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A New Entry of Practical and Chemoselective Iodocarbenoids for Carbonyl Iodomethylenation

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Direct oxidative addition of CHI_3 to the Mg-$TiCl_4$ bimetallic species resulted in the generation of a highly chemoselective and practically convenient iodomethylenetitanium complex, which efficiently effected condensation even with enolizable or inert carbonyl compounds, such as sterically congested ketones, to provide vinyl iodide compounds

Keywords: Vinyl iodide; Oxidative addition; Carbenoids; Methylenation; Bimetallic species.

INTRODUCTION

Formation of C = C bonds by means of metallocarbenes constitutes a particularly valuable strategy. The importance of vinyl iodides as building blocks for the construction of useful molecules such as *N*-vinylheterocycles and aryl vinyl ethers, alkenyl sulfides, enamides, alkylidene complexes,[1] acetylenes,[2] and dienes[3] makes their availability by such processes important. In spite of the vast number of titanium-carbene-mediated carbonyl-olefinations,[4,5] remarkably few reactions of iodocarbenoids are described except for the $CHI_3/CrCl_2$-[6a] and $Ph_3P = CHI$-[6b]promoted iodomethylenation of aldehydes or ketones with iodoforms. These processes do not generally extend to enolizable and sterically hindered ketones, and the use of very expensive $CrCl_2$ is unavoidable. In addition to carbonyl-iodomethylenation, several syntheses of vinyl iodides employ iodination of alkenylboronic acid or NaHMDS-promoted coupling of CH_2I_2 with $ArCH_2Br$.[7] In searching for a new and practical strategy based on the concept of the C–I bond activation promoted by the highly active Ti-Mg bimetallic species, we turned our attention to the elaboration of iodoform initiated by simple metal–iodine exchanges.

We here report the protocols whereby direct oxidative addition of CHI_3 to the Mg-$TiCl_4$ bimetallic species[5] resulted in the generation of a highly chemoselective and practically convenient iodomethylenetitanium complex (Scheme 1), which efficiently effected condensation even with enolizable or inert carbonyl compounds, such as sterically congested ketones, to provide vinyl iodide compounds.

RESULTS AND DISCUSSION

Believing a Mg-Ti inorganic-Grignard reagent[5,8] might be more reactive than either titanium (II) complexes[9a] or Mg-Hg-species,[9b] which had been used to activate *gem*-dihalides, we explored the oxidative addition of CHI_3 to the Mg/$TiCl_4$ system. Expectedly, as the data in Table 1 show, exposure of the simple cyclic ketone **1a** to $TiCl_4$/Mg/CHI_3 in CH_2Cl_2 and the electron-pair donor (EPD) additive dimethoxyethane (DME) at 0°C did indeed produce the desired vinyl iodide **1b** (Table 1).

As the data in Table 1 show, adding a solution of **1b** (1.0 mmol) in DME (1.2 mL) to a mixture of CHI_3 (1 mmol), $TiCl_4$ (3 mmol), and Mg (8 mmol) in 3 mL of CH_2Cl_2 at 0°C followed by stirring at 0°C for 2 h gave a 75% yield of **1b** (entry 1). Most revealing was the effect of the amount of Mg relative to titanium chloride on this process. Use of a 2:6 $TiCl_4$/Mg ratio improved the vinyl iodide formation. The iodomethylenation product **1b** was obtained in 90% yield (entry 2). Replacing DME with tetrahydrofuran (THF) gave a slightly diminished yield of 70% (entries 3 and 4). Replacing DME with other additives including acetonitrile, NEt_3, and pyridine gave no reaction (entry 5). Extension of these observations to other traps confirms their generality.

The use of ethylcyclohexanone **2a** also gave satis-

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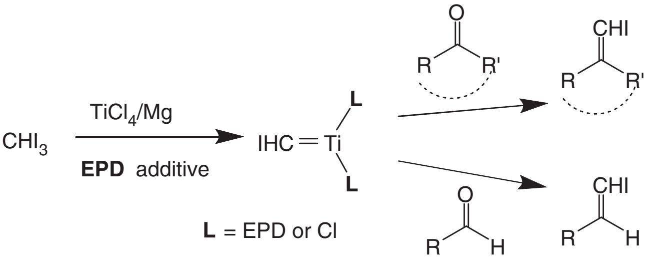
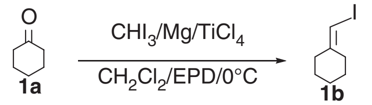


