# Generation of Reactive Low-Valent Titanium Species Using Metal−Arenes as Efficient Organic Reductants for $TiCl_3$: Applications to Organic Synthesis

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A comprehensive study on the use of metal−arene systems as organic reductants for $TiCl_3$ has resulted in an efficient method for the generation of highly reactive low-valent titanium (LVT) reagents. The activated titanium species could be prepared by refluxing a mixture of substoichiometric amounts of arenes, $TiCl_3$, and Li/Mg in THF or DME. Among the LVT reagents screened, $TiCl_3$−Li−naphthalene−THF (reagent **I**) was the best for coupling of carbonyls to olefins. The reagent could carry out the McMurry olefination of both aromatic and aliphatic substrates at a lower temperature and in a much reduced time as compared to the conventional procedures. Subtle changes in the method of preparation of the LVT reagents influenced the stereoisomeric ratio of the olefins. The reagent was also useful for the synthesis of *O*- and *N*- heterocycles and vicinal diamines via intramolecular carbonyl coupling and reductive duplication of imines, respectively.

## Introduction

Due to the unique features of high oxophilicity and reducing power, low valent titanium (LVT) reagents have gained widespread acceptance in organic synthesis.[1] In particular, the remarkable scope of LVT reagents to effect reductive coupling of carbonyls (McMurry reaction) has resulted in a variety of applications such as synthesis of strained olefins,[1] heterocyclic compounds,[1c,2] and macrocyclic ring systems[1,3] to complex natural products including paclitaxel.[4]

For this purpose, a lexicon of reactive LVT reagents have been developed by reducing titanium salts with a variety of inorganic reducing agents[5] such as Zn, Mg, Li, $C_8K$, Zn−Cu, LAH, etc. In contrast, the soluble organic reductants have received scarce attention[6] for this purpose. Recent reports[7] on the use of metal−arene combinations as potential organic reductants in organometallic electron transfer processes prompted us to explore their utility as efficient organic reductants for the generation of the activated LVT reagents.

Earlier, it has been shown by us[8−10] and others[11] that the reducing ability of LVT-based reagents can be rationally tuned by the simple addition of cosolvents,[8] external ligands,[9] and chemical redox agents.[10] We envisaged that the use of metal−arenes for reducing Ti salts might produce the LVT species which would be coordinated with the arenes. The coordination, in turn, might activate the LVT reagents by augmenting the electron density on the LVT species and also possibly by increasing their solubility in an organic medium. In this context, it is worth noting that another SET agent, the low-valent Sm species, scores over the LVT species in terms of their reactivity. This may be partly attributed[12] to the solubility of the Sm species in a variety of polar solvents. The LVT-based reagents, on the other hand, are insoluble in organic solvents, which affects their reactivity necessitating prolonged heating in most of the LVT-mediated reactions including McMurry olefination. In addition,

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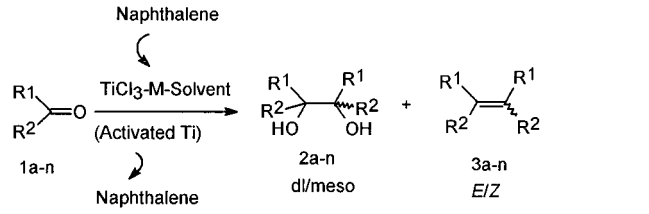
**Scheme 1**




a series: $R^1$ = Ph, $R^2$ = Me
b series: $R^1$ = 2-Naph, $R^2$ = Me
c series: $R^1$ = 4-MeC6H4, $R^2$ = Me
d series: $R^1$ = 4-*t*-BuC6H4, $R^2$ = Me
e series: $R^1$ = Ph, $R^2$ = H
f series: $R^1$ = 4-ClC6H4, $R^2$ = H
g series: $R^1$ = 4-OMeC6H4, $R^2$ = H
h series: $R^1$ = 3,4-OMeC6H3, $R^2$ = H
i series: $R^1$ = $R^2$ = Ph
j series: $R^1$ = $R^2$ = *cy*-Hex
k series: $R^1$ = $R^2$ = *cy*-Pent
l series: $R^1$ = PhCH2, $R^2$ = H
m series: $R^1$ = C6H13, $R^2$ = H
n series: $R^1$ = $R^2$ = *iso*-Prop

although a catalytic process[2d] in LVT is in hand, most of the LVT-mediated synthetic ventures require the use of superstoichiometric amounts of the reagents due to the heterogeneity of the reaction conditions.

