Titanium and zirconium neopentyl chloro complexes, MNp$_x$Cl$_{4-x}$ (x = 1–4)

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Abstract

The comproportionation reaction between the titanium and zirconium homoleptic neopentyl complexes, TiNp$_4$ and ZrNp$_4$ (Np = 2,2'-dimethylpropyl; CH$_2$CMe$_3$) and the metal tetrachlorides, TiCl$_4$ and ZrCl$_4$ provides a facile route to all of the titanium and zirconium neopentyl chloro complexes, MNp$_x$Cl$_{4-x}$ (x = 1,2,3). All the complexes described are moisture-sensitive, and in the case of the titanium complexes, light-sensitive also. The stability of the complexes at room temperature has also been estimated. The neopentyl chloro complexes, and the isotopically labelled species (where (Np-d) = CH(D)CMe$_3$), have been spectroscopically characterised, the ^{1}H NMR resonance of the CH$_2$ protons displays an increasing shift to high frequency in the series MNp$_4$, MNp$_3$Cl, MNp$_2$Cl$_2$, MNpCl$_3$. A modified synthesis of Me$_3$CCHDCl from Me$_3$CCHDOH is reported. © 1997 Elsevier Science S.A.

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1. Introduction

In early studies of the chemistry of metal–carbon σ-bonds it was thought that the metal–carbon bond strength was low, and that this accounted for the apparent low stability of metal alkyls. The thermodynamic strength of metal–carbon bonds has now been established [1], and metal–carbon bonds are stable provided that kinetically facile decomposition routes are prevented. The most important decomposition reaction is β-elimination, converting a metal alkyl into metal hydride and alkene, a reaction which can be prevented by employing alkyl groups which have no β-hydrogens. Other decomposition routes include intra- and intermolecular α-elimination [2], which reactions generally have sufficiently high activation energies that they can be prevented by avoiding elevated temperatures. Many alkyl complexes of early transition metals, including those stabilised by cyclopentadienyl ligands, are also prone to homolytic photochemical M–C bond cleavage, and require handling in the absence of light.

The simplest alkyl ligands containing no β-hydrogens are methyl and neopentyl (2,2'-dimethylpropyl),

and the chemistry of TiMe$_x$Cl$_{4-x}$ and its bromide analogues has been extensively studied [3], and TiMeX$_3$ complexes (X = Cl, NMe$_2$, OR) are widely employed in organic synthesis [4]. The chemistry of Ti(Me$_3$CCH$_2$)$_x$Cl$_{4-x}$ and the zirconium analogues have been less widely studied. The homoleptic tetraneopentyls of all the Group 4 metals have been described, along with their thermal stabilities, and comparisons with MMe$_4$ and M(CH$_2$SiMe$_3$)$_4$ [5,6]. Wengrovius and Schrock investigated the possibility of preparing alkylidenes by α-elimination from ZrNp$_2$X$_2$L$_2$, and also observed that addition of ligands including PMe$_3$ and TMEDA to ZrNp$_3$Cl causes disproportionation into ZrNp$_4$ and ZrNp$_2$Cl$_2$L$_2$ [7]. The solid-state structure of ZrNp$_3$Cl has been determined and consists of a metal-based polymer with repeating Zr–Cl–Zr–Cl units [8]. Recently, the syntheses of TiNpCl$_3$, Ti(CH$_2$CHMe$_2$)Cl$_3$ and Ti(CH$_2$SiMe$_3$)Cl$_3$ have been reported [9], and the crystal structure of Ti(CH$_2$SiMe$_3$)Cl$_3$ has been described [10]. It has been suggested that reaction of TiMeCl$_3$ with 2-methyl propene (isobutylene) gives TiNpCl$_3$ [11], although we have been unable to repeat this reaction.

