Supporting information

A Simple and Practical Catalytic Electron Transfer System Composed of TiCl₄ and Yb: Application in Carbonyl Olefination and Insight into Mechanism

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General methods

All reactions were carried out under nitrogen atmosphere using the standard Schlenk techniques or in a glove box. The solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. All substrates are commercially available and were used without further purification. Metal ytterbium (purity: > 99%) as an ingot was shattered prior to use, which then was directly used without chemical pretreatment. NMR spectra were recorded on a Bruker AVANCE ECA-400 instrument at 400 MHz (¹H) or 100 MHz (¹³C) using CDCl₃ as solvent. The chemical shift values (δ) are given in parts per million (ppm) and are referred to the residual peak of the deuterated solvent (CDCl₃).The known alkenes were identified by comparing their spectral data with those reported in the literatures.¹⁻²⁴

General procedure for the coupling reaction of ketones and aldehydes promoted by Yb/TiCl₄.

To a 50 mL Schlenk bottle was added Yb sand (0.173 g, 1.0 mmol), THF (8 mL), and TiCl₄ (0.33 mL, 0.3 mmol), this mixture was stirred at room temperature for 5 minutes. To the resulting suspension was added 1.0 mmol ketone or aldehyde. After stirring for 5-7 h at 70 °C (monitored by TLC), the reaction was quenched with 0.1 M hydrochloric acid, and the mixture was extracted with CHCl₃ (10 mL×3). The combined organic layer was washed with water and dried over anhydrous MgSO₄. After filtration and removal of solvents under reduced pressure, the residue was purified by silica gel column chromatography to afford the corresponding olefins.

General procedure for the cross coupling reaction between different carbonyl compounds promoted by Yb/TiCl₄.

The mixture of Yb sand (0.173 g, 1.0 mmol) and TiCl₄ (0.33 mL, 0.3 mmol) in THF (8 mL) was allowed to stir at room temperature for 5 minutes. This mixture was added to a solution of two different carbonyl compounds (molar ratio: 1:1) in THF (5mL). After stirring for 5-7 h at 70 °C (monitored by TLC), the reaction was quenched with 0.1 M hydrochloric acid, and the mixture

was extracted with $CHCl_3$ (10 mL×3). The combined organic layer was washed with water, dried over anhydrous MgSO₄. After filtration and removal of solvents under reduced pressure, the residue was purified by silica gel column chromatography to afford the corresponding products.

3,3'-(but-2-ene-2,3-diyl)bis(chlorobenzene) (2hh)

¹H NMR (400 MHz, CDCl₃) δ 7.31-7.22 (m, 2.05H), 7.13-7.10 (m, 0.68H), 7.04-6.96 (m, 6H), 6.78-6.75(m, 2H), 2.12 (s, 6H), 1.85 (s, 1.92H). ¹³C NMR (100 MHz, CDCl₃) δ 146.00 (s, MeCAr), 145.89 (s, MeCAr), 134.12 (s, Ar), 133.60 (s, Ar), 132.85 (s, Ar), 132.83 (s, Ar), 129.63 (s, Ar), 128.99 (s, Ar), 128.35 (s, Ar), 127.51 (s, Ar), 126.68 (s, Ar), 126.45 (s, Ar), 126.10 (s, Ar), 22.38 (s, *Me*), 21.34 (s, *Me*). Anal. Calcd. for C₁₆H₁₄Cl₂(%): C 69.33, H 5.09; found C 69.29, H 5.04.

4,4'-(but-2-ene-2,3-diyl)bis(1,2-dichlorobenzene) (2ii)

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, 0.5H), 7.34 (d, 0.5H), 7.15 (d, 2H), 7.11 (d, 2H), 7.09-7.06 (m, 0.5H), 6.72-6.69 (m, 2H), 2.11 (s, 6H), 1.84 (s, 1.5H). ¹³C NMR (100 MHz, CDCl₃) δ 143.97 (s, CH₃CAr), 143.79 (s, CH₃CAr), 132.54 (s, Ar), 132.47 (s, Ar), 132.07 (s, Ar), 130.77 (s, Ar), 130.47 (s, Ar), 130.23 (s, Ar), 130.17 (s, Ar), 129.96 (s, Ar), 128.83 (s, Ar), 127.78 (s, Ar), 22.40 (s, CH₃), 21.44 (s, CH₃). Anal. Calcd. for C₁₆H₁₂Cl₄ (%): C 55.53, H 3.49; found C 55.48, H 3.46.