## Results and Discussion

**Preparation of the Activated LVT Reagents with Metal−Arenes: Influence on McMurry Olefination.** For this study, a set of reactive LVT reagents was generated in situ by reducing $TiCl_3$ with different combinations of metals and arenes. The potential of these LVT reagents in McMurry olefination was then investigated using coupling of acetophenone ($R^1$ = Ph, $R^2$= $CH_3$; **1a**) to 2,3-diphenyl-2-butene (**3a**) as the model reaction (Scheme 1, Table 1). In most of the experiments, 0.25 equiv of the arenes with respect to $TiCl_3$ was used. In the initial trials, a combination of Mg and different arenes was evaluated as the reductants. Thus, when a mixture of $TiCl_3$, Mg, and phenanthrene in THF was refluxed for 3 h, a viscous but homogeneous LVT species (reagent **A**) was formed. In comparison, the inorganic reducing agents produce a suspension of the LVT reagent. Addition of **1a** to the reagent **A** at 25 °C and subsequent stirring furnished the intermediate pinacol **2a** (51% yield) as the major product along with 33% of the stilbene **3a** (run 1) within 3 h. The yield of the stilbene **3a** could be augmented to 66%, even at 25 °C, using anthracene (reagent **B**) as the electron carrier (run 2) and increased further to 73% with reagent **C**, prepared by using Mg−naphthalene as the reductant (run 3). In contrast, when the reaction was carried out at 25 °C using the conventional McMurry reagent ($TiCl_3$−Li−THF)[13a] (reagent **D**), the pinacol **2a** was isolated as the sole product (87%) even after prolonged (16 h) stirring (run 4). This clearly indicated the efficacy of Mg−naphthalene as an organic reductant for the generation of the LVT reagent.

Changing the metal to sodium in the above reagent protocol, i.e., Na−naphthalene, however, was found to be less efficient for the olefination reaction. Reaction of **1a** with the LVT reagent (reagent **E**) generated by Na−naphthalene and $TiCl_3$ afforded mainly the pinacol **2a** (65%) along with only 25% of the stilbene **3a** (run 5). Because of the smaller size of Li metal, Li−arenes are known[7a] to be superior reducing agents for metal salts. Hence, we used Li in conjunction with different arenes for the preparation of the LVT species. The LVT reagents (reagents **F** and **G**) produced with Li−phenanthrene and Li−biphenyl both appeared less effective for the designated transformation, wherein the pinacol **2a** was obtained as the major product in 48% and 58% yields, respectively (runs 6 and 7). On the other hand, the Li−anthracene combination generated another new LVT species (reagent **H**) which smoothly furnished the desired stilbene **3a** in 70% yield at 25 °C within 3 h (run 8). However, best result was obtained with the LVT reagent prepared by refluxing a mixture of Li, naphthalene, and $TiCl_3$ in THF for 3 h (reagent **I**). Reaction of **1a** with it, under refluxing temperature, produced the stilbene **3a** (89%) within 1.5 h (run 9). However, reduction of **1a** with Li−naphthalene alone (in the absence of $TiCl_3$), led to a complex mixture of products along with the recovery of the substrate. This clearly demonstrated that the activated LVT species was only responsible for the McMurry reaction. Interestingly, the reagent **I** was also effective in producing the stilbene even at lower temperatures and in a shorter time. For example, **3a** was obtained in 77% and 65% yields, respectively, at 25 °C and −15 °C (runs 10 and 11). In contrast, although the conventional McMurry reagent ($TiCl_3$−Li−THF)[13a] (reagent **D**) provided **3a** with the same yield, it required refluxing for 16 h (run 14).