The solution [12] and gas-phase [13] structures of MeTiCl$_3$ are now recognised to contain tetrahedral carbon and titanium atoms, undistorted by α-agostic inter-

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actions, although the solid-state structure, determined by X-ray diffraction [14], shows a Ti–Cl–Ti bridged dimer, with potential agostic interactions. The solid-state structures of the diphosphine adducts MeTiCl$_3$(dmpe) and EtTiCl$_3$(dmpe) do demonstrate the presence of α- and β-agostic interactions [15]. Calculations have suggested that the formation of agostic interactions is not favoured in pseudo-tetrahedral RTiCl$_3$ complexes, but is favoured for pseudo-octahedral complexes, RTiCl$_3$(L$_2$), where L$_2$ could potentially be diphosphine or bridging chloride ligands [16]. Neopentyl complexes of titanium and zirconium have the potential to satisfy their formal electron deficiency through the formation of α- or, less likely, γ-agostic interactions. The solid-state infra-red spectra of both ZrNp$_4$ and ZrNp$_3$Cl contain features, near 2700 cm^{-1}, which might indicate agostic interactions.

In this paper we describe the synthesis and spectroscopic characterisation of the series of titanium and zirconium neopentyl chlorides, Np$_x$MCl$_{4-x}$ (M = Ti, Zr; x = 1,2,3,4); the thermal sensitivity of some of these complexes prevents their isolation.

2. Results and discussion

The homoleptic neopentyl complexes, TiNp$_4$ and ZrNp$_4$ were prepared according to literature [5,6] procedures by the alkylation of the tetrachlorides using Me$_3$CCH$_2$MgCl, and were purified by vacuum sublima-

tion. Although it has been shown that reactions between TiCl$_4$ and lithium alkyls in hydrocarbon solvents give the highest yields when an excess of TiCl$_4$ is used [9], the excess TiCl$_4$ coordinating the LiCl to produce TiCl$_4$ · (LiCl)$_n$, we have not encountered magnesium halide adducts in reactions using NpMgCl in ether solvents. The isolated yield of the titanium complex is only 20%, a consequence of thermal decomposition during sublimation and, to a lesser extent, reduction of TiCl$_4$ by the alkylating agent; we have not explored the use of alternative titanium precursors which might be less prone to reduction, e.g. Ti(OPr^i)$_4$, since we believe the main reason for the poor isolated yield to be losses during sublimation. The deuterium-labelled complexes, M[CH(D)CMe$_3$]$_4$, M(Np-d)$_4$ (M = Ti, Zr) were similarly prepared using the labelled Grignard, Me$_3$CCH(D)MgCl. The ^{1}H NMR spectra of both TiNp$_4$ and ZrNp$_4$ in benzene-d_6 are in agreement with those reported by Mowat and Wilkinson [6].

The labelled neopentyl chloride, Me$_3$CCH(D)Cl, required for the synthesis of the Grignard reagent, was prepared in excellent yield from neopentyl alcohol-d, Me$_3$CCH(D)OH, by a two-step route involving conversion to the tosylate and displacement of tosylate by chloride ion, as LiCl, using 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) as solvent. In our hands, this method appears superior to previously reported syntheses employing either dimethylsulfoxide (DMSO) [17] or hexamethylphosphoramide (HMPA) as solvent [18]; the use of DMSO produces a volatile
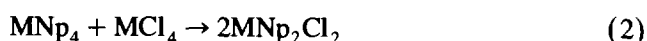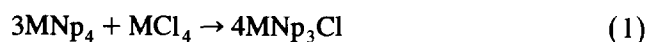
Table 1
Spectroscopic data characterising the complexes described [a]

