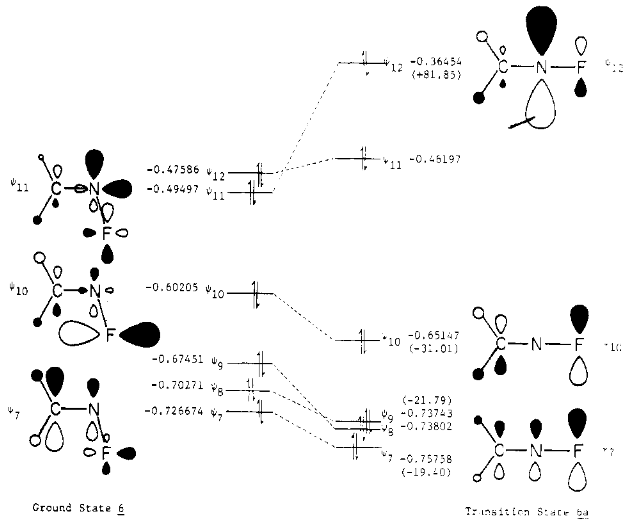


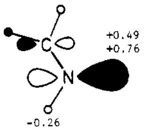
		H_a	H_b	C_{2pz}	N_{2s}	N_{2px}	N_{2pz}	F_{2s}	F_{2px}	F_{2pz}
	ψ_{11}	-0.13	+0.24	-0.11	+0.45	+0.40	+0.54	+0.04	-0.31	-0.45
6	ψ_{10}	-0.28	+0.17	-0.25	0.0	-0.13	+0.24	+0.09	+0.82	-0.11
	ψ_7	+0.30	-0.37	+0.50	+0.09	+0.03	+0.30	-0.15	+0.28	-0.14
	ψ_{12}	-0.32	+0.32	-0.12	0.0	0.0	+0.89	0.0	0.0	-0.39
6a	ψ_{10}	-0.30	+0.30	-0.44	0.0	0.0	-0.05	0.0	0.0	+0.67
	ψ_7	+0.18	-0.18	+0.33	0.0	0.0	+0.43	0.0	0.0	+0.64

Figure 5. Calculated (6-31G) frontier orbital energies (au), eigenvectors, and the net change in orbital energies (kcal/mol) for the molecular orbitals containing the nitrogen lone pair in *N*-fluoroformimine (**6**) and its transition state for inversion, **6a**. (See ref 13.)

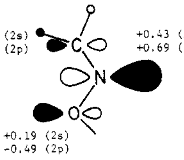
Table I. Computed (6-31G) Inversion Barriers for CH_2=N—X and the Increase in Orbital Energies upon Nitrogen Inversion

compd	X	inversion barrier, kcal/mol	ΔE for $\pi_{CH_2} - n$	ΔE for $\pi_{CH_2} + n$
3	CN	14.4	35.55	12.96
5	H	25.2	42.90	36.60
4	$^+N{\equiv}N$:	28.2	79.57	20.24
1	OH	59.5	63.81	25.55
6	F	77.4	81.85	−21.79

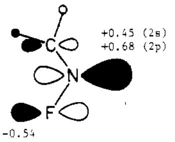
sition state for nitrogen inversion. In all three model compounds the lone pair on nitrogen resides principally in an sp^2 orbital as seen by the eigenvectors for the HOMO (ψ_8) in **5** and the NHOMO (ψ_{11}) in **1** and **6**. When the



5 (ψ_8)



1 (ψ_{11})



6 (ψ_{11})

nitrogen lone pair is directed along the *x* axis the magnitude of the coefficients reflects the relative contribution of the substitutent on nitrogen to these particular molecular orbitals.

A similar observation was made for the corresponding $\pi_{CH_2} - n$ orbitals in the *N*-cyano and *N*-diazoformimines **3** and **4**.[7b] In all five model substrates that we have studied using the extended 6-31G basis set, this particular molecular orbital consistently exhibits the largest increase in energy on going to the transition state. The lower energy ($\pi_{CH_2} + n$) bonding combination of this MO, that also contains the nitrogen lone-pair, shows an increase in orbital energy (Table I) with the exception of the fluoro derivative. The anomalously high increase in orbital energy noted for the diazo derivative **4** is presumably due to its unusually strong σ inductive effect and to the fact that the diazo portion of the molecule is nonlinear in the ground state, decreasing its effectiveness to extend the conjugation by resonance delocalization.

In summary, we have corroborated earlier suggestions[1] that electron-withdrawing substituents at nitrogen markedly increase the inversion barrier, and we have identified the molecular orbital that contributes most significantly to the activation energy as an "allyl type" MO containing the nitrogen lone pair.

Acknowledgment. We gratefully acknowledge support from the National Institutes of Health (Grant No. ES 00761-08) and the National Science Foundation (Grant No. CHE-80-06520).

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On the Mechanism of the Titanium-Induced Reductive Coupling of Ketones to Olefins

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The reductive coupling of ketones, induced by low-valent titanium, was studied by using benzophenone and cyclohexanone as model compounds. The reaction conditions were optimized. It is essential that $TiCl_3$ is reduced completely before addition of the ketone. The reaction mechanism is deduced from ESR measurements. Both the inorganic and organic part of the radical reaction are discussed. Various techniques were invoked to obtain a model for the actual coupling site. The coupling reaction occurs on the surface of an active titanium specimen.

In the early seventies three groups of investigators[2-4] established that low-valent Ti, prepared by the action of strong reducing agents on $TiCl_3$ or $TiCl_4$ in THF, can abstract oxygen from ketones, leading to the formation of

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[1] On leave from Polish Academy of Sciences, Institute of Organic Chemistry, Kasprzaka 44/52, Warszawa, Poland.

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Table I. Optimum Reaction Conditions for the Formation of [M] with Different Reducing Agents

reducing agent	$TiCl_3$/ reductant molar ratio	temp of reduction	time of reduction,[a] h	yield, %	
				TPE[b]	CCH[c]
Li	1:3.2	reflux in THF	40	85	80
K	1:3.2	reflux in THF	12	>90	90
Mg	1:1.7	reflux in THF	3	>95	90
$LiAlH_4$	1:0.5	0 °C and reflux	0.5 1	>95	85

[a] The conditions used to perform the coupling (eq 2) were 20 h of reflux in THF in the CCH cases and 6 h at room temperature for TPE formation. [b] Tetraphenylethene. [c] Cyclohexylidenecyclohexane.

olefins. The process constitutes an easy one-flask synthetic route to highly strained olefins[5-7] which are almost impossible to obtain otherwise. The actual reductive coupling proceeds in two steps (eq 1 and 2). Particularly McMurry

$$TiCl_3 + \text{reducing agent} + \text{solvent} \xrightarrow{Ar} [M] \qquad (1)$$

$$[M] + \text{ketone} \xrightarrow[\text{solvent}]{Ar} [M,O] + \text{coupling products} \qquad (2)$$

and his co-workers[8] have extensively investigated the reaction, to which we refer as the McMurry reaction hereafter. Nevertheless, important details in the mechanism remained unclarified. For instance, the reaction was postulated [4] to proceed via a radical mechanism, but the occurrence of organic radicals had not yet been proved beyond doubt. In fact an alternative mechanism involving carbene intermediates has been proposed by Tyrlik[2] and Sobota.[9a]

Furthermore, the nature of the active coupling species, [M] and in particular the formal valence state of Ti in [M] and in its successor [M,O], was unknown. In order to clarify some of these points and to elucidate contradictory reports in the literature,[4-6,8-13] we performed an ESR study of the reaction, investigated its stoichiometry, and optimized the reaction parameters. The information we obtained is helpful in the interpretation of the mechanism of the McMurry reaction and is also useful otherwise, since yields and composition of the reaction products are strongly dependent upon the reaction conditions. We selected the coupling of benzophenone to tetraphenylethene (TPE) and of cyclohexanone to cyclohexylidenecyclohexane (CCH) as model reactions for aromatic and aliphatic ketones, respectively.

Optimization of the Reaction Conditions

(a) Choice of the Reducing Agent. Three classes of reducing agents are commonly employed to reduce $TiCl_3$ to [M]: alkali metals, e.g., Li or K,[6,8,14] group II metals, e.g., Mg[2,15] or Zn–Cu couple,[8,16] and metal hydrides, e.g., $LiAlH_4$.[4,5,12,17]

Table I summarizes the optimum reaction conditions we have established for selective examples from each of the three classes. It should be stressed at this point that it is essential to carry out the reduction of $TiCl_3$ to [M] to completion in order to obtain good and reproducible yields of olefin. Otherwise, side reactions such as hydrogenation may become dominant. It is likely that some of the peculiar results, e.g., formation of tetraphenylethane encountered in the $TiCl_3$–K–THF–benzophenone system,[8] are the result of side reactions caused by incomplete formation of [M].