The reactivity of the reagent **I** showed striking dependence on the nature of the reaction medium and the stoichiometry of the electron carrier used. The LVT species (reagent **J**) prepared with lesser amount of naphthalene (0.12 equiv with respect to $TiCl_3$) *i. e.*, Li−naphthalene-$TiCl_3$ also produced the stilbene albeit less efficiently. Thus, with reagent **J**, although compound **1a** gave the stilbene **3a** and the pinacol **2a** in 68% and 18% yields respectively (run 12), it required more time (6 h). The effect of the reaction medium was, however, more drastic. For this study, an LVT reagent (reagent **K**) was prepared by refluxing a mixture of $TiCl_3$ and Li−naphthalene in dimethoxyethane (DME) instead of THF. Reaction of **1a** with reagent **K** at 25 °C proceeded only up to the stage of pinacol formation that too with modest yield (34%) (run 13). Similar pinacol formation was reported with a reactive Mn reagent generated by reduction of Mn-salts with Li−naphthalenide.[7c]

**Steric Course of Stilbene Formation.** The study of the stereochemical outcome (*E*/*Z*) of the olefination with the above LVT reagents (reagents **A**-**K**) was revealing. In general, the reagents derived by using Mg−arenes, i.e., Mg−phenanthrene, Mg−anthracene and Mg−naphthalene as reductants led to the preferential formation of the *Z*-stilbene (Table 1, runs 1−3). A complete reversal in stereoselectivity was observed by switching over to alkali metal-based reductants. Thus, the *E*-isomer of **3a** was found to be the major product (Table 1, runs 5, 6, 8−10) when the reactions were carried out using the LVT reagents generated from $TiCl_3$ and Li−phenanthrene/Li−anthracene/Li−naphthalene and even Na−naphthalene.

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**Table 1. McMurry Olefination of Acetophenone (1a) with $TiCl_3$−Metal−Arene Systems**

| run | metal | arene[a] (equiv)[b] | time (h), temp (°C) | % yield[c] (dl/meso)[d] of **2a** | % yield[c] (*E*/*Z*)[d] of **3a** | unreacted **1a** (%)[c] |
|---|---|---|---|---|---|---|
| 1 | Mg | phenanthrene (0.25) [reagent **A**] | 3.0, 25 | 51 (68:32) | 33 (30:70) | 9 |
| 2 | Mg | anthracene (0.25) [reagent **B**] | 2.0, 25 | 22 (70:30) | 66 (25:75) | |
| 3 | Mg | naphthalene (0.25) [reagent **C**] | 2.0, 25 | 18 (60:40) | 73 (40:60) | |
| 4 | Li | nil [reagent **D**] | 16, 25 | 87 (75:25) | trace | |
| 5 | Na | naphthalene (0.25) [reagent **E**] | 2.0, 25 | 65 (80:20) | 25 (60:40) | 7 |
| 6 | Li | phenanthrene (0.25) [reagent **F**] | 2.5, 25 | 48 (77:23) | 35 (65:35) | 14 |
| 7 | Li | biphenyl (0.25) [reagent **G**] | 3.0, 25 | 58 (72:28) | 9 | 6 |
| 8 | Li | anthracene (0.25) [reagent **H**] | 3.0, 25 | trace | 70 (70:30) | |
| 9 | Li | naphthalene (0.25) [reagent **I**] | 1.5, reflux | nil | 89 (56:44) | |
| 10 | Li | naphthalene (0.25) [reagent **I**] | 2.0, 25 | trace | 77 (68:32) | |
| 11 | Li | naphthalene (0.25) [reagent **I**] | 6, −15 | 15 (80:20) | 65 (80:20) | |
| 12 | Li | naphthalene (0.12) [reagent **J**] | 6.0, 25 | 18 (75:25) | 68 (30:70) | |
| 13 | Li | naphthalene (0.25) [reagent **K**][e] | 5.0, 25 | 34 (90:10) | 5 | 32 |
| 14 | Li | nil [reagent **D**] | 16, reflux | | 89 (75:25) | |

[a] LVT species were generated in each case by refluxing a mixture of $TiCl_3$ and respective metal−arenes in THF for 3 h under Ar. [b] Figure denotes the stoichiometry of arenes with respect to $TiCl_3$ used. [c] Isolated yields. Products were fully characterized by $^1$H NMR, IR, mp and mass spectra. [d] The dl/meso and *E*/*Z* ratios were estimated[14] from $^1$H NMR analyses of crude product mixtures. [e] Instead of THF, DME was used as the solvent in this case.