Compound	^{1}H NMR data	^{13}C{^{1}H} NMR data
TiNp$_4$	2.06 [s, 8H, CH$_2$], 1.09 [s, 36H, CMe$_3$]	119.1 [CH$_2$], 37.6 [CMe$_3$], 34.4 [CMe_3]
TiNp$_3$Cl	2.69 [s, 6H, CH$_2$], 1.09 [s, 27H, CMe$_3$]	126.9 [CH$_2$], 38.9 [CMe$_3$], 33.8 [CMe_3]
TiNp$_2$Cl$_2$	3.30 [s, 4H, CH$_2$], 1.00 [s, 18H, CMe$_3$]	142.3 [CH$_2$], 37.1 [CMe$_3$], 32.3 [CMe_3]
TiNpCl$_3$	3.56 [s, 2H, CH$_2$], 1.08 [s, 9H, CMe$_3$]	163.2 [CH$_2$], 33.0 [CMe_3]
Ti(Np-d)$_4$	2.00 [br t, 4H, CHD], 1.09 [s, 36H, CMe$_3$]	118.5 [t, J = 16.5, CHD], 37.5 [CMe$_3$], 34.4 [Me]
Ti(Np-d)$_3$Cl	2.64 [br t, 3H, CHD], 1.07 [s, 27H, CMe$_3$]	
Ti(Np-d)$_2$Cl$_2$	3.25 [br t, 2H, CHD], 1.01 [s, 18H, CMe$_3$]	141.0 [t, J = 16.5, CHD], 32.2 [CMe_3]
Ti(Np-d)Cl$_3$	3.51 [t, J = 1.44, 1H, CHD], 1.09 [s, 9H, CMe$_3$]	
ZrNp$_4$	1.26 [s, 8H, CH$_2$], 1.08 [s, 36H, CMe$_3$]	102.5 [CH$_2$], 35.8 [CMe$_3$], 35.2 [CMe_3]
ZrNp$_3$Cl	1.63 [s, 6H, CH$_2$], 1.08 [s, 27H, CMe$_3$]	105.0 [CH$_2$], 34.9 [CMe_3]
ZrNp$_2$Cl$_2$	2.31 [s, 4H, CH$_2$], 1.09 [s, 18H, CMe$_3$]	113.8 [CH$_2$], 37.4 [CMe], 33.6 [CMe_3]
ZrNpCl$_3$	2.60 [br s, 2H, CH$_2$], 1.10 [s, 9H, CMe$_3$]	sample insufficiently soluble
Zr(Np-d)$_4$	1.21 [t, J = 1.64, 4H, CHD], 1.08 [s, 36H, CMe$_3$]	102.3 [t, J = 16.3, CHD], 35.2 [CMe_3]
Zr(Np-d)$_3$Cl	1.58 [br t, 3H, CHD], 1.09 [s, 27H, CMe$_3$]	104.8 [t, J = 16.4, CHD], 34.9 [CMe_3]
Zr(Np-d)$_2$Cl$_2$	2.25 [br t, 2H, CHD], 1.07 [s, 18H, CMe$_3$]	114.0 [t, J = 16.6, CHD], 34.2 [CMe_3]
Zr(Np-d)Cl$_3$	2.6 [br s, 1H, CHD], 1.10 [s, 9H, CMe$_3$]	sample insufficiently soluble
Me$_3$CCHDOH	3.27 [t, J = 1.56, 1H, CHD], 1.55 [s, 1H, OH], 0.92 [s, 9H, CMe$_3$]	
Me$_3$CCHDOTs	7.78 [d, J = 8.2, 2H, CH], 7.34 [d, J = 8.2, 2H, CH], 3.64 [t, J = 1.22, 1H, CHD], 2.25 [s, 3H, Me], 0.90 [s, 9H, CMe$_3$]	130.4 [CH], 128.5 [CH], 79.8 [t, J = 22.3, CHD], 32.2 [CMe$_3$], 26.6 [CMe$_3$], 22.3 [Me]
Me$_3$CCHDCl	3.32 [t, J = 1.60, CHD], 1.00 [s, 9H, CMe$_3$]	

[a] All data were recorded in CDCl$_3$ at 20 °C, at 250 MHz (^{1}H), or 62.5 MHz (^{13}C). Chemical shifts are in parts per million, coupling constants in hertz. The quaternary ^{13}C resonance was not observed for all compounds.

impurity which is difficult to remove (as noted by Weiss and Snyder [17]), and HMPA is a hazardous solvent.