2,2'-(but-2-ene-2,3-diyl)difuran (2ll)

¹H NMR (400 MHz, CDCl₃) δ 7.46-7.45 (m, 1.90H), 7.31-7.30 (m, 2H), 6.47-6.46 (d, 1.96H), 6.40-6.39 (m, 1.97H), 6.35-6.34 (m, 2H), 5.97-5.96 (m, 2H), 2.30 (s, 5.89H), 2.14 (s, 6H).¹³C NMR (100 MHz, CDCl₃) δ 155.85 (s, MeCAr), 155.42 (s, MeCAr), 141.25 (s, Ar), 140.80 (s, Ar), 124.14 (s, Ar), 123.28 (s, Ar), 111.00 (s, Ar), 110.95 (s, Ar), 109.63 (s, Ar), 107.50 (s, Ar), 19.08 (s, *Me*), 18.77 (s, *Me*). Anal. Calcd. for C₁₂H₁₂O₂ (%): C 76.57, H 6.43; found C 76.50, H, 6.41.

4,4'-(3,3-dimethylbut-1-ene-1,1-diyl)bis(chlorobenzene) (2gx)

¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.33-7.31 (m, 2H), 7.20 – 7.17 (m, 2H), 7.11 - 7.05 (m, 4H), 6.07 (s, 1H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 142.15 (s, Ar), 141.23 (s, Ar),138.80 (s, Ar),136.88 (s, Ar), 133.05 (s, Ar), 132.68 (s, Ar), 131.64 (s, Ar), 128.22 (s, Ar), 128.20 (s, Ar₂CCH), 128.14 (s, Ar₂CCH), 34.12 (s, CMe₃), 31.31 (s, CMe₃). Anal. Calcd. for C₁₈H₁₈Cl₂ (%): C 70.83, H 5.94; found C 70.71, H, 5.92. Melting point: 86-87 °C.

Preparation of Ti(IV) pinacolate (ROTi)



In a glove box, 48 mg (2 mmol) NaH was added very slowly to a solution of *meso*-1,2diphenylpinacol (214 mg, 1 mmol) in the mixed solvent of 5 mL THF and 10 mL toluene. The mixture was allowed to stir for 2 h at room temperature. The solvent was removed under vacuum and the residue was redissolved in 15 mL THF. TiCl₄ (2.2 mL, 2 mmol) was then added via syringe to the mixture rapidly at room temperature. After stirring for 2 h remove of the resulting NaCl precipitate gave a clear yellow solution, which was concentrated to 5 mL and crystallized at -35 °C to give **ROTi** as bright yellow cube crystals in 76% yield. ¹**H NMR** (400 MHz, THF-*d*₈, 25 °C) δ = 7.41-7.38 (m, 4H), 7.25-7.22 (m, 6H), 6.85 (s, 2H), the other two groups of peaks belong to THF and THF-*d*₈. ¹³**C NMR** (100 MHz, THF-*d*₈, 25 °C) δ = 137.2, 129.9, 128.7, 128.3, 104.1. Anal. Calcd. for C₃₀H₄₄Cl₆O₆Ti₂ (%): C 44.53; H 5.48. Found: C 44.50, H 5.46.

Peraparation of [(THF)₂TiCl₃]₂(µ-O) (OTi₂)

$$\begin{array}{c|cccc} HO & OH \\ Ph & Ph \\ Ph & Ph \end{array} \xrightarrow{2 \text{ NaH}} \xrightarrow{2 \text{ TiCl}_4} (\text{THF})_2 \text{Cl}_3 \text{Ti} - \text{O} - \text{TiCl}_3 (\text{THF})_2 \\ \hline \text{OTi}_2 \end{array}$$

In a glove box, 48 mg (2 mmol) NaH was added very slowly to a solution of tetraphenylpinacol (366 mg, 1 mmol) in 25 mL toluene. The mixture was allowed to stir for 2 h at room temperature, and the solvent was removed under vacuum. The residue was redissolved in 15 mL THF, then TiCl₄ (2.2 mL, 2 mmol) was added. After stirring for 24 h at room temperature, NaCl was removed by filtration and the solvent was removed under vacuum. The residue was carried out at -35 °C to give hexane and was dissolved in 3 mL toluene. Recrystallization was carried out at -35 °C to give **OTi**₂ as pale yellow crystals in 83% yield. Anal. Calcd. for $C_{16}H_{32}Cl_6O_5Ti_2$ (%): C 31.36; H 5.26. Found: C 31.22, H 5.25. The structure of this compound was determined by single crystal X-ray diffraction.