A comparison of the yields of olefin production (Table I) shows that however different the reduction conditions may be, the produced active [M] is in all cases equally efficient in performing the coupling. We take this as a first indication that the various reducing agents produce rather similar [M] species. Another indication hinting toward the similarity of all [M] is that in all cases, during the reduction (eq 1) the color of the reaction mixture changes from violet via blue, green, and brown to black. After the coupling (eq 2) the black color persists, which indicates that TiO_2 is not the final Ti derivative of the McMurry reaction. More proof of [M,O] being different from TiO_2 stems from the observation we made that after step 2 (eq 2) the unreactive [M,O] can be regenerated. A fresh portion of $LiAlH_4$ can restore [M,O] to the active form [M], which is capable of coupling a fresh batch of ketone in good yields.

(b) Choice of Solvent. The reactivity of [M] restricts the choice of solvents largely to hydrocarbons and ethers. We tried benzene, cyclopentadiene, hexane, furan, thiophene, pyridine, anisole, tetrahydrofuran, glyme, diglyme, and diethyl ether.

The combination reducing agent–solvent turned out to be critical. For instance, with Na and Mg, the reduction step 1 (eq 1) could practically only be performed in THF, while with Li, K, and $LiAlH_4$ the reaction could also be accomplished in glyme, diglyme, and diethyl ether with only small loss of yield (60–90% yield of TPE). In pyridine, step 1 could be performed with all reducing agents (as judged from the appearance of a black suspension) but no coupling (step 2) could be achieved. Using diethyl ether as a solvent, we observed the formation of a metallic mirror on the walls of the reaction vessel, but olefins were still formed in good yields (about 60% TPE).

Of all solvents tested, THF performed best in all instances. Variation of the concentration (between 30 and 500 mL of THF/0.02 mol of $TiCl_3$) had little effect upon the yield of TPE. Addition of THF (5–10% of the volume of the solvent for $LiAlH_4$ and ca. 60% of the solvent volume for Mg and K) to an otherwise unreactive solvent–reductant combination resulted in most instances in a rapid reduction of $TiCl_3$ to an active [M].

Another important observation was the detection after the reduction step of dehydrogenation products of the solvent, e.g., furane in the case of THF. The amount of

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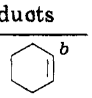
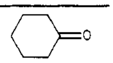
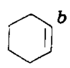
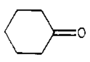
Table II. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$ to K[a]

	% olefin		% alcohol		% side products		% unreacted	
$TiCl_3$/K molar ratio	TPE	CCH	Ph_2CHOH	c-HxOH	Ph_2CH_2	 [b]	$Ph_2C{=}O$	
1:0.50	13	10	2	68	4	3	80	30
1:0.75	21		5		2		71	
1:1	27	20	3	28	2	5	65	45
1:1.5	44	35	5	15	3	4	47	42
1:2	63	50	6	11	3	3	26	30
1:2.5	80	70	4	11	2	4	17	15
1:2.75		72		9		5		13
1:3	86	75	4	8	3	3	6	12
1:3.1		80		12		1		5
1:3.2	93	90	8	5	0	2	0	0
1:3.3		87		6		5		0
1:3.5	94	88	1	9	4	2	0	0
1:4	90	92	3	5	4	2	1	0
1:5	92	86	6	5	2	0	1	1

[a] See the text for the experimental conditions. [b] Cyclohexene together with cyclohexane.

Table III. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$/Mg[a]

	% olefin		% alcohol		% side products		% unreacted	
$TiCl_3$/Mg molar ratio	TPE	CCH	Ph_2CHOH	c-HxOH	Ph_2CH_2	 [b]	$Ph_2C{=}O$	
1:0.25	22		3		2		73	
1:0.5	38	15	4	14	2	2	54	77
1:0.75	61	25	2	20	0	2	38	51
1:1	77	40	3	31	3	3	16	23
1:1.25	86	57	2	15	4	4	6	18
1:1.5	93	67	0	15	1	2	5	15
1:1.6		80		8		3		7
1:1.7	98	88	0	8	2	3	0	1
1:1.8		94		8		5		2
1:2	97	89	2	9	1	2	0	1
1:2.25	98		2		2		0	
1:2.5	96	85	2	12	4	1	0	0
1:3	98	89	3	5	0	2	0	3
1:4	95	85	2	7	3	5	1	1

[a] See the text for the experimental conditions. [b] Cyclohexene together with cyclohexane.

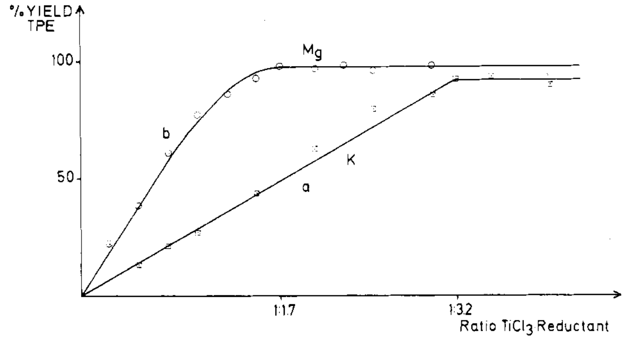


Figure 1. Percentage of TPE formed from benzophenone as a function of (a) the ratio of $TiCl_3$/K and (b) the ratio of $TiCl_3$/Mg.

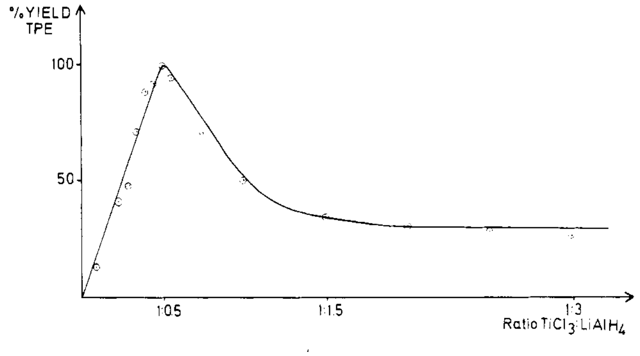


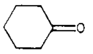
Figure 2. Percentage of TPE formed as a function of the ratio of $TiCl_3$/$LiAlH_4$.

dehydrogenation products seems to increase somewhat with the temperature at which step 1 is performed, but no quantitative measurements are presently available.

All above-mentioned facts fit the conclusion (to be worked out further below) that [M] is a suspension of titanium, mostly in the zero valency state. The colloidal system of small, active titanium particles may be stabilized by weak interactions with the solvent.

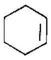
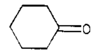
(c) Molar Ratio of $TiCl_3$ to Reducing Agent. Results of Tyrlik et al.[2] on the $TiCl_3$/Mg system had indicated that the yield of olefin depends upon the ratio of $TiCl_3$ to Mg, while for the $TiCl_3$/K system with $TiCl_3$/K ratios larger than 1:3, yields of olefin were reported[8] to be inferior. For the system $TiCl_3$/$LiAlH_4$ various ratios have been used.[4,5,11,13,17] No systematic optimization of this reaction parameter seems to have been performed so far. In each of the above mentioned systems we optimized the ratio of $TiCl_3$ to reducing agent with respect to the yield of tetraphenylethene (TPE) and cyclohexylidenecyclohexane (CCH), keeping the molar ratio of $TiCl_3$ to ketone at 1:1. We also determined a total product balance for each coupling. Side products in the coupling of benzophenone

Table IV. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3/LiAlH_4$[a]

$TiCl_3/LiAlH_4$ molar ratio	% olefin		% alcohol		% side products		% unreacted	
	TPE	CCH	Ph_2CHOH	c-HxOH	Ph_2CH_2	 [b]	$Ph_2C{=}O$	
1:0.10	13	11	4	9	0	0.5	86	81
1:0.20		19		38		0		46
1:0.25	41		3		0		60	
1:0.30	47	37	4	59	1	4	52	5
1:0.35	71		0		0		33	
1:0.40	88	42	2	53	1	3	9	1
1:0.45	91	46	3	49	1	1	5	1
1:0.50	99	68	2	32	0	0.5	0	1
1:0.55	93	62	6	33	1	0	1	1
1:0.60		60		34		0.5		3
1:0.75	70	45	5	50	1	1	20	2
1:1	50	36	4	61	1	1	43	2
1:1.5	35	23	4	74	1	2	33	4
1:2	30	18	4	86	0	1	66	0.5
1:2.5	28	14	4	83	1	1	67	4
1:3	26	15	1	80	1	2	77	0
1:4	24		4		0		75	
1:5	25		6		1		70	

[a] The reduction conditions were 0.5 h at 0 °C. See the text for further experimental conditions. [b] Cyclohexene together with cyclohexane.