**Table 2. Low Temperature McMurry Olefination of Aromatic Carbonyls with Reagent I**

| run | substrate | time (h)/temp (°C) | product (% yield)[a] | *E*/*Z*[b] |
|---|---|---|---|---|
| 1 | **1b** | 4.5/reflux | **3b** (68) | 60:40 |
| 2 | **1b** | 5.5/25 | **3b** (61) | 70:30 |
| 3 | **1c** | 2.5/25 | **3c** (72) | 78:22 |
| 4 | **1d** | 3.0/25 | **3d** (64)[c] | 76:24 |
| 5 | **1e** | 2.0/25 | **3e** (72) | 100 |
| 6 | **1f** | 2.0/25 | **3f** (70) | 100 |
| 7 | **1g** | 3.0/25 | **3g** (68) | 60:40 |
| 8 | **1h** | 5.5/0 to −10 | **3h** (65)[c] | 100 |
| 9 | **1i** | 7.0/25 | **3i** (78) | |

[a] Isolated yields of pure products, fully characterized by IR and $^1$H NMR spectra. [b] Stereoisomeric ratios of olefins were determined by comparing lit. data.[10,14] [c] 2% of **2d** was isolated. [d] 2% of **2h** was isolated.

**Table 3. Low Temperature McMurry Olefination of Aliphatic Carbonyls with Reagent I**

| run | substrate | time (h)/temp (°C) | product (% yield)[a] |
|---|---|---|---|
| 1 | **1j** | 6.5/reflux | **3j** (78) |
| 2 | **1k** | 8.0/25 | **3k** (72) |
| 3 | **1l** | 4.0/25 | **3l** (75) |
| 4 | **1m** | 5.5/25 | **3m** (47) |
| 5 | **1n** | 8.0/25 | **3n** (59) |

[a] Isolated yields of pure products, fully characterized by IR and $^1$H NMR spectra

The preponderance of *E*-olefination was augmented by carrying out the reaction at lower temperatures. Thus, lowering the reaction temperature from reflux to 25 °C to −15 °C resulted in progressively increased *E*-selectivity in the formation of **3a** from **1a** with reagent **I** (Table 1, runs 9−11). Surprisingly, the isomeric composition (*E*/*Z*) of the olefin **3a** was reversed (compare runs 10 and 12, Table 1) while changing the stoichiometry of naphthalene (0.25 equiv to 0.12 equiv). This observation was, however, inexplicable.

**Generality and Selectivity.** Based on the reactivity profile of different LVT reagents described in Table 1, the combination of $TiCl_3$−Li−naphthalene (0.25 equiv)-THF (reagent **I**) was found to be best suited for McMurry olefination and hence all the subsequent studies were carried out with this reagent only.

To explore the generality and scope of the reagent **I**, experiments were carried out using a variety of substituted aryl carbonyls, such as, aryl alkyl ketones (Table 2, runs 1−5), aryl aldehydes (Table 2, runs 6−9) and a diaryl ketone (Table 2, run 10) (Scheme 1). In all the cases, the respective olefins were obtained in good yields (65−78%) as the exclusive products. Interestingly, since the reagent **I** was effective for McMurry olefination even at lower temperatures, functional groups such as halogen, aryl-OMe, and methylenedioxy (Table 2, runs 7−9), which are otherwise incompatible under refluxing conditions,[8b,15] remained unaffected. Thus, the reagent also ensured excellent chemoselectivity in the McMurry olefination.

The general stereochemical features discussed earlier were also applicable with all these substrates. In these cases also, lowering of reaction temperature improved the *E*-selectivity. This was clearly evident with 2-naphthylmethyl ketone (**1b**) which produced more of the *E*-stilbene **3b** at 25 °C as compared to that under refluxing condition (Table 2, runs 1,2). Similarly, reactions of 4′-methylacetophenone (**1c**) and 4′-*tert*-butylacetophenone (**1d**) with reagent **I** at ambient temperature resulted in the predominant formation of the respective *E*-stilbenes as the major products (Table 2, runs 4, 5). The stereoselectivities of the stilbene formation were determined as carried out earlier[10] by $^1$H NMR spectroscopy.

