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THE TITANOCENE METHYLENE-ZINC HALIDE COMPLEX: A CONVENIENT SYNTHESIS AND ITS METHYLENATING ACTION ON UNSATURATED CARBON CENTERS[1]

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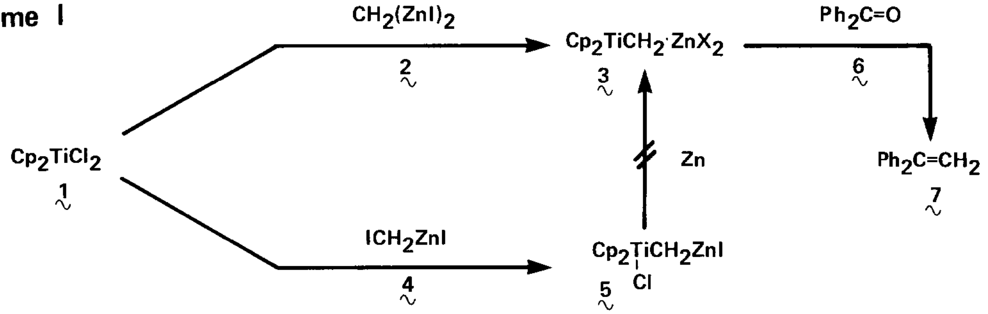
Abstract: The titanocene methylene-zinc halide complex, which can be conveniently prepared by treating titanocene dichloride with methylenezinc iodide in THF solution, readily methylenates ketones, nitriles, and alkynes.

The interaction of titanocene dichloride in toluene with pyrophoric alkyls, such as Me_3Al and Me_2Zn, produces titanocene methylene compounds complexed with the main-group metal halide. In the case of the reaction with Me_3Al, the so-called Tebbe reagent, $Cp_2TiCH_2AlClMe_2$, can be isolated in 45% yield after 60 h at room temperature.[2] The Tebbe reagent has proved of great value both in studies of the mechanism of olefin metathesis[2-5] and as a useful reagent for methylenating olefins,[2] ketones,[2-6] alkynes[5] and esters.[7] Its use suffers from the drawbacks of requiring long reaction times and the manipulation of hazardous Me_3Al.

Accordingly, we wish to report the discovery of a most convenient route to a titanocene methylene compound complexed with zinc halide and to present a survey of its reactions with a variety of organic substrates. The reagent can be prepared by allowing 9.0 g (138 mmol) of purified zinc dust to react under nitrogen and in 60 ml of THF with 50 mmol of CH_2I_2, which is added dropwise so as to maintain a reaction temperature of 45°C. After an additional hour the reaction mixture is filtered to give ∿45% yield of $CH_2(ZnI)_2$.[8] Then this reagent is added to an equivalent amount of Cp_2TiCl_2 suspended in THF and the resultant deep red solution stirred for 30-60 min. This solution can be used directly for various reactions or it can be kept at -78°C until the deep red precipitate of $Cp_2TiCH_2{\cdot}ZnX_2{\cdot}(THF)_x$ (**3**) settles out. This precipitate can be redissolved in toluene and used for reactions or spectroscopic measurements. The concentration of **3** in the original THF solution is determined by its reaction with benzophenone (**6**) to form 1,1-diphenylethene (**7**) (Scheme I). By this criterion, the yield of **3** ranges from 45 to 55% in the conversion of **1** by **2**. The ^1H NMR spectrum of **3** (X=Cl or I) in toluene-d_8 showed the characteristic singlets at δ 8.37 (2H) and 5.92 (10H) ppm as well as the two triplets of complexed THF. Reagent **3** is not formed when **1** is treated with ICH_2ZnI[9] and the resulting **5** treated with zinc;

