Table II. Spectral Data (IR, ^1H NMR) of Metallacycles 2

		^1H NMR (δ, C_6D_6, 25 °C)				
	IR ($\nu C{=}N$), cm^{-1}	N-$(SiMe_3)_2$ (54 H, s)	$NSiMe_3$ (9 H, s)	$SiMe_2$ (6 H, s)	CH_2 (2 H, br s)	*R*
2A	1615	–5.94	–18.30	6.01	25.21	–38.29 (3 H, s)
2B	1646	–6.37	–19.60	6.58	37.00	–37.18 (2 H, t), –19.17 (2 H, m), –9.95 (3 H, t)
2C	1643	–6.38	–16.59	7.33	36.73	–23.72 (1 H, hept), –13.65 (6 H, d)
2D	1627	–7.57	–20.73	7.63	47.15	–20.61 (2 H, s), –2.65 (2 H, d), 2.18 (2 H, t), 3.62 (1 H, t)
2E	1620	–7.57	–20.26	7.73	45.81	–20.38 (1 H, s), –2.42 (4 H, d), –2.18 (4 H, t), 3.62 (2 H, t)
2F	1618	–5.69	–17.29	7.27	18.29	–29.51 (1 H, dd), 12.0 (1 H, d), 11.6 (1 H, d)
2G	1640	–6.10	–21.25	7.08	34.98	–34.30 (2 H, t), –23.69 (2 H, t)
2H	1610	–6.08	–18.16	8.55	24.19	–11.26 (2 H, d), –2.52 (2 H, t), 6.61 (1 H, t)
2I	1630	–5.67	–19.50	7.47	22.45	–20.69 (1 H, d), –3.49 (1 H, t), 1.04 (1 H, d), 3.19 (1 H, t)
2J	1637	–8.50	–21.20	2.71	29.08	–50.30 (2 H, t), –6.15 (2 H, t)

bond stretching of azomethines. It is noteworthy that the stretching frequency of the unreacted $C\equiv N$ group of 2J (2080 cm^{-1}) was significantly lower than that of the free ligand (2150 cm^{-1}). This decrease in frequency might be attributable to the internal coordination of the cyano group on the coordinatively unsaturated uranium atom.[6]

^1H NMR spectra of compounds 2 (Table II) were remarkably simple. $(NSiMe_3)_2$ and $SiMe_3$ protons exhibit very sharp singlets at high fields whereas CH_2 protons appear as broad, dramatically deshielded signals.[7] Each set of protons on the inserted azomethines showed very good resolved signals that were easily assigned to the corresponding hydrogens.[8]

Experimental Section

All operations on the air- and moisture-sensitive metallacycle 1 were performed under argon atmosphere in Schlenk-type vessels.

The solvents were distilled from sodium benzophenone ketyl under argon just prior to use. ^1H NMR spectra were recorded on Bruker 400W spectrometer in C_6D_6. Chemical shifts are reported in ppm from external TMS. Gas chromatographic analyses of ketones were performed on XE60, 5% on Chromosorb NAW 100-120. Metallacycle 1 was easily synthetized from UCl_4 and Na $N(SiMe_3)_2$ in nearly quantitative yields according to a published procedure.[9] It was stored in the crystalline state or as standardized solutions in toluene or pentane (1–2 mol L^{-1}).

General Procedure for the Synthesis of the Metallacycles 2. To a stirred solution of 1 (1.8 mmol) in 10 mL of toluene was added slowly (2 min) at room temperature 1.8 mmol of nitrile in 10 mL of toluene. After 5 min, the solvent was removed under vacuum and the brown residue was extracted twice with 10 mL of pentane. The solution was filtered and evaporated to give satisfactorily pure 2 (more than 95%) as a brown microcrystalline powder. Yields on isolated product were reported in Table I.

General Procedure for Direct Synthesis of the Methyl Ketones. To a stirred solution of 1 (1.2 mmol) in 2 mL of pentane was added 1.2 mmol of nitrile within 5 min. After 5 min, the mixture was quenched with 2 mL of HCl (1 M). The organic layer was separated, washed with 1 mL of water, dried over sodium sulfate, diluted to 10 mL with pentane, and analyzed by VPC.