Some examples of the partially alkylated species, $TiNp_xCl_{4-x}$ and $ZrNp_xCl_{4-x}$ have been previously prepared by differing means, including: (i) the reaction of $TiCl_4$ or $ZrCl_4$ with 1, 2, or 3 equiv. of neopentyl lithium, neopentyl magnesium chloride or dineopentyl zinc; (ii) the stoichiometric reaction of MNp_4 with HCl; (iii) the comproportionation reaction between MNp_4 and the metal tetrachlorides. The first two reactions do not provide a general synthetic route applicable to all of these complexes. The comproportionation reaction between the homoleptic neopentyls, MNp_4, and the metal tetrachlorides provides the most satisfactory route to the mixed neopentyl chloro complexes, and with suitable control of reaction stoichiometry, according to Eqs. (1)–(3), pure samples of each of the partially alkylated species can be prepared, with the possible exception of $ZrNpCl_3$ (vide infra). Solution state ^1H and ^{13}C NMR data for these complexes are listed in Table 1.

$$3MNp_4 + MCl_4 \rightarrow 4MNp_3Cl \qquad (1)$$

$$MNp_4 + MCl_4 \rightarrow 2MNp_2Cl_2 \qquad (2)$$

$$MNp_4 + 3MCl_4 \rightarrow 4MNpCl_3 \qquad (3)$$

These comproportionation reactions were studied in situ by ^1H NMR spectroscopy, and each of the mixed neopentyl chloro complexes was characterised by ^1H and ^{13}C NMR spectroscopy. Monitoring the reactions of MNp_4 with MCl_4 has allowed us to determine the sequence of reaction steps by which the comproportionation reactions occur.

The room temperature reaction of $TiNp_4$ with 3 equiv. of $TiCl_4$ as a homogeneous solution in $CDCl_3$, monitored by ^1H NMR, reveals that the initial products of the reaction (5 min at 23 °C) are $TiNpCl_3$ and $TiNp_3Cl$ in a 1:1 molar ratio, with only a trace (< 5 mol%) of $TiNp_2Cl_2$, as determined by integration of the CH_2 resonances. The remainder of the sample is unreacted $TiNp_4$ and, NMR silent, $TiCl_4$. These observations are consistent with a simple mechanism for neopentyl exchange, namely the bimolecular exchange of one neopentyl and one chloride ligand, Eq. (4).

$$Np_4Ti + TiCl_4 \rightarrow TiNpCl_3 + TiNp_3Cl \qquad (4)$$
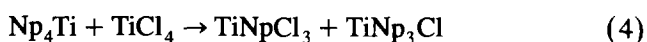
Subsequently the CH_2 resonances assigned to $TiNpCl_3$ and $TiNp_2Cl_2$ grow in intensity, and after 20 min at 23 °C the sample consists of pure (by NMR) $TiNpCl_3$. In the case of titanium, all the species are very soluble in $CDCl_3$ and the solution remains homogeneous throughout. As indicated above, other ratios of reactants allow the synthesis, after ca. 30 min at 23 °C of samples

containing essentially pure samples ($< 5\%$ of other species) of any of the titanium neopentyl chlorides. All the titanium neopentyl chloro complexes are highly soluble in chloroform-d, and presumably are either monomeric or dimeric in solution; the related $Ti(CH_2SiMe_3)Cl_3$ has been shown to be dimeric in the solid state, with two bridging chloride ligands [10].

For the titanium complexes the order of thermal stability is found to be $TiNp_4 > TiNpCl_3 > TiNp_3Cl > TiNp_2Cl_2$. Samples are stable in the absence of light at low temperatures (-20 °C), but were maintained at -196 °C for long term storage. The only product of the thermal decomposition reactions which can be identified by ^1H NMR is neopentane, the dark insoluble metal-containing products have not been identified.

