Intermolecular C–H Activation by Reactive Titanocene Alkylidene Intermediates

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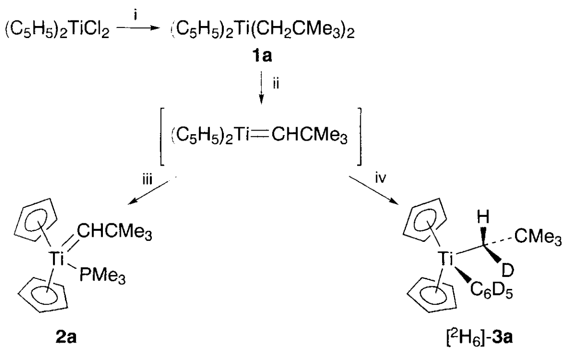
Thermal α-H abstraction from $(C_5H_4R)_2Ti(CH_2CMe_3)_2$ (R = H, Me) produces reactive titanocene neopentylidene intermediates under mild conditions, that can either be trapped with PMe_3 to yield the alkylidene complexes $(C_5H_4R)_2Ti(CHCMe_3)PMe_3$, or add C–H bonds of hydrocarbon substrates R′H (R′H = benzene, *p*-xylene) to the Ti=C double bond to produce $(C_5H_4R)_2Ti(CH_2CMe_3)R'$; an alternative reaction pathway, insertion of the alkylidene moiety into the cyclopentadienyl C–C bond, has been observed in the presence of THF.

The reactivity of transition-metal to nonmetal multiple bonds includes a wide variety of reaction types, a number of which are relevant to useful processes such as hydrocarbon oxidation, olefin metathesis and polymerisation.[1] Recent investigations of the reactivity of metal–nonmetal multiple bonds have involved activation of hydrocarbon C–H bonds by d^0-metal imido species. Intermolecular addition of a C–H bond to an M=NR functionality constitutes the microscopic reverse of α-elimination from metal–hydrocarbyl–amido complexes and has now been established for a number of transition metals (Zr,[2] Ti,[3] V,[4] Ta[5]). Although metal alkylidene species are, like imido complexes, also readily obtained *via* α-elimination, the corresponding reverse reactivity of metal–carbon double bonds in metal alkylidenes has to our knowledge been limited to a few intramolecular cases.[6,7] Here we describe the generation under mild conditions of reactive titanocene neopentylidene species that are able to effect intermolecular addition of both sp^2- and sp^3-C–H bonds to the Ti=CHR double bond.

Precursors of the neopentylidene species are the bis(neopentyl) complexes $(C_5H_4R)_2Ti(CH_2CMe_3)_2$ (R = H **1a**, Me **1b**). They can be isolated at or below 0 °C from the reaction of the corresponding dichlorides with $Mg(CH_2CMe_3)_2$·dioxane in diethyl ether. Complex **1a** has been previously described (but not spectroscopically characterised) as the product of the reaction between $(C_5H_5)_2$ $TiCl_2$ and neopentyllithium at −80 °C.[8] It can be stored as a solid for weeks at −40 °C, whereas **1b** is an oil and has to be used within a few days of preparation, even when stored cold. Compounds **1** decompose in solution at ambient temperatures *via* α-H abstraction to give neopentane and a titanocene neopentylidene species. The latter can be trapped with PMe_3 to give the thermally stable alkylidene complexes $(C_5H_4R)_2Ti(CHCMe_3)PMe_3$ (R = H **2a**, Me **2b**, Scheme 1). These show spectroscopic features typical of titanocene alkylidenes.[9] For example, **2a** has its ^1H- and ^{13}C-NMR Ti=CH– and Ti=CH– resonances at δ 12.32 (J_{PH} = 7.2 Hz) and δ 312.9 (J_{PC} = 27 Hz, J_{CH} = 110 Hz) respectively. The bisneopentyl complexes **1** are thus convenient precursors of titanocene alkylidene species under mild conditions.