Table V. Product Balance of the Coupling of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3/LiAlH_4$[a, b]

$TiCl_3/LiAlH_4$ molar ratio	% CCH	% c-HxOH	% 	% unreacted 
1:0.30	63	10	2	23
1:0.45	78	6	5	12
1:0.50	88	5	5	0
1:0.55	80	10	2	5
1:2	15	12	1	80

[a] The reduction conditions are 0.5 h at 0 °C and an additional 1 h at reflux in THF. For further experimental conditions see the text. [b] Cyclohexene together wtih cyclohexane.

to TPE are some diphenylmethanol together with minor amounts of diphenylmethane. In the coupling of cyclohexanone to CCH, side reactions gave cyclohexanol in addition to cyclohexene and cyclohexane. The latter two products were determined together. All analyses were performed by gas chromatography with an internal C_{12} standard. In addition, the percentages of TPE were also determined by UV analysis at λ_{max} = 309 nm; both methods gave the same results within experimental error.

Our results are summarized in Tables II–V and Figures 1 and 2. Each series of experiments was repeated at least three times, resulting in an accuracy of the tabulated numbers of about 5%. Judging from the percentages of olefin formed and the percentages of unreacted ketone it is clear that optimum conditions are reached at a $TiCl_3/K$ ratio of 1:3.2 (Table II) and at a $TiCl_3/Mg$ ratio of 1:1.7 (Table III). This is consistent with the formation of titanium formally in a zero-valent oxidation state (eq 3 and 4). A slight excess of reducing agent above the stoichiometric amount is necessary because $TiCl_3$ always contains some impurities ($TiCl_4$ and Ti oxychlorides) and because of very small amounts of peroxides in THF, even after a careful drying procedure. Our results corrobate McMurry's conclusion[8,14] that [M] prepared by K, Li, and similar reducing agents contains Ti(0).

$$TiCl_3 + 3K \rightarrow Ti(0) + 3KCl \tag{3}$$

$$2TiCl_3 + 3Mg \rightarrow 2Ti(0) + 3MgCl_2 \tag{4}$$

The situation in the $TiCl_3/LiAlH_4/THF$ combination is much more complicated. It is often supposed that [M] produced in this system contains a Ti(II) species.[5,13] However, it is known[18] that $TiCl_4$ reacts with large amounts of $LiAlH_4$ according to eq 5. We suggest that in our most active [M] produced at the $TiCl_3/LiAlH_4$ ratio of 1:0.5 (Tables IV and V), Al(0) is also present. We support this with the following arguments.

$$TiCl_4 + 4LiAlH_4 \rightarrow Ti(0) + Al(0) + 8H_2 + 4LiCl \tag{5}$$

First, in the electron microscope (see also section on the discussion of a model) only chlorine and no aluminium is lost when [M] is in the electron beam; if the volatile $AlCl_3$ were present, corresponding amounts of Cl and Al should be lost, as was observed in a control experiment.

Second, if [M] is prepared properly (Table I), we never observed in ESR experiments any splitting of the Ti signals due to the Al nuclear spin ($I = {}^5/_2$). Yet, it is known that if Ti(III) and Al(III) species interact, which would happen if in our system Al(III) compounds were present, an Al splitting occurs.[19–21] Only when [M] is made by using an excess of $LiAlH_4$ (e.g. 1:0.8 $TiCl_3/LiAlH_4$) do we observe small splittings due to Al.

Third, addition of a trace amount of $TiCl_3$ to AlH_3 in THF causes a complete disappearance of the white suspension of AlH_3 and the formation of gray-black Al(0) powder (unreactive toward water).

Fourth, addition of $AlCl_3$ to an ESR-inactive [M] results in a Ti(III) ESR signal the intensity of which increases with the amount of $AlCl_3$. This result can only mean that the low-valent titanium in [M] is oxidized, while Al(III)

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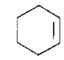
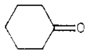
Table VI. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$/ketone[a]

$TiCl_3$/ketone molar ratio	% olefin		% Ph_2CHOH	c-HxOH	% side products		% unreacted ketone	
	TPE	CCH			Ph_2CH_2	c-HxH + 	$Ph_2C{=}O$	
5:1	94	90	4	8	2	2	0	0
4:1	90	85	4	8	1	5	2	1
3:1	97	87	2	6	0	2	0	1
2:1	92	88	5	10	0	3	0	0
1:1	92	86	6	5	1	4	0	1
1:1.25	86	76	5	8	1	3	5	5
1:1.5	75	64	8	9	2	2	13	23
1:1.75	68	50	8	10	1	5	20	32
1:2	47	40	5	8	1	2	42	50
1:2.5	31	34	4	5	2	3[b]	60	55
1:3	25	28	6	10	1	3[b]	67	55
1:4	20	21	5	8	0	2[b]	70	62
1:5	12	13	8	7	1	1[b]	72	72
1:10	6	10	4	12	0	4[b]	88	76

[a] The ratio of $TiCl_3$ to K was fixed at 1:3.2. [b] In addition to the compounds given, 1-4% of dicyclohexylpinacol were also observed.

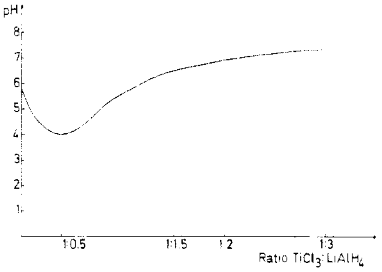


Figure 3. Values of pH of aqueous solutions obtained by hydrolysis of various [M] as a function of the ratio of $TiCl_3$/$LiAlH_4$.

is reduced. In other words, Al(III) and low-valent titanium cannot coexist together. These results suggest that Al(0) and not Al(III) is present in [M].

Further, one can conceive on purely stoichiometric grounds that the formation, formally, of Ti(0) and Al(0) proceeds via eq 6. One consequence of such a stoichiometry is that Ti(0) can already be formed at a $TiCl_3$/$LiAlH_4$ ratio of 1:0.6, while incomplete reduction to, formally, Ti(II) or Ti(I) would require ratios of 1:0.2 and 1:0.4, respectively.

$$5TiCl_3 + 3LiAlH_4 \rightarrow 5Ti(0) + 3Al(0) + 12HCl + 3LiCl \quad (6)$$

Experimentally we find (Tables IV and V) optimum coupling conditions at a $TiCl_3$/$LiAlH_4$ ratio of 1:0.5. Keeping in mind that a small portion of the reducing agent is consumed by impurities, we suggest that the formal oxidation state of Ti in the $TiCl_3$/$LiAlH_4$ system is close to Ti(I). Another consequence is that HCl is formed at high ratios of $TiCl_3$ to $LiAlH_4$, whereas H_2 is formed at low ratios. The amount of HCl must then depend upon the $TiCl_3$/$LiAlH_4$ ratio and will probably be adsorbed/chemisorbed on titanium. In other words, the stoichiometry predicts the amount of HCl to go through a maximum as a function of the $TiCl_3$/$LiAlH_4$ ratio. Hydrolysis of the corresponding [M] must give aqueous solutions of which the pH goes through a minimum. Indeed we found such a minimum (Figure 3). In the $TiCl_3$/Mg system such a pH effect was not observed, as could be expected.

Further inspection of the data (Tables II–V) shows that the use of excessive amounts of K or Mg in these systems does not have any influence upon the yield of the reaction.

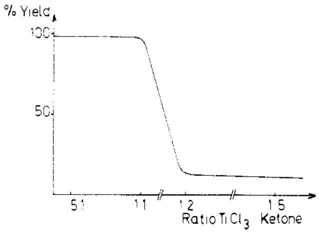


Figure 4. Percentage of TPE formed from benzophenone as a function of the ratio of $TiCl_3$/benzophenone keeping the $TiCl_3$/reducing agent ratio constant at the optimum value.

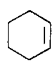
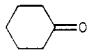
In contrast, the olefin percentage in the $TiCl_3$/$LiAlH_4$ system reaches a peak at 1:0.5, decreases, and levels off to a constant value beyond 1:2. We noted the similarity of this curve with the pH curve and speculate that high coupling activity corresponds with high HCl concentration.

Not only HCl but also H_2 can be adsorbed/chemisorbed on titanium. The presence of large amounts of activated hydrogen could explain the large amounts of cyclohexanol formed particularly with decreasing ratios of $TiCl_3$ to $LiAlH_4$ (Table IV). Preliminary experiments, in which [M] was refluxed for an additional hour after complete reduction, showed (Table V) a marked decrease in cyclohexanol production to values also encountered in the K and Mg systems.

(d) Molar Ratio of $TiCl_3$ to Ketone. Since Tyrlik et al.[2] had found indications that the $TiCl_3$/ketone ratio could be important, we optimized this parameter in the McMurry reaction.