In the case of zirconium, qualitative studies of the kinetics of the comproportionation reactions are complicated by the insolubility, in benzene-d_6 and chloroform-d, of polymeric $ZrCl_4$, and the sparing solubility of $ZrNpCl_3$, which compound we presume has an extended chloride-bridged structure. The remaining zirconium species, $ZrNp_2Cl_2$ and $ZrNp_3Cl$, as well as $ZrNp_4$, are soluble in both chloroform and benzene, although the solid-state structure of $ZrNp_3Cl$ consists of a Zr–Cl–Zr–Cl linear polymer. When 3 equiv. of $ZrNp_4$ is reacted with 1 equiv. of $ZrCl_4$ in $CDCl_3$ the ^1H NMR spectrum after 30 min at 20 °C shows approximately equimolar $ZrNp_4$ and $ZrNp_3Cl$. The spectrum does not show signals assigned to either $ZrNp_2Cl_2$ or the sparingly soluble $ZrNpCl_3$; the sample does, however, contain unreacted $ZrCl_4$. After 120 min at 20 °C the sample consists of pure $ZrNp_3Cl$. These observations are consistent with a mechanism where the rate determining step is attack of $ZrNp_4$ on solid $ZrCl_4$ to give soluble species ($ZrNpCl_3$, $ZrNp_2Cl_2$ and $ZrNp_3Cl$) which then react rapidly with the excess $ZrNp_4$ in solution giving $ZrNp_3Cl$. At this reaction stoichiometry, the concentration of $ZrNpCl_3$ and $ZrNp_2Cl_2$ is always too low to observe by ^1H NMR. Attempts to study the intermediates produced by other reaction stoichiometries are frustrated by solubility difficulties, although we have successfully prepared solutions containing $ZrNp_2Cl_2$ and $ZrNpCl_3$ as the final products. The preparation of $ZrNpCl_3$ appears to require the use of an excess of $ZrCl_4$ (i.e. more than 3 equiv.), and the final products of the reactions always include solid material consisting of excess $ZrCl_4$ and undissolved $ZrNpCl_3$.

The zirconium neopentyl complexes do not show any significant light-sensitivity, and are moderately thermally stable. Solutions of $ZrNp_2Cl_2$ or $ZrNp_3Cl$ in benzene-d_6 begin to darken after standing at room temperature for 1 h, and NMR spectra show the formation of traces of neopentane (2,2-dimethylpropane). Both compounds are stable for many weeks at -20 °C, but samples were stored at -196 °C, where they are stable indefinitely. The order of thermal stability of the zirco-

nium species is the same as that of their titanium analogues: $ZrNp_4 > ZrNpCl_3 > ZrNp_3Cl > ZrNp_2Cl_2$.

Studies of the NMR spectra (^1H, ^{13}C and $^{47,49}Ti$) of the complete series of methyl titanium complexes, together with carbon, silicon, tin and lead analogues, XMe_nCl_{4-x} (X = C, Si, Sn, Pb, Ti; n = 0–4), have demonstrated that the ^{13}C chemical shifts of the methyl titanium complexes are consistently to high frequency of the other compounds, e.g. 69 ppm for Me_4Ti, −9 to 31.4 ppm for the other Me_4X compounds [19]. The ^{13}C chemical shift of $ZrMe_4$, the only methyl zirconium complex studied, is δ 33.2 ppm. The unusual ^{13}C NMR shifts of the titanium complexes have been ascribed to the presence of low-lying empty d orbitals which overlap strongly with the π-component of the Ti–C bond, leading to a large paramagnetic contribution to the ^{13}C chemical shifts. The ^{13}C chemical shifts of the CH_2 resonances of the neopentyl titanium and zirconium complexes described in the current work show similar trends. In both the ^1H and ^{13}C NMR spectra the CH_2 resonance moves to higher frequency in the series $MNp_4 < MNp_3Cl < MNp_2Cl_2 < MNpCl_3$ for both titanium and zirconium. The chemical shifts of these CH_2 resonances are to higher frequency in all the titanium complexes than their zirconium analogues, and, given the additional alkyl group, all are to higher frequency than the analogous titanium methyl complex.