One of the striking limitations[16] of the McMurry reaction is its inability to effectively couple aliphatic carbonyls to olefins. The relatively strong alkyl−oxygen bonds in the intermediate pinacolates[17] necessitates prolonged refluxing for the required deoxygenation. Even then, the yields of the product olefins are often unsatisfactory. However, using the present soluble LVT reagent (reagent **I**), reductive couplings of alicyclic ketones **1j** and **1k**, aliphatic aldehydes **1l** and **1m** including the sterically hindered ketone **1n** to their respective olefins were achieved at ambient temperature and in yields almost comparable to those with aromatic carbonyls (Scheme 1, Table 3).

**Synthesis of Heterocyclic Compounds.** The scope of the reagent **I** was further extended for the synthesis

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**Table 4. Synthesis of Heterocyclic Compounds *via* McMurry Olefination with Reagent I**

| run | substrate | product | yield (%) | rep yield[a] (ref) |
|---|---|---|---|---|
| 1 | **4a** | **5a** | 55 | 55 (2a) |
| 2 | **4b** | **5b** | 52 | 56 (2a) |
| 3 | **4c** | **5c** | 60 | 75 (2b) |

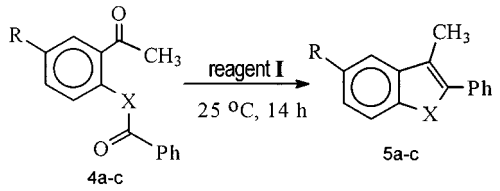
[a] The reactions were carried out at reflux temperature.

**Table 5. Imino-Pinacol Coupling with Reagent I**

| run | substrate | products (% yields) | rep yields (%) | ref |
|---|---|---|---|---|
| 1 | **6a** | **7a** (45[a]) **8a** (30) | **7a** (78) **8a** (0) | 19a |
| 2 | **6b** | **7b** (52[a]) **8b** (28) | **7b** (80) **8b** (0) | 19b |

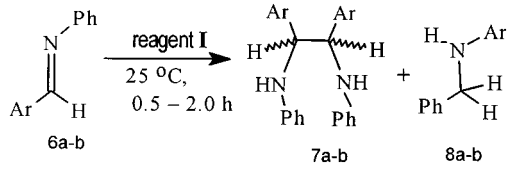
[a] The dl/meso ratios were 65:35 and 3:7 for **7a** and **7b**, respectively.

**Scheme 2**




4a X = O; R = H
4b X = O; R = OMe
4c X = NH; R = H

**Scheme 3**




a Ar = Ph
b Ar = 2-$OHC_6H_4$

of heterocycles via intramolecular keto-ester[2a] and keto-amide[2b] cyclization reaction developed earlier by us and other laboratories. Thus, reaction of 2-(benzoyloxy)-acetophenone (**4a**) and 2-(benzoyloxy)-5-(methoxy)acetophenone (**4b**) with reagent **I** afforded the corresponding benzofurans **5a** and **5b**, respectively, in moderate yields (Scheme 2). Similarly, reaction of 2-(*N*-benzoylamino)-acetophenone (**4c**) furnished 2-phenyl-3-methyl indole (**5c**) in only 2 h at 25 °C (Scheme 2). These results were comparable with those previously reported.[2a,2b] Thus, the LVT reagent **I** appeared to be better for the synthesis of heterocycles via McMurry coupling as the reaction could be carried out at room temperature.

**Synthesis of Vicinal Diamines.** Vicinal diamines find extensive applications in radiopharmaceuticals and as complexing agents and chiral auxiliaries.[18] In view of their frequent occurrence in natural products and medicinal compounds, we have earlier developed an LVT mediated synthesis of them via an imino-pinacol coupling reaction.[19a] In this study, the utility of the activated reagent **I** for the coupling of imino substrates was also explored (Scheme 3). Thus, addition of *N*-benzylideneaniline (**6a**) to the reagent **I** at 25 °C furnished *N*1,*N*2-di(phenyl)-1,2-diphenyl-1,2-ethanediamine (**7a**) in 45%