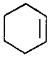
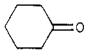
The results of the experiments in the $TiCl_3$/K (1:3.2), the $TiCl_3$/Mg (1:1.7) and the $TiCl_3$/$LiAlH_4$ (1:0.5) systems are given in Tables VI–IX and Figure 4. Each experiment was performed at least twice. The tabulated values represent averages, and their accuracy is about 5%. Three factors attract attention. First, at low $TiCl_3$/ketone ratios small amounts of pinacol are formed. Second, in the system $TiCl_3$/$LiAlH_4$/cyclohexanone the amount of cyclohexanol production can again be reduced drastically by refluxing [M] for about 1 h after its formation. Third, the most efficient ratio $TiCl_3$/ketone ratio is 1:1; at lower ratios the additional amount of ketone is left unreacted. Per titanium atom only one ketone molecule can be coupled. In other words, it is unlikely that the coupling proceeds on a single Ti atom but rather takes place on the surface

Table VII. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$/ketone[a]

$TiCl_3$/ketone molar ratio	% olefin		% alcohol		% side products		% unreacted ketone	
	TPE	CCH	Ph_2CHOH	c-HxOH	Ph_2CH_2	c-HxH + 	$Ph_2C{=}O$	
5:1	99	90	1	5	1	3	0	0
4:1	94	93	2	5	2	2	0	1
3:1	97	87	2	8	1	3	1	1
2:1	92	88	6	6	0	4	1	0
1:1	94	88	5	6	1	5	0	2
1:1.25	82	80	6	10	1	3	10	9
1:1.5	77	71	6	16	1	2	14	10
1:1.75	72	58	4	12	2	5	20	21
1:2	45	49	7	13	0	4[b]	44	30
1:2.5	35	43	5	10	2	3[b]	55	40
1:3	27	33	3	12	1	5[b]	65	48
1:4	18	20	2	8	0	4[b]	77	65
1:5	12	14	4	7	0	3[b]	86	72
1:10	10	10	2	8	1	4[b]	88	76

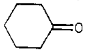
[a] The $TiCl_3$/Mg ratio was fixed at 1:1.7. [b] Additional amounts (1-2%) of dicyclohexylpinacol were observed.

Table VIII. Product Balance of the Coupling of Benzophenone to TPE and of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$/Ketone[a]

$TiCl_3$/ketone molar ratio	% olefin		% alcohol		% side products		% unreacted ketone	
	TPE	CCH	Ph_2CHOH	c-HxOH	Ph_2CH_2	c-HxH + 	$Ph_2C{=}O$	
5:1	94	68	4	32	1	0.5	0	0.5
4:1	92	68	6	30	1	1	1	2
3:1	96	72	4	25	1	0.5	0	1
2:1	99	73	0	28	0	1	0	1
1:1	91	66	6	30	2	0	1	2
1:1.25	88	58	5	32	1	0.5	5	9
1:1.50	76	44	7	32	0	2	15	20
1:1.75	71	35	4	44	1	1	22	44
1:2	43	25	6	35	2	0[b]	49	38
1:2.5	27	21	5	29	1	1[b]	65	46
1:3	22	18	6	23	1	0[b]	70	55
1:4	17	13	4	20	2	0[b]	72	65
1:5	12	10	6	15	1	0.5[b]	75	71
1:10	7	8	4	10	0	0.5[b]	80	82

[a] The $TiCl_3$/$LiAlH_4$ ratio was fixed at 1:0.5. The reduction conditions were 0.5 h at 0 °C. [b] Additional amounts (1-3%) of dicyclohexylpinacol were observed.

Table IX. Product Balance of the Coupling of Cyclohexanone to CCH as a Function of the Molar Ratio of $TiCl_3$/Ketone[a]

$TiCl_3$/ketone molar ratio	% CCH	% c-HxOH	% side products, c-HxH + 	% unreacted ketone, 
5:1	85	8	3	3
4:1	85	10	2	1
1:1.5	66	10	2	20
1:2	44	13	2	42
1:5	13	12	1[b]	70

[a] The $TiCl_3$/$LiAlH_4$ ratio was fixed at 1:0.5. The reduction conditions were 0.5 h at 0 °C and, in addition, 1 h at reflux in THF. [b] An additional 2% of dicyclohexylpinacol was observed.

of a Ti microcrystallite or Ti cluster.

Hydrolysis Experiments during the Reduction of $TiCl_3$

In 1976, Tyrlik et al.[22] studied the reduction of $TiCl_3$·3THF with Mg. They prepared [M] by using a ratio of $TiCl_3$ to Mg of 1:2.5 (eq 7 and 8). After various reduction

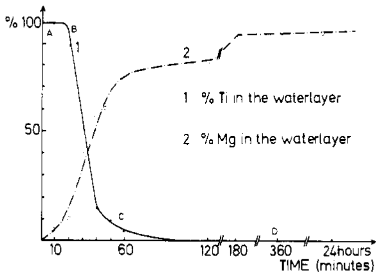


Figure 5. Study of the hydrolysis of [M] in the $TiCl_3$/Mg system.

$$TiCl_3{\cdot}3THF + Mg \xrightarrow{Ar} [M] \quad (7)$$

$$[M] + H_2O \rightarrow$$
$$\text{gas + black precipitate + water soluble substances} \quad (8)$$

times they hydrolyzed the reaction mixture and investigated the composition of the precipitate and the water

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[22] S. Tyrlik and I. Wolochowicz, *Bull. Acad. Pol. Sci, Ser. Sci. Chim.*, 24, 341 (1976).

layer. They found that after 24 h of reduction, 65% of the Mg and all Ti was consumed to form [M].

We repeated these experiments using a 1:1.7 $TiCl_3/Mg$ ratio under our optimal reaction conditions (Table I). The results are given in Figure 5. Any titanium present in the water layer should be due to unreacted $TiCl_3$, while the Mg in the water layer represents $MgCl_2$[22] formed by reaction.

The reduction has an induction period, since during the time interval AB (Figure 5) all titanium is recovered in the water layer. Only a little Mg is consumed. Probably, traces of peroxides are removed from the solvent, and at least one of the solid components (e.g., $TiCl_3$) goes into solution so that the precursor complex can be formed (e.g., $TiCl_3 \cdot 3THF$) during this period. The color of the reaction slurry changes from purple ($TiCl_3$) to blue ($TiCl_3 \cdot 3THF$).

During the second interval, BC, the amount of Ti in the water layer drops drastically, and Mg is about 60% consumed. The color of the reaction mixture changes from blue via green (ca. 15 min after the starting time) to brown (after ca. 25 min) to black (after ca. 30 min). We suggest that in this period, BC, the $TiCl_3$ is reduced to the active coupling species, which gives water-insoluble components after hydrolysis. During the period CD the amount of Ti in the water layer decreases to zero, and the amount of consumed Mg reaches 95%; that is to say after about 3 h of reflux, [M] is completely formed, and all the Mg is used.

We found that at a 1:2.5 $TiCl_3/Mg$ ratio no more than 70% of the Mg had reacted after completion of the reduction. (The remainder was left as unreacted Mg metal.) These results are further support of the conclusion that Ti(0) is the active species in the $TiCl_3/Mg$ system.

Experiments with Other Metals and Dicyclopentadienyltitanium Dichloride

In an effort to increase the number of coupling reagents we prepared some other metal slurries (Co, Ni, Fe, Sn, and Cr) by the Rieke method,[23] i.e., a reduction of the metal chloride by $LiAlH_4$. None of these metals showed any activity toward the coupling of ketones under the experimental circumstances in which titanium is successful. It should be noted that these metals have a considerably lower redox potential than titanium. Interestingly, it is reported[24,25] that low-valent tungsten, vanadium, and molybdenum compounds can be used as coupling reagents, although these metals also have low redox potentials. In the case of tungsten it was proved[24] that the coupling proceeds via a carbene intermediate.

Since in our system [M] is rather heterogeneous, we thought it worthwhile to investigate a seemingly simpler system, $Cp_2TiCl_2/LiAlH_4/THF$. The low-valent Ti complex formed after reduction showed, however, no coupling activity. Electron-spin resonance spectra taken during the reduction of Cp_2TiCl_2 showed a transient signal with $g = 1.979$, which can be assigned[19] to $(Cp_2TiCl)_2$. After complete reduction an intense signal with $g = 1.992$ is observed, as a result of the formation [19] of $Cp_2TiH(THF)$. The latter compound is known[26] to be rather stable and has apparently no coupling activity. High stability and high reactivity are often mutually exclusive properties. The high activity of our [M] could be due to a stability that is border line. The subtle difference between THF as a solvent on the one hand and diethyl ether or anisole on the other hand seems to be sufficient in that the former [M] can remain as small particles, whereas the latter [M] coagulates to a metallic mirror. In contrast, the stabilizing influence of the solvent as ligands should not be too high. Strong chelating agents such as cyclopentadiene or pyridine equally prevent the coupling in the $TiCl_3$ systems (vide supra), although the reduction could be accomplished.

Electron Spin Resonance Studies

Although the yield of the coupling in the different systems is roughly the same, we suggested already that the composition and formal valency state of Ti in the different [M]'s is not completely equal. For this reason we will discuss the systems $TiCl_3/Mg$ and $TiCl_3/K$ separately from $TiCl_3/LiAlH_4$.