We have prepared mono-deuterated neopentyl [M–CH(D)CMe₃] analogues of the complexes described in this work, and screened them for the presence of agostic interactions. The resonances due to the CHD group appear as 1:1:1 triplets in both the ^1H and $^{13}C\{^1H\}$ NMR spectra due to coupling to the deuterium nucleus. The ^1H resonance usually appears as a broad triplet, and the geminal coupling constant $^2J_{H-D}$ has only been resolved in a few cases. Ground-state agostic interactions can be detected by a number of means [20], one of which is the presence of a large temperature-dependent isotope shift, or isotopic perturbation of resonance (IPR) between the ^1H NMR resonances of M–CH₂R and M–CHDR isotopomers. This experiment should be carried out using a solution containing isotopomerically pure complexes, e.g. of $Ti(CH_2CMe_3)_2Cl_2$ and $Ti(CHDCMe_3)_2Cl_2$; however, a solution containing both complexes would rapidly scramble the alkyl groups, yielding a statistical mixture of the two starting complexes and $Ti(CH_2CMe_3)(CHDCMe_3)Cl_2$. The ^1H NMR isotope shift which it is experimentally feasible to obtain is that between the CHD resonance [δ(CHD)] of the isotopically labelled compound and the residual CH_2 resonance [δ(CH₂)R] in samples of the isotopically labelled compound, both values being obtained from the same spectrum. The chemical shift data for the titanium and zirconium neopentyl chloro complexes show no large (> 0.1 ppm) temperature-dependent isotope shifts (IPR) which might be associated with pro-

tons in bridging (agostic) environments; instead, these compounds display small isotope shifts which are essentially temperature invariant. We conclude that these measurements provide no evidence in favour of structural distortion in these complexes. Whilst the observation of IPR is diagnostic of a structural distortion, the absence of IPR is not proof of the absence of structural distortion.

In conclusion, we have demonstrated that all the neopentyl chloro complexes of titanium and zirconium are accessible, the few thermally-stable examples have been previously reported. Spectroscopic measurements do not provide conclusive evidence for agostic interactions in these complexes in solution. Future studies will develop the coordination chemistry of these complexes, isolating ligand adducts, such as $TiNpCl_3(tmeda)$, and structurally characterising $ZrNp_2Cl_2$.

3. Experimental

Air- and moisture-sensitive compounds were manipulated under a nitrogen atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Varian VXR-200 (^1H), Bruker AC-250 (^1H and ^{13}C) and Varian VXR-400 (^{13}C and variable-temperature ^1H) spectrometers. Spectra used to determine isotope shifts and $^2J_{H-D}$ geminal coupling constants were recorded with digitisation better than 0.3 Hz per point, where possible. Solvents were pre-dried over molecular sieves and distilled from appropriate drying agents, $CDCl_3$ was vacuum distilled from P_2O_5. Me_3CCH_2OH and $ZrCl_4$ were purchased from Aldrich and used as-received. $Me_3CCHDOH$ was prepared from $Me_3CC(O)H$ (Aldrich) by reduction with $LiAlD_4$ [21], which was prepared by the reaction between LiD (Aldrich, 98 + at.% D) and $AlCl_3$ in diethyl ether. $Me_3CCHDOTs$ (Ts = p-toluenesulfonyl) was prepared from the alcohol according to a literature procedure [18]. All the titanium complexes described are light sensitive and were prepared and handled in vessels wrapped with aluminium foil under subdued lighting.