Scheme 1 *Reactions and conditions*: i, $Mg(CH_2CMe_3)_2$·dioxane, Et_2O, 10 min, 20 °C, work-up < 0 °C, 60% isolated yield; ii, $-CMe_4$, 20 °C; iii, PMe_3, pentane, 72% isolated yield; iv, C_6D_6

In the absence of phosphine, addition of C–H bonds of hydrocarbon solvents to the Ti=C bond in the unsaturated alkylidene intermediate is observed at ambient temperature. Complex **1a** reacts in neat C_6D_6 to produce quantitatively (by NMR) the [1-^{2}H] neopentyl [$^2H_5$] phenyl complex $(C_5H_5)_2Ti(CHDCMe_3)(C_6D_5)$ [$^2H_6$]-**3a**, with the selective incorporation of one deuterium on the neopentyl α-carbon (Scheme 1). This is evident from (*a*) the $^1J_{CD}$ coupling constant of 18 Hz, (*b*) the isotope shift Δδ of −1.0 ppm in the ^{13}C-NMR spectrum of [$^2H_6$]-**3a** by comparison with separately prepared non-deuteriated **3a**, and (*c*) the inequivalence of the diastereotopic C_5H_5-ligands in [$^2H_6$]-**3a**. The reaction follows simple first-order kinetics over the temperature range 12.9–40.4 °C, and kinetic parameters were determined from an Arrhenius plot (of seven *k*-determinations over the cited temperature range) as $\Delta H^‡$ = 18.2(5) kcal mol^{-1} and $\Delta S^‡$ = −11.9(8) kcal mol^{-1} K^{-1} (1 cal = 4.184 J). A comparison with the kinetic parameters of the thermal decomposition of $(C_5Me_5)_2TiMe_2$ (*via* α-H abstraction followed by intramolecular trapping by C–H activation of the C_5Me_5-ligand Me-groups)[6a] of $\Delta H^‡$ = 27.6 kcal mol^{-1} and $\Delta S^‡$ = −2.8 kcal mol^{-1} K^{-1} shows that α-H abstraction in **1a** is much more facile, and that the transition state has a higher degree of organisation, presumably due to the large CMe_3 substituents on the alkyl groups. In solution at 20 °C, **1a** has a half-life of 56 min, while this is only 20 min for the methylcyclopentadienyl derivative **1b**, showing that alkyl substitution on the cyclopentadienyl ligand facilitates the α-H abstraction process.

Intermolecular activation of benzylic sp^3-CH bonds was also observed: reaction of **1a** with [$^2H_{10}$]-*p*-xylene produces $(C_5H_5)_2Ti(CHDCMe_3)(CD_2C_6D_4CD_3$-*p*) ([$^2H_{10}$]-**4**), although in this solvent, unlike in benzene, paramagnetic side products are formed. In mixed alkyl–benzyl complexes of this kind, the benzylic α-hydrogens are themselves susceptible to α-H abstraction, leading eventually to bis(benzylic) products. Thus in protio-*p*-xylene **1a** is transformed *via* transient protio-**4** to the bis benzylic product $(C_5H_5)_2Ti(CH_2C_6H_4Me$-*p*$)_2$ **5**.[†]

Attempts at intermolecular activation of aliphatic C–H bonds on titanocene alkylidene intermediates have so far produced inconclusive results. In alkane solvents (*n*-pentane, cyclohexane) complexes **1** produce dark poorly-soluble materials, suggesting reduction of the metal centre. However, in the presence of a few equivalents of THF a product is formed concurrently that indicates at least one alternative reaction pathway for these unsaturated alkylidene intermediates. Based on ^1H- and ^{13}C-NMR data[‡] the product was identified as a cyclohexadienyl complex, $(C_5H_5)[\eta^5\text{-}C_5H_5C(H)CMe_3]Ti(THF)$ **6**, a compound apparently derived from an expansion of the cyclopentadienyl ring by insertion of the alkylidene moiety into one of the C–C bonds. The compound slowly decomposes under reaction conditions, liberating *tert*-butylbenzene. The latter was identified by NMR spectroscopy (^1H, ^{13}C) and GC through comparison with an authentic sample. Cyclopentadienyl ring expansion has been observed in some cyclopentadienyl–metal–acyl complexes (M = Ti[10], Ta[11], U[12]), where the reaction is believed to involve the acyl as a ‘Fischer’-type carbene that inserts into the C_5H_5 C–C bond. It is unprecedented for early transition metal alkylidenes, and the precise mechanism of the observed reaction is as yet unclear.