Redissolution of 2 in pentane followed by hydrolysis as described above afforded methyl ketones in similar yields.

Registry No. 1, 72472-77-6; **2** (R = CH_3), 113765-70-1; **2** (R = $CH_3CH_2CH_2$), 113765-71-2; **2** (R = $(CH_3)_2CH$), 121029-64-9; **2** (R = $C_6H_5CH_2$), 121029-65-0; **2** (R = $(C_6H_5)_2CH$), 121029-66-1; **2** (R = $CH_2 = CH$), 121029-67-2; **2** (R = $BrCH_2CH_2$), 121029-68-3; **2** (R = C_6H_5), 113765-72-3; **2** (R = *o*-ClC_6H_4), 121029-69-4; **2** (R = $N\equiv CCH_2CH_2$), 121029-70-7; CH_3CN, 75-05-8; $CH_3CH_2CH_2CN$, 109-74-0; $(CH_3)_2CHCN$, 78-82-0; $C_8H_5CH_2CN$, 140-29-4; $(C_6H_5)_2CHCN$, 86-29-3; $CH_2{=}CHCN$, 107-13-1; $BrCH_2CH_2CN$, 2417-90-5; C_6H_5CN, 100-47-0; *o*-ClC_6H_5CN, 873-32-5; $NCCH_2CH_2CN$, 110-61-2; $CH_3C(O)CH_3$, 67-64-1; $CH_3CH_2CH_2C(O)CH_3$, 107-87-9; $(CH_3)_2CHC(O)CH_3$, 563-80-4; $C_6H_5CH_2C(O)CH_3$, 103-79-7; $(C_6H_5)_2CHC(O)CH_3$, 781-35-1; $CH_2{=}CHC(O)CH_3$, 78-94-4; $BrCH_2CH_2C(O)CH_3$, 28509-46-8; $C_6H_5C(O)CH_3$, 98-86-2; *o*-$ClC_6H_4C(O)CH_3$, 2142-68-9; $NCCH_2CH_2C(O)CH_3$, 927-56-0.

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[6] The lack of reactivity observed for the second cyano group, even if an excess of uranium reagent was added, is in good accordance with the internal coordination of this group on the uranium atom.

[7] The methylene singlet of 1 was strongly shielded (–118 ppm, C_6D_6, 25 °C) whereas the deshielding of the same protons in the metallacycles obtained after insertion of polar molecules into the U–C bond was a general feature (see ref 2, 3, 9 and also: Dormond, A.; Elbouadili, A.; Moise, C. J. *Less. Com. Met.* **1986**, *122*, 159).

[8] The considerable splitting and the good resolution of signals in ^1H NMR spectra of the metallacycles obtained after insertion in the uranium–methylene bond of 1 is a general feature for a wide range of organic molecules. Therefore, the utilization of the uranium metallacycle 1 as a shift reagent instead lanthanides complexes is under investigation.

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An Optimized Procedure for Titanium-Induced Carbonyl Coupling

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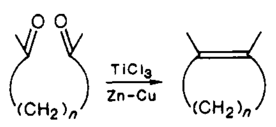
Fifteen years have passed since the discovery[1-3] that ketones and aldehydes undergo deoxygenative coupling to yield olefins on treatment with low-valent titanium. The reaction takes place equally well on all manner of substrates, be they saturated or unsaturated, aliphatic or aromatic, ketone or aldehyde. Furthermore, the reaction occurs both in an intermolecular sense on monocarbonyl compounds to yield acyclic alkenes and in an intramolecular sense on dicarbonyl compounds to yield cycloalkenes.[4]



Although our initial work[1] involved preparation of the low-valent titanium reagent by reduction of $TiCl_3$ with $LiAlH_4$ in tetrahydrofuran (THF), we soon found that

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[4] For reviews, see: (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411. (b) Lai, Y.-H. *Org. Prep. Proced.* **1980**, *12*, 361–391. (c) Welzel, P. *Nachr. Chem. Tech. Lab.* **1983**, *31*, 814–816. (d) McMurry, J. E. *Chem. Rev.*, in press.