Peraparation of [(µ-O)TiCl₂(THF)₂]₃ (OTi)



In a glove box, 48 mg NaH was added very slowly to a solution of tetraphenylpinacol (366 mg, 1 mmol) in 25 mL toluene. The mixture was allowed to stir for 2 h at room temperature and then the

solvent was removed under vacuum. The residue was redissolved in 15 mL THF, then TiCl₄ (2.2 mL, 2 mmol) was added. After stirring for 24 h at room temperature, NaCl was removed by filtration and the solvent was removed under vacuum. The residue was washed by hexane and the solid was dissolved in 3 mL toluene. Crystallization was carried out at -35 °C, giving [(μ -O)TiCl₂(THF)₂]₃ (**OTi**) as pale yellow crystals in 82% yield. Anal. Calcd. for C₂₄H₄₈Cl₆O₉Ti₃ (%): C 34.44; H 5.78. Found: C 34.81, H 5.63. The structure of this compound was determined by single crystal X-ray diffraction.

Copies of NMR Spectra for 2hh



Copies of NMR Spectra for 2ii



Copies of NMR Spectra for 2ll



Copies of NMR Spectra for 2gx



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Copies of NMR Spectra for ROTi





¹H NMR Spectra for the crude product of cross-deoxygenative coupling of Ph₂CO with cyclohexanone



¹H NMR Spectra for 2kv



¹H NMR Spectra for the crude product of cross-deoxygenative coupling of 9-Fluorenone with cyclopentanone



X-ray Crystallographic Analysis. Suitable crystals were sealed in the thin-wall glass capillaries under a microscope in the glove box. Data collections were performed on a Bruker SMART APEX (at 293K) or Bruker SMART APEX (II) (at 296K) diffractometer with CCD area detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT^[25] and SADABS^[26] to yield the reflection data file. The structure was solved by using SHELXTL program^[27]. Refinement was performed on F² anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. All the hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging-carbons were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance. CCDC 1000407 (OTi) CCDC 1000408 (ROTi), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

	ROTi	ОТі
Formula	$C_{30}H_{44}Cl_6O_6Ti_2$	$C_{24}H_{48}C_{16}O_9Ti_3$
Molecular Weight	809.15	837.02
Crystal color	bright yellow	pale yellow
Crystal dimens (mm)	0.15 x 0.10 x 0.10	0.20 x 0.20 x 0.15
Crystal system	Orthorhombic	Triclinic
Space group	Pbca	P-1
Unit cell dimensions		
<i>a</i> (Å)	13.085(5)	10.354(4)
<i>b</i> (Å)	12.063(5)	10.811(4)
<i>c</i> (Å)	23.777(9)	18.781(7)

Table 1 Crystal and Data Collection Parameters of ROTi and OTi

β (deg)	90	88
$V(Å^3)$	3753(2)	1850.4(11)
Ζ	4	2
<i>Dc</i> (g.cm ⁻³)	1.432	1.502
μ (mm ⁻¹)	0.890	1.107
F (000)	1672	864
Radiation ($\lambda = 0.710730$ Å)	Μο-Κα	Mo-K _a
Temperature (K)	293(2)	293(2)
Scan type	ω -2 $ heta$	ω -2 $ heta$
No. of unique reflections	3348 [R(int) = 0.0740]	6366 [R(int) = 0.0470]
Completeness to θ	99.9% [<i>θ</i> = 25.10]	97.8% [<i>θ</i> = 25.00]
h,k, l range	$-15 \le h \le 12$,	$-12 \le h \le 12$,
	$-14 \le k \le 14$,	$-12 \le k \le 12$,
	$-28 \le l \le 24$	$-15 \le 1 \le 22$
No. of reflections measured	14899	7743
Max. and min. Transmission	0.9162 and 0.8780	0.8515 and 0.8089
Data / restraints / parameters	3348 / 0 / 199	6366 / 0 / 379
Goodness-of-fit on F ²	1.001	1.003
Final R indices $[I \ge 2\sigma(I)]$	R1 = 0.0641,	R1 = 0.0516,
	wR2 = 0.1683	wR2 = 0.1046
<i>R</i> indices (all data)	R1 = 0.1282,	R1 = 0.0938,
	wR2 = 0.1906	wR2 = 0.1131
Largest diff. peak and hole ($e \cdot A^-$	0.825 and -0.316	0.430 and -0.456
3)		



Figure 1 Molecular structure of ROTi (thermal ellipsoids at 30% level; hydrogen atoms are omitted for clarity)



Figure 2 Molecular structure of **OTi** (thermal ellipsoids at 30% level; hydrogen atoms are omitted for clarity)

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