Scheme 1. $TiCl_4$-Mg bimetallic complex-promoted CHI transfer reaction of CHI_3.

factory results with the iodoform-$TiCl_4$-Mg system, giving 85% yield of **2b** as a 90:10 *E*/*Z* mixture (Table 2, entry 1). More gratifyingly, the reaction directly scales up; thus, vinyliodide **2b** was obtained in 80% yield on a 10-mmol scale using a 14 mmol of $TiCl_4$ and 42 mmol of Mg. Iodomethylenation onto the acyclic ketones **3a** and **4a** was equally effective (entries 2 and 3). As expected, the phenylthio group was completely unaffected. The sterically congested ketone **5a** presented no difficulties. For the iodomethylenation of **5a**, use of 5 equiv of $TiCl_4$ and 4 equiv of Mg proved most satisfactory, giving 78% yield of the desired vinyl iodide **5b** as a 90:10 *E*/*Z* mixture. Most pleasingly, due to the non-basic character of the titanium–iodomethylene complex, enolizable ketones[10,11] also proved to be a satisfactory trap (entries 6 and 7). Thus, 2-indanone **7a** and β-tetralone **8a** gave 78% and 76% yields, respectively, of the desired iodomethylenation products **7b** and **8b**.

Table 1. Effect of various EPD additive on the $TiCl_4$-Mg-mediated iodomethylenation of cyclohexanone **1b**



Entry	$TiCl_4$/Mg (equiv)	EPD additive	Yield[a] (%); **1b**
1	3:8	DME (1.2 mL)	75
2	2:6	DME (1.2 mL)	90
3	2:6	THF (1.2 mL)	55
4	3:8	THF (2.0 mL)	70
5	2:6 or 3:8	NEt_3, CH_3CN or pyridine	0

[a] Isolated yield

With an eye to extending these observations to other less reactive ketones, we explored the iodomethylenation of unsaturated ketones with CHI_3. Fortunately, exposing 1-acetylcyclohexene **9a** to the $TiCl_4$-Mg-CHI_3-DME system led to smooth iodomethylenation to give 82% of the desired 95:5 mixture of (*E*)- and (*Z*)-vinyl iodides **9b** (entry 8). On the other hand, using the acetophenone **10a** also gave satisfactory results wherein the vinyliodide **10b** was obtained in 75% yield (entry 9). Changing the carbonyl compounds to aldehydes, which are particularly prone to reduction and/or dimerization, led to equally gratifying results. Thus, reacting cyclohexanecarboxaldehyde **11a** with iodoform using a 2:6 $TiCl_4$/Mg ratio led to smooth iodomethylenation to give vinyl iodides **11b** in 82% yield as a 70:30 *E* and *Z* mixture (entry 10). The aromatic aldehyde **12a** also gave satisfactory results. Iodomethylenation of **12a** using a 3:8 $TiCl_4$/Mg ratio afforded a 90:10 mixture of (*E*)- and (*Z*)-vinyl iodides **12b** in 75% yield (entry 11).

CONCLUSIONS

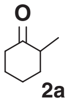
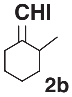
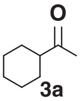
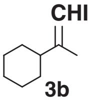
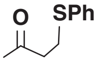
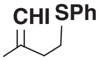
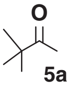
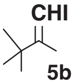
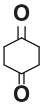
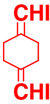
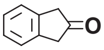
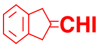
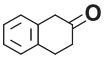
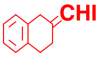
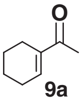
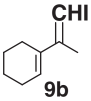
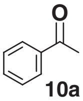
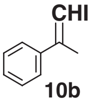
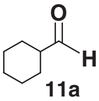
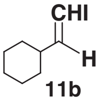
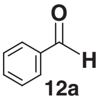
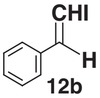
In conclusion, the successful application of the Mg-$TiCl_4$-promoted CHI transfer to various ketone and aldehyde carbonyl groups illustrated the extraordinary reactivity of this new titanium–iodomethylene complex. This oxidative addition of CHI_3 promoted by the Mg-Ti bimetallic complex not only represents an extremely simple, practical, and efficient synthesis of vinyl iodides but also offers the opportunity to discover other carbenoids derived from Mg-$TiCl_4$-polyhaloalkanes.[12] Not only is this iodocarbenoid non-basic but it also seems highly nucleophilic. The novel reactivity involved suggests several intriguing directions, which are currently under active investigation.