Systems $TiCl_3/Mg$ and $TiCl_3/K$. Since the phenomena observed in these systems are equal, we restrict our discussion to $TiCl_3/Mg$. Solid $TiCl_3$ is a polymeric substance and has no ESR signals. Upon solution in THF the chlorine bridges are depolymerized and a blue complex $TiCl_3 \cdot 3THF$[2] is formed, giving rise to a broad (about 1400 G) signal with $g = 1.880$. Part of this complex goes into solution (the solubility[27,28] is about 10^{-3} M) and a part precipitates to the bottom of the ESR tube. The solution gives a far more intense signal than the solid, suggesting that the complex in solution is more monomeric.

The ESR spectra of the reduction (step 1, eq 1) were recorded as a function of time as well as a function of the $TiCl_3/Mg$ ratio (see Experimental Section). Both series of experiments led to the same results. Upon addition of Mg a rather sharp Ti(III) signal ($g = 1.952$; $A(Ti) = 17$–18 G) starts to grow, superposed on the broad line of $TiCl_3 \cdot 3THF$, which itself decreases slowly in intensity during the reduction. The Ti(III) signal persists until the reduction is completed. After complete reduction with 1:1.7 $TiCl_3/Mg$, only an extremely weak signal with g between 1.956 and 1.960 remains, which we attribute to paramagnetic titanium species resulting from contact of [M] with air. Despite all precautions we were not able to avoid such contacts rigorously. The fact that [M] itself has no signal is consistent with a Ti(0) species.

The reduction potentials of the species involved and the fact that a Ti(III) signal persists until the end of the reduction strongly suggest that Ti(III) is first reduced to Ti(II) in a slow step, immediately followed by a fast further reduction to Ti(0). Under the reaction circumstances, Ti(III) and Ti(0) can thus coexist together, but Ti(III) and Ti(II) cannot. The coexistence of Ti(III) and Ti(0) provides us with an explanation for two rather surprising results reported in the literature.[8]

The first is that although the reduction of $TiCl_3$ with 3 equiv of Li after 1 h at reflux temperature was incomplete (much unreacted Li was recovered), the obtained black slurry coupled ketones to olefins surprisingly well. A $TiCl_3$/Li (or K)/ketone ratio of 1:3.5:0.25 is given as optimum. We offer the following explanation: after 1 h the reduction of $TiCl_3$ is incomplete, but, nevertheless, substantial amounts of Ti(0) are already formed. This Ti(0) performs the coupling. Since only a part of the titanium is present in an active form, only 0.25 mol of ketone can be coupled per mole of $TiCl_3$.

The second unexpected result occurred in a $TiCl_3$/K/benzophenone system. $TiCl_3$ and K (ratio 1:3.5) were

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[23] R. D. Rieke and P. M. Hudnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972).

[24] Y. Fujiwara, R. Ishikawa, F. Akijama, and S. Teranishi, *J. Org. Chem.*, **43**, 2477 (1978).

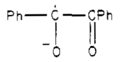
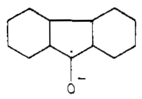
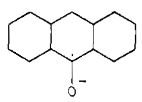
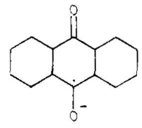
[25] T. A. Cooper, *J. Am. Chem. Soc.*, **95**, 4158 (1973).

[26] E. E. Van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 481 (1972).

[27] R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).

[28] G. W. A. Fowler, R. A. Hoodless, and R. A. Walton, *J. Chem. Soc.*, 5873 (1963).

Table X. Results of ESR. Experiments at Room Temperature during the Coupling of Ketones with [M] Prepared from $TiCl_3/Mg$ (1:1.7)

ketone added	ESR signal due to	*g* value	remarks
benzophenone	Ph_2—Ċ—O^-	2.0027	HFSC ortho, 2.52 G (lit.[29] 2.95 G) meta, 0.82 G (lit.[29] 1.10 G) para, 3.50 G (lit.[29] 3.40 G)
benzil	 $\mathrm{Ph-\underset{{}^{-}O}{\dot{C}}-\underset{O}{\overset{\|}{C}}Ph}$	2.0037	HFSC ortho, 0.99 G (lit.[30] 0.99 G) meta, 0.50 G (lit.[30] 0.36 G) para, 0.99 G (lit.[30] 1.12 G)
fluorenon		2.0034	
anthrone		2.0031	
anthraquinone		2.0036	no hyperfine splitting

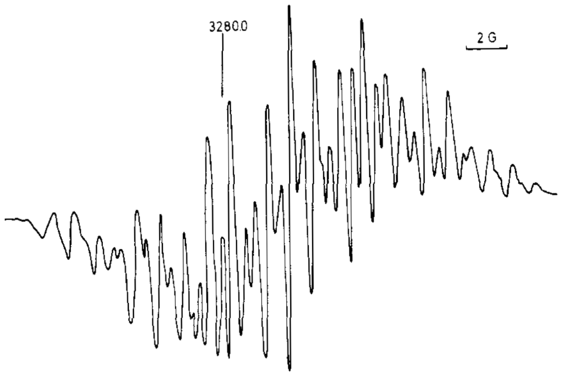


Figure 6. ESR spectrum of the benzophenone anion radical as recorded during the reaction of benzophenone with [M] produced from $TiCl_3/Mg$.

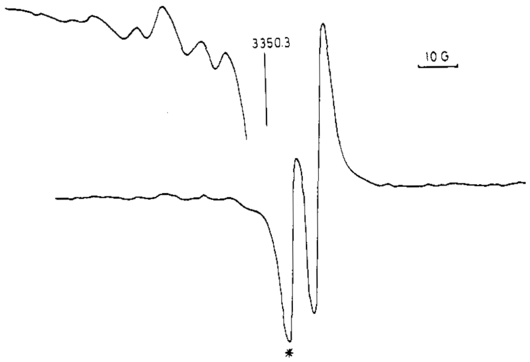


Figure 7. ESR spectrum of the titanium signals ($g < 2$) recorded during the coupling of ketones in the 1:0.5-$TiCl_3/LiAlH_4$ system. The impurity signal is marked with an asterix.

heated in THF for 1 h, after cooling benzophenone was added, and after a further 16 h of reflux tetraphenylethane was obtained in 80% yield instead of the expected TPE. Here again the coupling step was started with an incompletely formed Ti(0) species, i.e., during the coupling (olefin formation) new [M] is also formed by reduction of $TiCl_3$ with K, which are still present. At elevated temperatures (16 at reflux) the fresh [M] abstracts hydrogen from THF and is able to transfer it to the initially formed tetraphenylethene, giving the corresponding saturated hydrocarbon. The fact that in the experiment with Li the olefin remained intact is due to the (fortunate) circumstance that formation of new [M] is much slower with Li than with K (see Table I).

We recall that after complete reduction all [M] are ESR inactive, regardless of the reducing agent employed. Addition of benzophenone to [M] in the Mg system produces at room temperature within 2 min an ESR pattern ($g = 2.0027$) which increases in intensity, reaches its maximum in about 1 h, and decreases very slowly later on. The spectrum (Figure 6) consists of 40 lines and corresponds to the benzophenone anion radical. The hyperfine splitting constants (Table X) deviate slightly from those reported by Rieger and Fraenkel,[29] suggesting that in our system the organic radical is bonded to Ti. A further indication is that we occasionally observed Ti satellite lines ($A = 17$ G) on the organic signal, which can only be caused by direct interaction.

Neither during nor after the coupling reaction (step 2, eq 2) did we observe signals due to Ti specimens ($g < 2$). Also during the coupling of other aromatic ketones we invariably observed only signals of the corresponding anion radicals. These signals sometimes[31] showed very well resolved hyperfine splittings, again with indications of a link between the Ti and the organic radical (Table X). Unfortunately, the short relaxation times of the anion radicals of aliphatic ketones prevented their observation.

System $TiCl_3/LiAlH_4$. The reduction of $TiCl_3$ to [M] with $LiAlH_4$ was followed by recording ESR spectra as a function of the $TiCl_3/LiAlH_4$ ratio. The same signals (Table XI) were observed as those described in the $TiCl_3/Mg$ system. In the $LiAlH_4$ system the finally resulting [M] is equally ESR inactive. If here, as we suggested, the formal valency state of titanium is Ti(I), then [M] must be polymeric, or at least dimeric. The situation in the $LiAlH_4$ system during the coupling differs from the coupling in the Mg system. The spectra taken during the coupling, induced by [M] from a $TiCl_3/LiAlH_4$ ratio of 1:0.5, showed three groups of signals: one group with $g > 2$ due to organic anion radicals and two groups with $g < 2$ due to titanium species.

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(29) P. Rieger and G. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

(30) R. Dehl and G. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(31) The occurrence of hyperfine splittings depends inter alia on the radical concentration, a parameter which is difficult to control in our heterogeneous system.