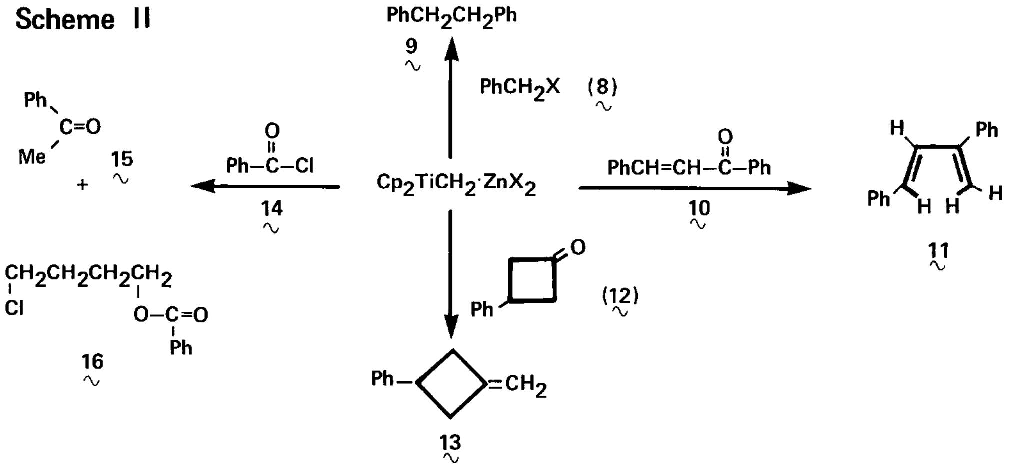
only brown decomposition products resulted (Scheme I).

Scheme I



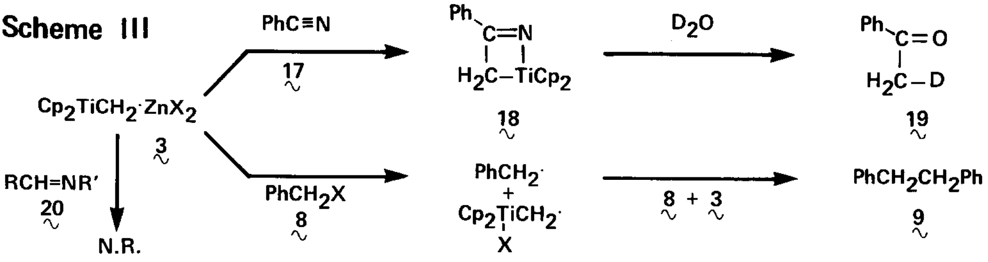
The titanocene methylene-zinc halide complex (3) is a most efficient reagent for methylenating ketones. At -10°C a toluene solution of 3 reacted essentially quantitatively with benzophenone (6) and gave >80% isolated yields of the corresponding methylene derivatives with chalcone (10) and with 3-phenylcyclobutanone (12) (Schemes I and II).[10] With benzoyl chloride (14), the predominant reaction of 3 was the ring opening of the complexed THF to yield 16 (45%); only a small amount of acetophenone (15, 20%) was obtained upon hydrolysis. With a reactive halide, such as benzyl chloride or bromide (8), no methylenation occurred but rather an electron-transfer coupling led to a >85% yield of bibenzyl (9) (Schemes II and III).

Scheme II



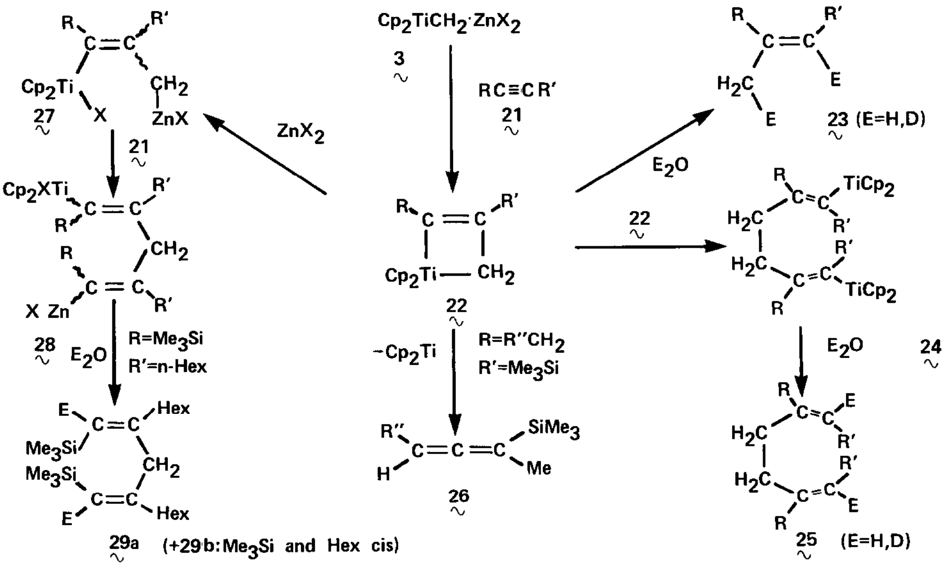
Toward carbon-nitrogen unsaturation, reagent 3 proved to be sensitive to steric factors. Benzalaniline (20: R=Ph, R'=Ph) and phenanthridine (20: R and R'=2,2'-biphenylene) did not react with 3, but benzonitrile (17) reacted at 45°C over 17 h in toluene to give a 70% isolated yield of acetophenone upon hydrolysis. That an alternative work-up with D_2O yielded deuterated 19 accords with the presence of precursor 18 (Scheme III).