EXPERIMENTAL

Typical procedure

Method A. A solution of cyclohexanone 1a (0.098 g, 1 mmol) in DME (1.2 mL) was added dropwise to a suspension consisting of Mg (146 mg, 6 mmol), $TiCl_4$ (0.21 mL, 2 mmol), CHI_3 (0.394 g, 1 mmol), and CH_2Cl_2 (3 mL) at 0°C. After stirring for 1–2 h at 0°C, a saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on

Table 2. Iodomethylenation of ketones and aldehydes with CHI_3-$TiCl_4$-Mg/DME (1.2 mL) at 0°C

Entry	Carbonyl compd (1 mmol)	$TiCl_4$/Mg (equiv)	Methylene product	Yield[a] % (*E*/*Z*)
1	 **2a**	2:6 14:42[c]	 **2b**	85–90:10[b] 80
2	 **3a**	3:8	 **3b**	85–60:40[b]
3	 **4a**	2:6	 **4b**	83–75:25[b]
4	 **5a**	5:4	 **5b**	78–90:10[b]
5	 **6a**	3:8	 **6b**	73
6	 **7a**	3:8	 **7b**	78
7	 **8a**	3:8	 **8b**	76–65:35[b]
8	 **9a**	3:8	 **9b**	82–95:5[b]
9	 **10a**	3:8	 **10b**	75–85:15[b]
10	 **11a**	2:6	 **11b**	82–70:30[d]
11	 **12a**	3:8	 **12b**	75–90:10[d]

NOESY may provide a further confirmation.

[a] Isolated yield.

[b] *E*/*Z* ratio based upon ^1H NMR and steric strain considerations.

[c] 10-mmol scale of **2a** and 12 mL of DME.

[d] *E*/*Z* ratio based on the *J*-value between the two vinyl protons.

silica gel (elution with hexane) to give (iodomethylene) cyclohexane **1b** (0.200 g, 90% yield) as a colorless oil: 1H NMR (400 MHz, $CDCl_3$) δ 1.54–1.49 (m, 6 H), 2.28–2.24 (m, 4 H), 5.75–5.74 (m, 1 H); 13C NMR (100 MHz, $CDCl_3$) 26.0, 26.9, 27.9, 35.9, 37.2, 71.1, 151.2; HRMS-EI Calcd for $C_7H_{11}I$: 221.9905. Found: 221.9911.

Method B. A solution of cyclohexanone **1a** (0.098 g, 1 mmol) in DME (1.2 mL) was added dropwise to a suspension consisting of Mg (194 mg, 8 mmol), $TiCl_4$ (0.32 mL, 3 mmol), CHI_3 (0.394 g, 1 mmol), and CH_2Cl_2 (3 mL) at 0°C. After stirring for 1–2 h at 0°C, a saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on silica gel (elution with hexane) to give (iodomethylene) cyclohexane **1b** (0.170 g, 75% yield) as a colorless oil:

Method C. A solution of cyclohexanone **1a** (0.098 g, 1 mmol) in THF (2.0 mL) was added dropwise to a suspension consisting of Mg (146 mg, 6 mmol), $TiCl_4$ (0.21 mL, 2 mmol), CHI_3 (0.394 g, 1 mmol), and CH_2Cl_2 (3 mL) at 0°C. After stirring for 1–2 h at 0°C, a saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on silica gel (elution with hexane) to give (iodomethylene) cyclohexane **1b** (0.150 g, 70% yield) as a colorless oil.

1-(Iodomethylene)-2-methylcyclohexane 2b. Following the procedure of method A, iodomethylenation of **2a** (0.110 g, 1 mmol) afforded **2b** (0.201 g, 85%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, $CDCl_3$) 1.03 (d, *J* = 7.2 Hz, 3 H), 1.35–1.71 (m, 6 H), 1.94–2.01 (m, 1 H), 2.25–2.30 (m, 1 H), 2.62–2.65 (m, 1 H), 5.71 and 5.76 (2 bs, total 1 H, ratio ~10:90); *Z*- and *E*-isomers: 13C NMR (100 MHz, $CDCl_3$) 18.6, 25.0, 27.3, 36.1, 36.3, 40.2, 70.9, 155.1; HRMS-EI Calcd for $C_8H_{13}I$: 236.0062. Found: 236.0060.