Table XI. Results of the ESR Experiments at Room Temperature during the Reaction of Some Ketones, Alcohols, and Alkenes with [M] Prepared from $TiCl_3/LiAlH_4$ (1:0.5)

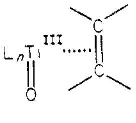
		Ti signals	
substrate	organic g signal	impurity signal[b]	reaction signal[a]
benzophenone	2.0027 ($Ph_2\dot{C}—O^-$)	$g = 1.955$, $A = 17.5$ G	$g = 1.950-1.951$, $A = 17$ G
fluorenone	2.0032	$g = 1.954-1.953$, $A = 17$ G	$g = 1.950-1.951$, $A = 17.5-18$ G
acetophenone	2.0030[c]	$g = 1.953-1.954$, $A =$ 17-17.5 G	$g = 1.950$, $A = 18$ G
3-pentanone	none	$g = 1.954$, $A = 17$ G[d]	$g = 1.954-1.955$, $A = 17-17.5$ G
cyclohexanone	none	$g = 1.955$, $A = 17-17.5$ G	$g = 1.950-1.951$, $A = 16.5-17$ G
cyclohexanol[a]	none	$g = 1.954-1.955$, $A = 17-17.5$ G	
3-pentanol[e]	none	$g = 1.955-1.956$, $A = 17.5-18$ G	
benzhydrol[e]	none	$g = 1.950-1.952$, $A = 17-17.5$ G	
tetraphenylethene[f]	none	$g = 1.954$, $A = 17-18$ G (weak signal)	
2,3-dimethyl-2-butene[f]	none	$g = 1.955$, $A = 16-17$ G (weak signal)	

[a] The reaction signal is due to formation of [M,O]. [b] The impurity signal is due to reaction of [M] with air. [c] The origin of this signal is not known with certainty. [d] The impurity signal can only be distinguished from the reaction signal in Q-band EPR spectra. [e] Alcohols give rise to only one Ti signal. [f] Olefines give rise to only one Ti signal.

With benzophenone, fluorenone, anthrone, and benzil we found g values and hyperfine splitting constants equal to those in the $TiCl_3/Mg$ system. The only difference is that the signals now disappear faster (in about 20 min).

The observation of the two Ti signals ($g < 2$; see Figure 7) is independent of the nature of the ketone. Even with aliphatic ketones, which do not show organic signals, the same Ti signals are observed as with aromatic ketones (Table XI). Q-band ESR measurements proved decisively that two separate Ti species are present and not one species with an anisotropic signal. One of the two signals, the one of which the intensity remained constant during the coupling, could be assigned to a Ti species originating from reaction of [M] with air. The other signal increases inintensity during the coupling, reveals satellite bands with A(Ti) between 17 and 18 G, and is almost symmetrical at the end of the reaction. Such characteristics point to the formation of [M,O] as a monomeric Ti(III) species. Because the reductive coupling requires two electrons per ketone molecule and because the $TiCl_3$/ketone ratio is 1:1, [M] from $TiCl_3/LiAlH_4$ must formally contain Ti(I) compounds at the beginning of the coupling. The ESR phenomena show that [M] must be polymeric (dimeric) before coupling and that sometime during the coupling (eq 2) the titanium is broken down into Ti monomers. This process is accompanied by H_2 evolution.

Further information about the nature of [M,O] stems from ESR spectra obtained after addition of $TiCl_3$ to alkenes (e.g., 2,3-dimethyl-2-butene or TPE). The signals were very similar to those of [M,O] and must be due to Ti(III) which is π bonded to the olefinic bond. We interpret the time-dependent Ti signal in the $TiCl_3/LiAlH_4$ system as due to [M,O], containing Ti(III) π bonded to the produced alkene. A model for [M,O] would be as follows, with L = THF, Cl, or other ligands.



Further Studies on the Nature of [M]. Discussion of a Model

We attempted to obtain more information on the nature of [M] via electron microscopy, thermogravimetry, and infrared spectroscopy.

A few drops of the [M]-containing suspension were quickly transferred to an electron microscope, avoiding contact with air as much as possible. The [M] prepared from $LiAlH_4$ looked totally amorphous, whereas in samples of [M] prepared from $TiCl_3/K$ and $TiCl_3/Mg$ distinct microcrystals were visible. Apart from the direct view, we also worked in the diffraction mode and performed microelemental analyses (elements with $Z > 11$) on selected spots. The results showed that the composition of the samples is heterogeneous in all cases. Atomic ratios of Ti to other elements were random; the only correlations that seem to exist are between K/Cl ≈ 1:1 and Mg/Cl ≈ 1:2 at the position of the microcrystals. Occasionally we encountered spots with a Ti content over 95%. In samples of [M] from $TiCl_3/LiAlH_4$ it was often observed that the Cl content decreased under prolonged (~20 s) illumination by the electron beam, whereas the Ti and Al contents remained unchanged. As stated earlier, it is our interpretation that HCl is boiled off. In a control experiment it was verified that pure $AlCl_3$ is completely evaporated within 5 s under the experimental conditions prevailing in the electron microscope.

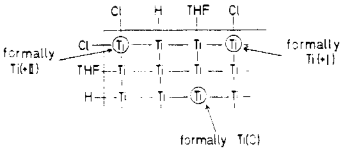


Figure 8. Possible model of an active titanium particle.

When [M] is put on a thermobalance under inert atmosphere, two distinct mass jumps were noted. One could be correlated to loss of the ligand THF. At still higher temperatures a slow decrease in mass occurred in the $TiCl_3/LiAlH_4$ system. We could detect HCl in the effluent gases.

Infrared studies on [M] showed inter alia a band near 1728 cm^{-1}; such bands are commonly[32] assigned to Ti–H stretchings. The combination of evidence led to the following working model of [M]. It consists of a carrier of Al and LiCl or other metal chlorides (KCl, $MgCl_2$) depending upon the reducing agent used. On this carrier is the active titanium dispersed at random. A picture of such a titanium particle is given in Figure 8. The inner side resembles metallic titanium. At the surface titanium can be in a higher valency state, when bonded to chlorine in particular. The number and strength of the ligand bonds determine the formal valency state of a particular titanium atom at a particular position on the surface. The formal bulk valency state is then an average over all titanium atoms. When Mg or K are used as reducing agents, not many strong titanium–ligand bonds are present, and the

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[32] R. J. H. Clark in "Comprehensive Inorganic Chemistry", Vol. III, J. C. Bailar, H. J. Emeléus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson Eds., Pergamon Press, New York, 1980, p 362.

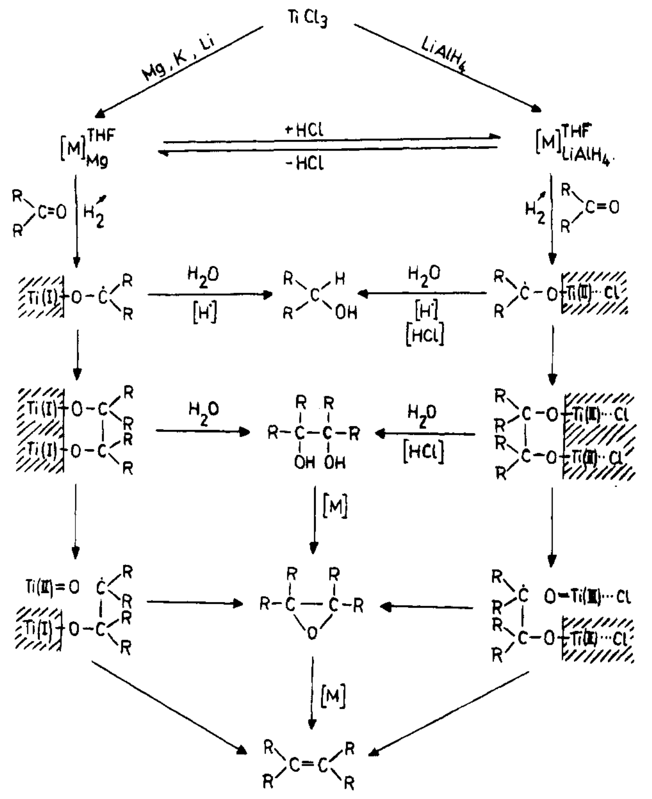
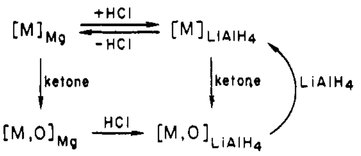


Figure 9. Proposed organic part of the reaction mechanism.

bulk oxidation state is close to zero. With $LiAlH_4$ much HCl is formed and chemisorbed, resulting in an average bulk valency state of ca. +1. Since, however, no monomeric Ti species are present in [M], it does not show ESR activity regardless of the method of preparation.