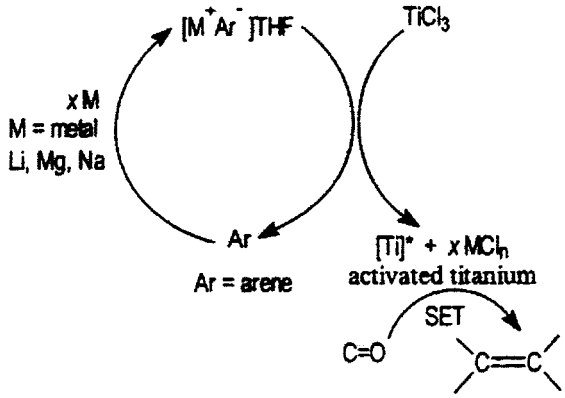



**Figure 1.** Possible route to activated LVT species using soluble organic reductants.

yield in only 0.5 h. However, competitive unimolecular reduction also produced *N*-benzyl aniline (**8a**) in an appreciable amount (30%). Similar reaction on *N*-(2-hydroxybenzylidene)aniline (**7a**) with reagent **I** produced the corresponding dimeric product **7b** in 52% yield after 1.5 h, along with 28% of the monoamine **8b**. Thus, the reagent **I** was capable of carrying out the imino-pinacol coupling, albeit less efficiently than the LVT reagent ($TiCl_3$−Li/THF) used earlier.[19a,b] The poorer result might be due to the formation of the mono-amines, formed by unimolecular reductions.

**Mechanistic Aspects.** The high reactivity of the LVT reagent prepared by reducing $TiCl_3$ with Li−naphthalene could be rationalized on the basis of a soluble model. The redox properties of both $Li^+$/Li and naphthalene/lithium−naphthalenide should be similar as their standard redox potential values are same (∼ −3.0 eV).[7a] However, based on the previous report[7a] on metal−arene mediated generation of reactive metals, it appears that the soluble naphthalenide anion is the actual reducing species for $TiCl_3$ in this case. During this process, the free arene is liberated to take part in continuing the redox cycle (Figure 1). It is, thus, imperative that unlike the report[6] by Clive et al., the arene need not be present in stoichiometric amounts. At the same time, the study revealed that rather than a catalytic quantity, a minimum of 0.25 equiv of the arene was required for optimum activity. This possibly might be accounted by considering a coordination of the arene with LVT species.

Earlier, the nature of the active Ti species has been put to considerable debate.[1c,16,20] The mechanism of action and active sites are known to differ in homogeneous and heterogeneous cases.[21] In analogy to Dams et al.,[16] it is proposed that LVT species generated in the present case mostly exist in the zero valent state. We also envisage that the new homogeneous LVT reagents were possibly organometallic Ti(0) complexes generated by coordination of the LVT species with the arenes used. This would then result in their higher activity. It is important to note that while the McMurry reagent ($TiCl_3$−Li−THF) is obtained as a colloidal suspension,[1] reagent **I** was homogeneous

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in nature. Thus, the redox-active arenes play a dual role of acting both as the electron carrier and also as ligand, thereby augmenting the reactivity.

Mechanistically, the McMurry olefination is widely regarded[1] to proceed via the initial formation of the titanium pinacolates followed by their deoxygenation under forcing experimental conditions to give the olefins. More recently, Ephritikhine has proposed[22a,b] another interesting mechanism involving metallocarbenoid species which also accounted for the generation of alkanes/alkenes in the above reaction via direct deoxygenation of the carbonyl substrates. In addition, the mechanism could also explain the dimerization of aliphatic ketones to olefins even at room temperature with the LVT reagent prepared from $TiCl_4$/Li(Hg). However, as suggested by them, the carbenoid mechanism is primarily operative for McMurry olefination of especially hindered aliphatic substrates and may well be the case with one of the chosen substrates, **1n**. In contrast, the other substrates of the present study do not have any significant steric hindrance and thus would follow the classical pinacolate route. Hence, their smooth dimerization to the respective olefins at lower temperatures could only possibly be explained by considering activation of the LVT species through ligation with the arene as proposed above. This argument was also substantiated by the fact that the conventional McMurry reagent (Reagent **D**) produced the pinacol only at room temperature.