(1-Iodoprop-1-en-2-yl)cyclohexane 3b. Following the procedure of method B, iodomethylenation of **3a** (0.126 g, 1 mmol) afforded **3b** (0.225 g, 85%) as a colorless oil 1 (*Z*- and *E*-isomers): 1H NMR (400 MHz, $CDCl_3$) 1.08–1.75 (m, 10 H), 1.73 and 1.76 (2 s, total 3 H, ratio ~1:1), 2.06–2.14 and 2.44–2.55 (2 m, total 1 H, ratio ~1:1), 5.72 and 5.90 (2 bs, total 1 H, ratio ~40:60); *Z*- and *E*-isomers: 13C NMR (100 MHz, $CDCl_3$) 20.1 and 22.6; 26.0 and 26.3; 30.0 and 31.8; 46.6 and 48.2; 72.6 and 74.9; 151.2 and 152.9; HRMS-EI Calcd for $C_9H_{15}I$: 250.0218. Found: 250.0212.

2-(Iodomethylene)-4-(phenylthio)butane 4b. Following the procedure of method A, iodomethylenation of **4a** (0.180 g, 1 mmol) afforded **4b** (0.252 g, 83%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, $CDCl_3$) 1.82 and 1.90 (2 s, total 3 H, ratio ~2.4:1), 2.47–2.53 (m, 2 H), 2.96–3.00 (m, 2 H), 5.93 and 5.96 (2 bs, total 1 H, ratio ~25:75), 7.39–7.18 (m, 5 H); *Z*- and *E*-isomers: 13C NMR (100 MHz, $CDCl_3$) 23.5 and 23.6; 30.5 and 31.9; 38.5 and 38.8; 76.8; 126.1 and 126.2; 128.8 and 128.9; 129.5, and 129.6; 145.3 and 145.6 ; HRMS-EI Calcd for $C_{11}H_{13}IS$: 303.9783. Found: 303.9788.

1-Iodo-2,3,3-trimethylbut-1-ene 5b. Adding a ~0.9 M solution of **5a** in DME to a mixture of CHI_3 (1 mmol), $TiCl_4$ (5 mmol) and Mg (4 mmol) in 3 mL of CH_2Cl_2 at 0°C followed by stirring at 0°C for 2 h afforded **5b** (0.175 g, 78%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, $CDCl_3$) 1.08 (s, 9 H), 1.86 (s, 3 H), 5.92 and 6.02 (2 bs, total 1 H, ratio ~10:90); *Z*- and *E*-isomers 13C NMR (100 MHz, $CDCl_3$) 21.9, 28.9, 38.9, 75.4, 155.1; HRMS-EI Calcd for $C_7H_{13}I$: 224.0062. Found: 224.0071.

1,4-bis(Iodomethylene)cyclohexane 6b. Following the procedure of method B, iodomethylenation of **6a** (0.112 g, 1 mmol) afforded **6b** (0.263 g, 73%) as a colorless oil: 1H NMR (400 MHz, $CDCl_3$) 2.31 (s, 4 H), 5.94 (s, 2 H); 13C NMR (100 MHz, $CDCl_3$) 35.7, 36.9, 73.2, 148.7; HRMS-EI Calcd for C8H10I$_2$: 359.8872. Found: 359.8870.

2-(Iodomethylene)indane 7b. Following the procedure of method B, iodomethylenation of **7a** (0.132 g, 1 mmol) afforded **7b** (0.200 g, 78%) as a colorless oil: 1H NMR (400 MHz, $CDCl_3$) 3.64 (s, 2 H), 3.74 (s, 2 H), 6.16 (s, 1 H), 7.14–7.24 (m, 4 H); 13C NMR (100 MHz, $CDCl_3$) 40.2, 44.1, 71.5, 124.6, 124.8, 125.9, 126.7, 126.8, 140.5, 151.8; HRMS-EI Calcd for C10H9I: 255.9749. Found: 255.9743.