In the model of [M] we have developed so far, the formal oxidation state of Ti depends upon whether H_2 or HCl is adsorbed/chemisorbed. Hydrogen ligands are characteristic for the Mg system and HCl ligands for the $LiAlH_4$ system. Exchange of H_2 by HCl must then transfer the [M] of the Mg system into [M] of the $LiAlH_4$ system and vice versa. Indeed, bubling of dry HCl gas through [M] prepared from $TiCl_3$/Mg gives an active [M] which shows upon addition of, e.g., benzophenone, the two Ti signals ($g < 2$) characteristic of the $TiCl_3/LiAlH_4$ system. The reverse process, the removal of HCl from the $TiCl_3/LiAlH_4$ reaction slurry, can be performed by using an excess of $LiAlH_4$. It was gratifying to see that at low $TiCl_3/LiAlH_4$ ratios the addition of benzophenone no longer produced Ti signals but only signals of the organic anion radical. Such behavior is characteristic for the $TiCl_3$/Mg system. We conclude that the process shown in eq 9 takes place.

Scheme I



$$[M]_{Mg}{}^{THF} \underset{-HCl}{\overset{HCl}{\rightleftarrows}} [M]_{LiAlH_4}{}^{THF} \qquad (9)$$

Another consequence of the model is that an [M] → [M,O] change in the $LiAlH_4$ system means an Ti(I) → Ti(III) change, whereas in the Mg system it means a Ti(0) → Ti(II) change. To prove the Ti(II) state in [M,O] of the latter system, we carried out the coupling of benzophenone to completion, that is until *all* ESR signals including these of the organic anion had disappeared. If the now-formed [M,O] contains Ti(II), it should be possible to oxidize it to Ti(III). Indeed, bubbling of dry HCl gas through the final mixture produced a system which showed in the ESR spectrum the two Ti signals characteristic of the $LiAlH_4$ system. Futhermore, preliminary experiments showed that a fresh batch of $LiAlH_4$ (ca. 0.01 mol/0.02 mol of $TiCl_3$) could transform an inactive [M,O] into an active [M] capable of coupling a fresh batch (0.02 mol) of benzophenone (see Scheme I). Further work to complete this picture is in progress.

Reaction Mechanism and Discussion of the Organic Aspects

Now that the connection is made between [M] prepared by K or Mg on the one hand and [M] prepared by $LiAlH_4$ on the other, we are in a position to propose a general reaction mechanism (see Figures 9 and 10) which is con-

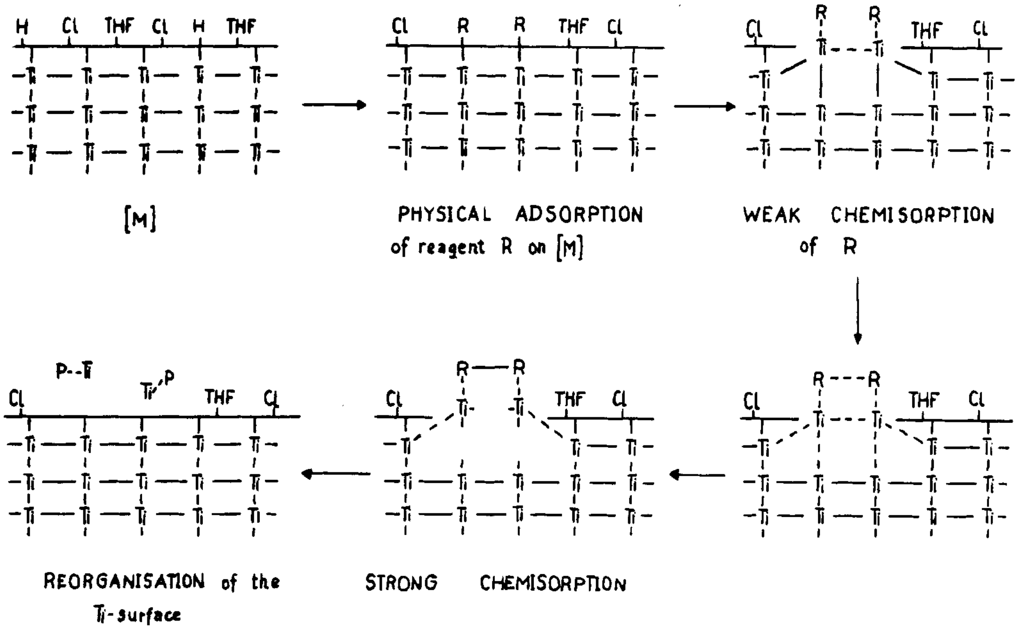


Figure 10. Proposed inorganic part of the reaction mechanism; R represents the reagent molecule (ketone) and P the product molecule (olefin).

sistent with all available experimental evidence.

In the first step the ketone becomes attached to [M] and one electron is transferred from the titanium to the ketone, yielding the organic anion radical. This radical dimerizes to a titanium pinacolate in the second step. The titanium then withdraws in consecutive steps two oxygen atoms from the pinacolate, and the formed olefin is kept π bonded to Ti in the postreaction [M,O] complex.

A similar, but less detailed, mechanism was already put forward by McMurry et al.[8] In what follows we will discuss the separate steps.

Due to the interaction of the ketone with [M], hydrogen gas is evoluted. The ketone becomes attached to a free active site on titanium, and the coupling process via a radical mechanism is started by an electron transfer from Ti to the ketone molecule. Quantitative measurements of the radical concentrations have not yet been performed, but the behavior of the ESR phenomena with time clearly suggests that the spectra are the reflection of the bulk of the reaction process. At this point it may be advantageous to consider some factors that determine the reactivity of [M] toward coupling. Necessary prerequisites of the metal are a strong affinity for oxygen and a redox potential exceeding the redox potential of organic ketones. Furthermore, we suggest that the solvent used as ligand should have just sufficient chelating properties to prevent the coagulation of the Ti particles ("solvated metal"). If the link between ketone and Ti involves d–π bonding, the availability of d orbitals is necessary. The electron transfer could proceed via back-donation.

The anion radicals can now react in two ways: they either dimerize to titanium pinacolate or form alcohols (and hydrocarbons to a lesser extent) by uptake of adsorbed activated hydrogen. The hydrogen source is $LiAlH_4$ and/or THF, the latter when K or Mg is used as the reductant. Reflux of [M], prior to the addition of the ketone, results in a decrease of the alcohol production.

The majority of anion radicals will dimerize under proper experimental conditions. We speculate that *this* step is rate determining and *not* the subsequent fission of the C–O bonds. Though conclusive evidence is still lacking, the assumption fits in with the following observations. The amount of hydrogenation products of the anion radicals is higher than that of any other side reaction product, suggesting that the anion radical is a longer living intermediate. Also, the coupling rate for aliphatic ketones is much lower than for aromatic ones, and as a consequence the amount of alcohol production is higher with aliphatic ketones. This suggests that there is a relatively important accumulation of radical anions, consistent with the occurrence of a sizeable energy barrier just behind them. The cause of the barrier could be that dimerization requires the encounter of two radicals in a correct orientation on neighboring Ti centers. This process is statistically unfavorable and is subjected to the effects of steric hindrance. The view offers an explanation why strongly hindered ketones such as di-*tert*-butyl ketone, *tert*-butyl isopropyl ketone, and *tert*-butyl neopentyl ketone form only the corresponding alcohols when subjected to the McMurry reaction.[33] If the abstraction of oxygen from the pinacolate were the most difficult step, the corresponding pinacols should be formed.

After the formation of the titanium pinacolate the two C–O bonds are broken in consecutive steps as is proved by the occurrence of an epoxide as a side product in the coupling of mesityl oxide. The formation of an epoxide via the produced olefin is very unlikely.

The result of the total process is an olefin π bonded to [M,O]. Preliminary experiments have shown that it is possible to reconvert [M,O] to active [M] with a fresh batch of $LiAlH_4$.

The organic part of the mechanism is equal for all systems, regardless of the reducing agent. Finally, the occurrence of carbenes as intermediates in an alternative reaction pathway can be rejected. Despite considerable effort, we never succeeded in trapping carbenes with the usual reagents such as diazomethane and vinyl ether.

Experimental Section

Instrumentation. We used the following apparatus: Du Pont Instruments 951 thermogravimetric analyzer, Du Pont Instruments R90 thermal analyzer, Varian E-112 Q-band ESR spectrometer, Varian E4 and E 101 X-band ESR spectrometers, JEOL PS 100 ^1H NMR spectrometer, Varian Aerograph 1400 gas chromatograph (the length of the column was 1.19 m, and it was packed with 15% Dexsil on Chromosorb W), Perkin-Elmer 580 IR spectrophotometer, JEOL 01-SG2 mass spectrometer, Cecil Instruments CE 303 grating UV spectophotometer; Philips transmission electron microscope with energy-dispersive X-ray emission analysis and selected area electron diffraction (100 kV, Model EM 300). The EDXRA system consists of a KEVEX Si–Li semiconductor detector and a Link Systems computer. All melting points are uncorrected.