Scheme III



Although the Tebbe reagent forms adducts readily with alkynes (*e.g.*, 22) and thereby methylates them in a *syn*-manner,[5] reagent 3 causes principally the methylenative dimerization of alkynes. For example, 1-decyne (21: R=n-C_8H_{17}, R'=H) reacted with 3 to yield, upon deuterolysis, 30% of a 60:40 mixture of 2-methyl-1-decene and 1-undecene [the former being dideuterated as shown in 23 (Scheme IV, R=n-C_8H_{17}, R'=H)] and 45% of dimer 25 (R=n-C_8H_{17}, R'=H).[11] The deuteration patterns in 23 and 25 indicate that 22[3] and 24 are their precursors. Similarly, phenylacetylene (21, R=Ph, R'=H) and 3 produced, upon D_2O treatment, 10% of 23 (R=Ph, R'=H) and 48% of a 3:1 mixture of diphenyl-1,5-hexadienes (25a: R=Ph, R'=H; 25b: R=H, R'=Ph).[12] With diphenylacetylene and 3, the principal product in 22% yield was the known 1,2,5,6-tetraphenyl-1,5-hexadiene (25: R=Ph, R'=Ph).[13]

Scheme IV



The behavior of the alkyne, trimethyl(1-octynyl)silane (**21**: $R=n\text{-}C_6H_{13}$; $R'=SiMe_3$), with **3** differed in two respects from that of the foregoing alkynes: 1) a small amount of allene (5% **26**: $R''=n\text{-}C_5H_{11}$) was formed;[14] and 2) the principal methylenated dimers (20%) had the structures shown in **29**.[15] Some 32% of the product was the same methylated vinylsilane (**23**: $R=n\text{-}C_6H_{13}$; $R'=SiMe_3$) as that formed from Cp_2TiCl_2 and $MeAlCl_2$.[16] The novel dimers **29** can readily be explained as arising by the insertion of further **21** into the allylic C-Zn bond of **27**. Again, the deuteration patterns in **23** and **29** support the presence of **22** and **28** as reactive intermediates. Finally, allene **26** could readily form by a facile *beta*-hydride elimination in **22**, a process rich in precedent.[17]

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(10) Treatment of Cp_2ZrCl_2 with $CH_2(ZnI)_2$ in THF gave a yellow solution that converted Ph_2CO to $Ph_2C=CH_2$ (70%).

(11) Compound **25** ($R=n\text{-}C_8H_{17}$, $R'=H$): ^1H NMR ($CDCl_3$) the 4H-singlet at 4.73 becomes a 2H-singlet in 25 (E=D). By analogy with **25** (R=Ph, R'=Ph), the dimer from 1-decyne most likely has the R and R' trans.

(12) Both **25a** (mp 45-46.5°C) and **25b** (mp 77.5-78°C) are known compounds: G.B. Butler and J. Brooks, *J. Org. Chem.*, **28**, 2699 (1963) and H.P. Koch, *J. Chem. Soc.*, 1111 (1948).

(13) Compound **25** (R=Ph, R'=Ph), mp 146.5-147.5°C, is a known compound: R. Luckenbach and N. Müller, *Z. Naturforsch.*, **34B**, 464 (1979).

(14) Compound **26** has a characteristic IR band at 1930 cm^{-1}.

(15) Compounds **29a** and **29b** display very similar ^1H NMR ($CDCl_3$) spectra but show distinctive vinyl proton signals at 5.00 (**29a**, t, $J \sim 1$ Hz) and 5.17 (**29b**, br. s, $J < 0.5$ Hz); in **29a**, the vinyl H and the cis-CH_2 of the hexyl group are coupled.

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