2-(Iodomethylene)-1,2,3,4-tetrahydronaphthalene 8b. Following the procedure of method B, iodomethylenation of **8a** (0.146 g, 1 mmol) afforded **8b** (0.205 g, 76%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, $CDCl_3$) 2.50–2.53 and 2.57-–2.60 (2 m, total 2 H, ratio ~35:65), 2.78–2.81 and 283–2.86 (2 m, total 2 H, ratio ~1:1.6), 3.55 (s, 2 H), 6.05 and 6.07 (2 s, total 1 H, ratio ~35:65), 7.08-7.17 (m, 4 H); *Z*- and *E*-isomers: 13C NMR (100 MHz, $CDCl_3$) 29.4 and 30.6; 33.7 and 34.3; 38.8 and 39.6; 73.2 and 73.5; 125.8 and 126.2; 126.3 and 127.3; 127.8 and 128.2; 128.6 and 135.0; 135.8 and 136.8; 137.6 and 147.3; HRMS-EI Calcd for C11H11I: 269.9905. Found: 269.9901.

(*E*)-1-(1-Iodoprop-1-en-2-yl)cyclohexene 9b. Following the procedure of method B, iodomethylenation of **9a** (0.124 g, 1 mmol) afforded **9b** (0.203 g, 82%, *E*/*Z* >95:5) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, CDCl$_3$) 1.54-2.16 (m, 11 H), 5.93–5.94 (m, 1 H), 6.22–6.23 (m, 1 H); *Z*- and *E*-isomers 13C NMR (100 MHz, CDCl$_3$) 21.9, 22.2, 22.6, 25.8, 26.2, 76.3, 126.1, 135.5, 147.2; HRMS-EI Calcd for C9H13I: 248.0062. Found: 248.0065.

(1-Iodoprop-1-en-2-yl)benzene 10b. Following the procedure of method B, iodomethylenation of **10a** (0.120 g, 1 mmol) afforded **10b** (0.183 g, 75%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, CDCl$_3$) 2.20 and 2.26 (d, *J* = 2.8), total 3 H, ratio ~1:4), 6.25 and 6.50 (q, *J* = 2.8), total 1 H, ratio ~15:85), 7.13-7.38 (m, 5 H); *Z*- and *E*-isomers: 13C NMR (100 MHz, CDCl$_3$) 24.4 and 26.5; 79.1; 126.2 and 127.0; 127.4 and 127.6; 127.8 and 128.2; 128.4 and 128.5; 141.4 and 147.1; HRMS-EI Calcd for C9H9I: 243.9748. Found: 243.9752.

2-(Iodopvinyl)cyclohexane 11b. Following the procedure of method A, iodomethylenation of **11a** (0.112 g, 1 mmol) afforded **11b** (0.194 g, 82%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, CDCl$_3$) 1.04-1.38 (m, 5 H), 1.63–1.71 (m, 5 H), 1.94–2.05 and 2.24–2.35 (2 m, total 1 H, ratio ~30:70), 5.95 (dd, *J* = 14.0, 1.2 Hz, 0.69 H, *E*), 5.96 (dd, *J* = 8.4, 7.2 Hz, 0.31 H, *Z*), 6.04 (dd, *J* = 7.2, 0.6 Hz, 0.31 H, *Z*), 6.46 (dd, *J* = 14.0, 7.0 Hz, 0.69 H, *E*): *Z*- and *E*-isomers: 13C NMR (100 MHz, CDCl$_3$) 25.5 and 25.7; 25.86 and 25.9; 31.3 and 32.0; 43.6 and 44.5; 73.2 and 74.5; 146.2 and 152.1; HRMS-EI Calcd for C8H13I: 236.0062. Found: 236.0066.

2-(Iodopvinyl)benzene 12b. Following the procedure of method B, iodomethylenation of **12a** (0.106 g, 1 mmol) afforded **12b** (0.173 g, 75%) as a colorless oil (*Z*- and *E*-isomers): 1H NMR (400 MHz, CDCl$_3$) 6.55 (d, *J* = 8.4) and 6.83 (d, *J* = 15.2), total 1 H, ratio ~10:90), 7.26–7.62 (m, 6 H); *Z*- and *E*-isomers: 13C NMR (100 MHz, CDCl$_3$) 79.2 (*Z* and *E*); 126.0 (*Z* and *E*); 128.1 and 128.3; 128.5 and 128.7; 137.7 and 138.7; 145.0 (*Z* and *E*); HRMS-EI Calcd for C8H13I: 229.9592. Found: 229.9586.

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12. Further studies will determine whether these bimetallic-species promoted oxidative additions will be generally useful for employment with polyhaloalkanes.