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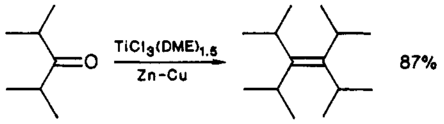
variations in the age, history, and source of $TiCl_3$ caused problems with reproducibility. In attempts to overcome the difficulties, we subsequently introduced the use of $TiCl_3/K$,[5] $TiCl_3/Li$,[6] and then $TiCl_3/Zn-Cu$.[7] Other workers have also attempted to improve the coupling reaction, and uses of the reagent systems $TiCl_4/Zn/pyridine$[8] and $TiCl_3/K/graphite$[9-11] have been reported. With these numerous reagent systems available, it is understandable why confusion exists in the literature, why low yields are sometimes reported for carbonyl-coupling reactions, and why we occasionally read of workers using procedures that we ourselves abandoned a decade ago.

We now report clear experimental details of an optimized procedure that gives reproducibly high yields in every case it has been used. The key to this new procedure is that even aged and ineffective batches of $TiCl_3$ can be reproducibly converted into a $TiCl_3$/dimethoxyethane solvate that is purified by crystallization. The resultant $TiCl_3(DME)_{1.5}$ complex is by far the most effective titanium source we have used for coupling. As an example of the efficacy of this new procedure, the coupling of diisopropyl ketone to yield tetraisopropylethylene was originally reported[12] to take place in 12% yield using $TiCl_3/LiAlH_4$. We improved the yield to 37% by using $TiCl_3/Zn-Cu$,[7] and we now find that the reaction takes place in 87% yield using $TiCl_3(DME)_{1.5}/Zn-Cu$.



Intermolecular couplings leading to acyclic alkenes, and intramolecular couplings leading to small-ring cycloalkenes (ring sizes 3–7), are best carried out by rapid addition of the substrate to a reagent prepared by using 3 equiv of $TiCl_3(DME)_{1.5}$ per equivalent of carbonyl compound. More difficult intramolecular couplings leading to medium- and large-ring cycloalkenes require a lengthy addition time to achieve high dilution, and the use of 4 or more equivalents of titanium reagent per carbonyl group.

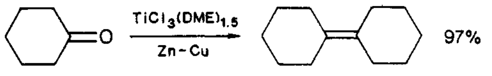
Experimental Section

1-Alkyl-1,4-dihydronicotinamides. Dimethoxyethane (DME) was distilled from potassium metal under an argon atmosphere; pentane was distilled from CaH_2 and deoxygenated prior to use by purging with argon for 10 min. All manipulations were carried out under an atmosphere of argon, and all transfers were done using Schlenk apparatus.

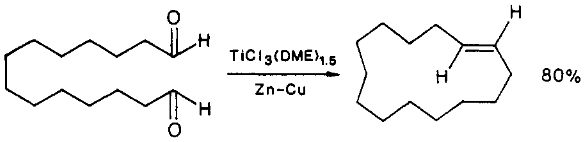
Preparation of $TiCl_3(DME)_{1.5}$.[13] $TiCl_3$ (25.0 g, 0.162 mol) was suspended in 350 mL of dry DME, and the mixture was refluxed for 2 days under argon. After the mixture was cooled to room temperature, filtration under argon, washing with pentane, and drying under vacuum gave the fluffy, blue crystalline $TiCl_3(DME)_{1.5}$ (32.0 g, 80%) that was used in the coupling reaction. The solvate is air-sensitive but can be stored indefinitely under argon at room temperature.

Preparation of Zinc–Copper Couple. Zinc–copper couple was prepared by adding zinc dust (9.8 g, 150 mmol) to 40 mL of nitrogen-purged water, purging the slurry with nitrogen for 15 min, and then adding $CuSO_4$ (0.75 g, 4.7 mmol). The black slurry was filtered under nitrogen, washed with deoxygenated (nitrogen-purged) water, acetone, and ether, and then dried under vacuum. The couple can be stored indefinitely in a Schlenk tube under nitrogen.