Competition between ring expansion and C–H addition was observed in aromatic solvents in the presence of THF (4 equiv. per Ti), allowing an estimate of the relative trapping efficiency of the alkylidene intermediate by the aromatic substrates. In C_6D_6, the ring expansion product **6** and the C–H addition product $[^2H_6]$-**3a** are formed in a 23 : 77 ratio from **1a**, as determined by NMR.§ A normal isotope effect appears to be present in the trapping of the alkylidene intermediate by C–H bonds, as the ratio **6** to **3a** decreases to 4 : 96 for the reaction in C_6H_6 under otherwise identical conditions. The ring-expansion to C–H addition ratio increases to approximately 45 : 55 in $[^2H_{10}]$-*p*-xylene, showing that xylene is a less efficient trapping agent for the neopentylidene intermediate than benzene.

In conclusion, titanocene bis(neopentyl) complexes form convenient precursors of unsaturated alkylidene species that are able to effect intermolecular C–H activation. One possible reason for the readily observed intermolecular C–H activation in this system is that it may have difficulties in forming dimers: no evidence was obtained for formation of 1,3-dimetallacyclobutane species similar to $[(C_5H_5)_2Ti(\mu\text{-}CH_2)]_2$[13] (for comparison, the molybdenum complex $(C_5H_5)Mo(CH_2CMe_3)_2(NO)$ forms dimeric $(C_5H_5)_2Mo_2(NO)(CHCMe_3)(\mu\text{-}NO)$-$(\mu\text{-}CHCMe_3)$ upon loss of neopentane).[14] In the absence of favourable intramolecular C–H activation pathways, it allows trapping of the Ti=C functionality by intermolecular addition of C–H bonds. The efficiency of this trapping is substrate-dependent, as can be seen from competition experiments with the ring-expansion reaction in the presence of THF. Thus, it appears that intermolecular addition of C–H bonds to transition metal–heteroatom double bonds does not necessarily require a very high polarity of the latter.

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Footnotes

† Thermolysis (20 °C) of independently prepared (though impure) $(C_5H_5)_2Ti(CH_2CMe_3)(CH_2Ph)$ in C_6D_6 in the presence of PMe_3 produced the benzylidene complex $(C_5H_5)_2Ti(CHPh)PMe_3$ as the main product: ^{1}H-NMR δ 13.25 (Ti = C*H*Ph, d, J_{PH} = 8.8 Hz); ^{13}C-NMR δ 293.2 (Ti=CHPh, d, J_{PC} = 29; d J_{CH} = 117 Hz).

‡ **6** ^{1}H-NMR (300 MHz, $[^2H_{10}]$-*p*-xylene): δ 0.01 (s, 9H, CMe_3), 0.13 (1H, CH_ACMe_3), 4.36 (2H, *o*-CH_B), 4.53 (1H, *p*-CH_D), 5.40 (2H, *m*-CH_C), 6.12 (s, 5H, C_5H_5); THF resonances are very broad. $J(H_AH_B)$ = 1.8, $J(H_BH_C)$ = 7.8, $J(H_CH_D)$ = 7.3, $J(H_BH_D)$ = 1.2 Hz. ^{13}C-NMR (75.4 MHz, $[^2H_{10}]$-*p*-xylene): δ 22.1 (q, 122 Hz, CMe_3), 26.1 (d, 135, C_A), 29.8 (s, CMe_3), 92.1 (d, 165, C_B), 96.0 (d, 165, C_D), 103.1 (d, 164, C_C), 106.53 (d, 171, C_5H_5); THF resonances very broad.

§ Typical experiments with 0.05 mol dm^{-3} **1a**, 0.20 mol dm^{-3} THF solutions in aromatic solvent. Product ratio was determined from integrated ^{1}H-NMR intensities after approximately 2 h reaction time at 25 °C. The reaction mixture in C_6H_6 was pumped dry and redissolved in C_6D_6 after which the product ratio was immediately determined by NMR.

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