Materials. Solvents (Aldrich) were thoroughly dried over sodium wire and $LiAlH_4$ (when appropriate) and redistilled under N_2 prior to use. $TiCl_3$ (Alfa Ventron) was stored under Ar. Benzophenone and cyclohexanone (Aldrich) were used without further purification. All manipulations with $TiCl_3$ and [M] were carried out either in a glovebox or in Schlenk-type glassware under argon.

Preparation of [M]. With Mg or K. In a glovebox 3.12 g (0.02 mol) $TiCl_3$ was accurately weighed into a three-necked flask. Then 60 mL of dry solvent (usually THF) was added. To the stirred slurry the desired amount of Grignard magnesium was added from a Schlenk-tube under argon. The mixture was refluxed for 3 h, at which time all the Mg had reacted and the color of the mixture had changed from violet via blue, green, and brown to black. Instead of Mg, an equivalent amount of K, freshly cut and washed with hexane, can be used. A reflux time of 12 h is necessary to complete the reduction.

With $LiAlH_4$. The $TiCl_3$/THF mixture was cooled to 0 °C, and the desired amount of $LiAlH_4$ was added in small portions to keep the vigorous reaction (H_2 evolution) under control. After the addition, the reaction mixture was stirred at 0 °C for 30 min. If hydrogenation as a side reaction is to be minimized, the black suspension of [M] is refluxed for an additional hour.

Procedure for the Coupling Reactions. The desired amount of ketone was added via a Schlenk tube to the cooled, black suspension of [M]. A rapid evolution of H_2 was observed particularly with $LiAlH_4$ as the reducing agent. After the addition, the mixture was stirred at room temperature for ca. 6 h in the case of benzophenone or refluxed for ca. 20 h in the case of cyclohexanone. During the reaction a gentle stream of argon was maintained. Experiments had shown that the above reaction times are sufficient to obtain complete coupling. The reaction was then quenched by adding 40 mL of 2 N hydrochloric acid, and the reaction mixture was extracted three times with 10 mL of $CHCl_3$. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated.

In a typical preparative experiment [M] was generated from 3.12 g (0.02 mol) of $TiCl_3$ and 0.38 g (0.01 mol) of $LiAlH_4$ in 60 mL of THF as described. Then 3.64 g (0.02 mol) of benzophenone or 1.96 g (0.02 mol) of cyclohexanone was added and the mixture worked up as above. A yield of 3 g (90%) of TPE was obtained after column chromatography [length 20 cm, adsorbent Al_2O_3, eluant petroleum ether bp 60/80 °C] and recrystallization from acetic acid; mp 222–223 °C (lit.[34] mp 222 °C). Yield of 1.4 g (85

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(33) R. Dams, M. Malinowski, and H. J. Geise, unpublished results.

(34) W. Schlenk and E. Bergman, *Justus Liebigs Ann. Chem.*, **463**, 1 (1928).

%) CCH was isolated after column chromatography and recrystallization from ethanol; mp 51–52 °C (lit.[35] mp 53.5–54.5 °C).

Product Balances. In the experiments performed to obtain the product balances, THF was added (if necessary) before the workup in order to restore the original volume. Then a 10-mL sample was hydrolyzed by 10 mL of 2 N HCl and extracted with $CHCl_3$ (benzophenon case) or pentane and ether (cyclohexanone experiments). A 1-mL extract was mixed with 1 mL of an internal standard solution of dodecane by using calibrated micropipets and analyzed by gas chromatography. Concentrations of TPE were also measured by UV analysis starting from a 2-mL sample treated in the usual way and diluted to the desired dilution factor. Absorbances at λ_{max} = 309 nm ($CHCl_3$) were compared against absorbances of standard solutions of TPE. No interferences were observed.

ESR Measurements. The reduction of $TiCl_3$ with Mg at a 1:1.7 $TiCl_3$/Mg ratio was followed by ESR. At regular intervals (about every 30 min) an aliquot of the reaction mixture was transferred with the help of a syringe into the ESR tube, which was flushed before with Ar and carefully closed immediately after being filled. Spectra were recorded at room temperature. Step 1 (eq 1) was also followed as a function of the $TiCl_3$/Mg ratio ranging from 1:0.2 to 1:1.8. In each case [M] was prepared as stated (3 h reflux) by using the same ESR conditions as before. The results were completely analoguous; i.e., for example, a spectrum of [M] with a 1:0.8 $TiCl_3$/Mg ratio was equivalent to one recorded with a 1:1.7 $TiCl_3$/Mg ratio after half the reduction time.

The reduction of $TiCl_3$ by $LiAlH_4$ is fast and was only followed as a function of $TiCl_3/LiAlH_4$ ratios. For each ratio, the reaction mixture was prepared by addition of the appropriate amount of $LiAlH_4$ to an ice-cooled $TiCl_3$–THF mixture. After the addition, the mixture was allowed to warm to room temperature and stirred for 30 min under an argon atmosphere. As before, samples were transferred into an ESR tube under a vigorous Ar stream, and room-temperature spectra recorded.

The coupling (eq 2) was studied by starting from an [M], generated under optimal conditions (Table I), which showed no ESR activity. Then, again under a vigorous Ar stream, the ketone was added in one portion up to a $TiCl_3$/ketone ratio of 1:1. After hydrogen evolution, the tubes were closed, and ESR signals were followed with respect to time at room temperature.

The ESR tubes, solvents, and reagents were checked to be inactive in the ESR spectrometer.

Acknowledgment. Much of this investigation could not have been performed without the equipment kindly put at our disposal by other institutes. We express our sincerest gratitude to Professor Dr. J. Reedijk (State University Leiden, The Netherlands), Dr. P. Van der Put (Technical University Delft, The Netherlands), and Professor Dr. D. Schoemaker (Department of Physics, UIA) for their permission to use the X-band and Q-band ESR spectrometers and above all for their professional expertise. The help of Drs. P. Bloch with the electron microscope and of Professor Dr. M. Herman (University of Antwerp, RUCA) with the IR spectroscopy and thermogravimetry is gratefully acknowledged. Professor Dr. F. Alderweireldt, Dr. E. Esmans, Dr. R. Dommisse, and Mr. Y. Luyten (University of Antwerp, RUCA) are thanked for their assistance with the gas chromatographic analyses and for recording NMR and mass spectra. Dr. Jerzy Herlich and Dr. I. Wolochowicz (Technical University, Warsaw, Poland) are thanked for stimulating discussions and critical remarks. M. M. is grateful for receiving a postdoctoral grant within the framework of the Polish-Belgian Exchange Treaties. R. Dams thanks the Belgian organization IWONL for a predoctoral grant.

Registry No. Benzophenone, 119-61-9; cyclohexanone, 108-94-1; tetraphenylethene, 632-51-9; cyclohexylidenecyclohexane, 4233-18-5; benzil, 134-81-6; fluorenone, 486-25-9; anthrone, 90-44-8; anthraquinone, 84-65-1; benzophenone radical ion 1−, 16592-08-8; benzil radical ion 1−, 16827-94-4; fluorenone radical ion 1−, 3101-67-5; anthrone radical ion 1−, 34500-64-6; anthraquinone radical ion 1−, 3426-73-1; acetophenone, 98-86-2; 3-pentanone, 96-22-0; cyclohexanol, 108-93-0; 3-pentanol, 584-02-1; benzhydrol, 91-01-0; 2,3-dimethyl-2-butene, 563-79-1; $TiCl_3$, 7705-07-9.

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[35] R. Criegee, E. Vogel, and H. Hoger, *Chem. Ber.*, **85**, 144 (1952).

Inert Carbon Free Radicals. 2. Monofunctionalized Tetradecachlorotriphenylmethyl Radicals and Related Compounds

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Perchlorinated triphenylmethyl radicals, and their nonradical α-H precursors, with hydrogen (2), carboxy (3), carbomethoxy (4), ammonium carboxylate (5), bromo (6), iodo (7), and methyl (8) substituents in the 4-position have been synthesized and their reactivities studied. The radicals are completely disassociated even in the solid (magnetic susceptibility), and their radical character is not changed by O_2 or highly reactive chemical agents. Their decomposition points in air range from 270 °C to beyond 300 °C. Their remarkable spectra (ESR, UV–vis, and IR) are given and interpreted. A novel substitutive–oxidative decarboxylation with I_2 has been found in carboxy radical 3.

Some years ago, the authors reported the discovery of the so-called "inert carbon free radicals".[1] These are trivalent carbon species which are completely disassociated even in crystalline form, do not react with oxygen in solution or with typical radical reagents (nitric oxide, quinone, hydroquinone, toluene, etc.), and are remarkably inert toward reactive chemical species (concentrated H_2SO_4, concentrated HNO_3, Cl_2, Br_2, etc.). Furthermore, in air they withstand temperatures as high as 300 °C. Their chemical inertness and thermal stability are traced to steric shielding rather than to electronic effects.[1a] The

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[1] (a) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Ballester, M.; Riera, J.; Castañer, J. Spanish Patent 311 621 (1965); U.S. Patent 3 347 941 (1967); Canadian Patent 805 963 (1969).

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