich for his helpful remarks.

References

1 T. Mukaiyama, T. Sato and J. Hanna, *Chem. Lett.*, 1973, 1041.
2 S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chim. Fr.*, 1973, 2147.
3 J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, 1974, **96**, 4708.
4 Y. H. Lai, *Org. Prep. Proced. Int.*, 1980, **12**, 363.
5 R. Dams, M. Malinowski, I. Westdorp and H. J. Geise, *J. Org. Chem.*, 1982, **47**, 248.
6 M. Malinowski, *Synthesis*, 1987, 732.
7 M. Malinowski and L. Kaczmarek, *Synthesis*, 1987, 1013.
8 M. Malinowski, *J. Prakt. Chem.*, 1988, **330**, 811.
9 M. Malinowski and L. Kaczmarek, *J. Prakt. Chem.*, 1988, **330**, 154.
10 R. Dams, M. Malinowski and H. J. Geise, *Bull. Soc. Chim. Belg.*, 1981, **90**, 1141.
11 R. Dams, M. Malinowski and H. J. Geise, *Transition Met. Chem.*, 1982, **7**, 37.
12 L. Kaczmarek, M. Malinowski and R. Balicki, *Bull. Soc. Chim. Belg.*, 1988, **97**, 787.
13 R. Balicki, L. Kaczmarek and M. Malinowski, *Synth. Commun.*, 1989, **19**, 897.
14 *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology*, eds. H. Fischer and K.-H. Hellwege, Springer, Berlin, 1980, vol II/9 d1, pp. 451, 871–872.
15 B. H. J. Bielski and J. M. Gebicki, *Atlas of ESR Spectra*, Academic, N.Y., 1967, p. 584.
16 P. Sobota, T. Pluzinski and S. Rummel, *Tetrahedron*, 1981, **37**, 939.
17 G. L'Abbe, *Chem. Rev.*, 1969, **69**, 345.
18 S. Tyrlik and I. Wolochowicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1976, **25**, 341.

Paper 0/04813E
Received 25*th October* 1990
Accepted 20*th December* 1990