## Conclusion

The present investigation describes an efficient strategy for the generation of reactive LVT species by reducing $TiCl_3$ with in situ formed metal-arenide systems acting as the soluble organic reductants. Thus, the addition of a substoichiometric amount of an electron carrier, e. g., naphthalene to a mixture of Li−$TiCl_3$, provided an easy access to a reactive homogeneous LVT species. The applicability of the LVT reagent for carrying out SET-induced coupling processes such as inter- and intramolecular carbonyl coupling reactions as well as iminopinacol couplings under milder conditions are reported. A facile entry to biologically important benzofurans, indoles, and vicinal diamines under milder conditions further augments the utility of the reagent system. The present study unfolds a potentially important variation in the preparation of activated LVT reagent using soluble organic reductants instead of conventional inorganic species (under a complete heterogeneous condition). The present finding is likely to enhance the utility of LVT reagents in a multitude of synthetic endeavors and will open up new avenues in preparative chemistry.

## Experimental Section

**General Methods.** General information regarding instruments, techniques, and source of chemicals used were the same as mentioned in our previous publication.[10] Lithium rods cut into small pieces were used for the reduction of $TiCl_3$.

**General Method for the Preparation of Activated LVT reagents.** To a stirred suspension of Li (33 mmol, 0.23 g) in dry THF (20 mL) under argon was successively added $TiCl_3$ (10 mmol, 1.55 g) in THF (20 mL) and arene (2.5 mmol) at room temperature. After refluxing for 3 h, a thick dense homogeneous black mass of activated Ti species was obtained in each case. The modified LVT reagent was then allowed to cool to ambient temperature and used for the subsequent reactions.

**General Procedure of Reductive Coupling of Carbonyl/Imino Substrates with Reagent I.** To the activated LVT reagent, prepared as above, was added the substrate **1a**−**n** (2.5 mmol) or **6a** and **7a** (4 mmol) in THF (5 mL) and the reaction mixture was stirred at temperatures indicated in the Tables 1−3 and 5. After disappearance of the substrate (cf. TLC), the reaction mixture was diluted with hexane, quenched with aqueous saturated $NH_4Cl$ solution, and the supernatant was passed through a bed of Celite. The eluent was extracted with a mixture of ethyl acetate−hexane (1:4) and the organic extract was washed with brine and dried ($Na_2SO_4$). Removal of solvent in vacuo yielded the crude product from which naphthalene was removed by vacuum sublimation (50 °C/10 mm) and the residue subjected to preparative TLC to afford the respective products (yields and the ratio of *E*/*Z* mixtures are presented in respective Tables). The products were characterized on the basis of their spectral ($^1$H NMR, MS, and IR) and physical data which were found to be in agreement with those of authentic samples and literature data.[9,10,14,19]

**Typical Procedure of Reductive Coupling of Acetophenone (1a) using Reagent I.** To a stirred solution of the reagent **I** was added **1a** (0.3 g, 2.5 mmol) in THF (5 mL) and the reaction mixture was stirred at temperatures indicated in Table 1. After disappearance of the substrate (cf. TLC), the reaction mixture was diluted with hexane and quenched with aqueous saturated $NH_4Cl$ solution and the supernatant was passed through a bed of Celite. The eluent was worked-up as above and the crude product was subjected to preparative TLC (silica gel, EtOAc/hexane (5/95)) to afford the known compound[10,14] **3a** (the yield and stereoisomeric ratio is given in Table 1).

**Synthesis of Furans, 5a,b, and Indole, 5c, using Reagent I.** Similar reactions of reagent **I** with keto-esters **4a** and **4b** and keto-amide **4c** (2.5 mmol, 10 mL THF) according to the above-mentioned procedure afforded the intramolecularly coupled *O*-/*N*- heterocycles **5a**−**c**. Spectroscopic data (NMR, IR, MS) and physical constants of the isolated products were in full agreement with the authentic samples.[2a,b]

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**Supporting Information Available:** The physical and spectral (IR, $^1$H NMR, and mass) data for **3a**−**3n**, **5a**−**5c**, and **7a**, **7b** (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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