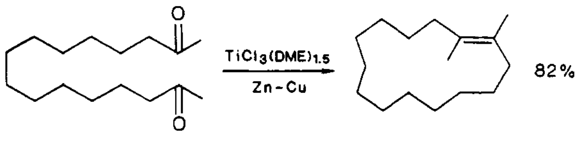
Example of an Intermolecular Coupling: Cyclohexylidenecyclohexane. $TiCl_3(DME)_{1.5}$ (5.2 g, 17.9 mmol) and Zn–Cu (4.9 g, 69 mmol) were transferred under argon to a flask containing 100 mL of DME, and the resulting mixture was refluxed for 2 h to yield a black suspension. Cyclohexanone (0.44 g, 4.5 mmol) in 10 mL of DME was added, and the mixture was refluxed for 8 h. After being cooled to room temperature, the reaction mixture was diluted with pentane (100 mL), filtered through a pad of Florisil, and concentrated at the rotary evaporation to yield cyclohexylidenecyclohexane (0.36 g, 97%) as white crystals, mp 52.5–53.5 °C. If a 3:1 ratio of $TiCl_3(DME)_{1.5}$ to carbonyl compound is used instead of 4:1, the yield decreases from 97% to 94%; if a 2:1 ratio is used, the yield is 75%.



Example of a Macrocyclic Intramolecular Dialdehyde Coupling: Cyclotetradecene. $TiCl_3(DME)_{1.5}$ (5.2 g, 17.8 mmol) and zinc–copper couple (3.80 g, 58.1 mmol) were added to a dry argon-filled flask and were stirred vigorously while DME (150 mL) was added by syringe. After the mixture was heated at 80 °C for 4 h to form the active titanium coupling reagent, tetradecanedial (0.50 g, 2.20 mmol) in 50 mL of DME was added via syringe pump over a period of 35 h. The reaction was heated an additional 6 h after addition was complete and was then cooled to room temperature. Pentane (160 mL) was added to the reaction flask, and the reaction slurry was filtered through a small (5 cm × 10 cm) pad of Florisil to remove metal salts. After washing the Florisil pad with an additional 100 mL of pentane, the filtrates were combined and concentrated at 0 °C under reduced pressure to give pure cyclotetradecene (340 mg, 80%) as a colorless oil. NMR and capillary GC analysis indicated that the product was a 9:1 mixture of *E* and *Z* isomers. ^{13}C NMR (*E* isomer): δ 23.8, 24.3, 25.3, 26.5, 27.6, 31.6, 131.6.



Example of a Macrocyclic Intramolecular Diketone Coupling: 1,2-Dimethylcyclotetradecene. $TiCl_3(DME)_{1.5}$ (4.6 g, 15.7 mmol) and Zn–Cu couple (3.1 g, 47.6 mmol) were placed in a dry argon-filled flask, 150 mL of DME was added, and the mixture was refluxed for 5 h. 2,15-Hexadecanedione (0.50 g, 2.0 mmol) in 50 mL of dry DME was added by syringe pump over a period of 35 h while the reaction temperature was maintained at 80 °C, and the mixture was stirred an additional 8 h after addition was complete. After being cooled to room temperature and the addition of 150 mL of pentane, the reaction mixture was filtered through Florisil and concentrated under reduced pressure to yield 1,2-dimethylcyclotetradecene (360 mg, 82%) as a 92:8 mixture of *E* and *Z* isomers. ^{13}C NMR (*E* isomer): δ 18.4, 24.1, 25.3, 25.5, 26.3, 27.4, 33.5, 128.5.



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[13] Redox titrations of the $TiCl_3$/DME solvate against benzoquinone show a 1:1.97 ratio of $TiCl_3$ to DME, but X-ray studies by Professor Carlo Floriani, Université de Lausanne, show that the actual stoichiometry of the purified solvate is $TiCl_3(DME)_{1.5}$. Our material must therefore contain solvent of crystallization. We thank Professor Floriani for this information.