3.1. Preparation of $Me_3CCHDCl$

A solution of $Me_3CCHDOTs$ (15.3 g, 63 mmol) and dried LiCl (2.9 g, 68 mmol, 1.08 × theory) in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 30 ml) was stirred in a sealed Young's ampoule at 90 °C for 48 h. The volatiles were removed under reduced pressure (23 °C, 0.01 mmHg) and identified as pure $Me_3CCHDCl$, by comparison of its NMR spectrum with that reported [18]. Yield, 6.5 g, 96%. Isotopic purity (estimated by ^1H NMR) > 95 at.% D.

3.2. Preparation of Me$_3$CCHDMgCl [1]

A suspension of activated magnesium turnings (3 g, 125 mmol, stirred under N$_2$ for 2 days) in refluxing diethyl ether (80 ml) was treated dropwise (addition taking 3 h) with a solution of Me$_3$CCHDCl (6.5 g, 60.5 mmol) and BrCH$_2$CH$_2$Br (1.0 ml, 11.6 mmol) in diethyl ether (20 ml). The mixture was refluxed for 15 h to give a yellow solution. The solution was cooled to room temperature, filtered and the residue was washed with diethyl ether (20 ml). Aliquots (1 ml) of the resulting solution were titrated against a standardised toluene solution of propanol using 1,10-phenanthroline as indicator. Yield 120 ml of 0.4 M solution, 48 mmol, 79.3%.

3.3. Preparation of (Me$_3$CCH$_2$)$_4$Zr and (Me$_3$CCHD)$_4$Zr

These two isotopomers were prepared according to the same method. A suspension of ZrCl$_4$ (0.466 g, 2 mmol) in hexane (20 ml) was cooled to 0 °C and treated dropwise over 15 min with a diethyl ether solution of Me$_3$CCH$_2$MgCl or Me$_3$CCHDMgCl (6 mmol). The mixture was stirred at 20 °C for 18 h giving a cloudy brown solution. The solution was filtered and the volatiles removed under reduced pressure leaving a pale-brown solid which was sublimed (50 °C, 0.01 mmHg) to give colourless crystals. Yield, 0.39 g, 69% based on NpMgCl.

3.4. Preparation of (Me$_3$CCH$_2$)$_4$Ti and (Me$_3$CCHD)$_4$Ti

These two isotopomers were prepared according to the same method. Neat TiCl$_4$ (0.22 ml, 2 mmol) was added to diethyl ether at − 78 °C precipitating the etherate, TiCl$_4$(Et$_2$O)$_2$, and this suspension was treated dropwise over 20 min with a diethyl ether solution of Me$_3$CCH$_2$MgCl or Me$_3$CCHDMgCl (8 mmol). During the addition the solution developed a very dark colour. The mixture was stirred in the dark at 20 °C for 4 h. The solution was filtered and the volatiles removed under reduced pressure leaving a black oil. Sublimation under reduced pressure (40 °C, ca. 0.01 mmHg) gave pale yellow crystals. Yield, 0.13 g, 20% based on TiCl$_4$. The product decomposes slowly at room temperature and on exposure to light; it was thus stored in the dark at − 20 °C, where it is stable for a few days.

3.5. Reaction of TiNp$_4$ with TiCl$_4$, preparation of TiNp$_3$Cl, TiNp$_2$Cl and TiNpCl$_3$

A 5 mm NMR tube was loaded in the glovebox with TiNp$_4$ (30 mg, 90 μmol) and attached to the Schlenk

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line. The tube was cooled to − 196 °C and CDCl$_3$ (0.2–0.3 ml) transferred under vacuum. The solution was warmed to room temperature giving a yellow solution which was cooled to − 78 °C and treated dropwise with a solution of TiCl$_4$ (270 μmol) in CDCl$_3$. The solution was frozen at − 196 °C and the NMR tube was flame-sealed under vacuum. The NMR tube was warmed to room temperature, the solution rapidly turned orange. The reaction was monitored by ^{1}H NMR, which showed initial formation of a mixture of species (see text for details), and after 2 h at 20 °C in the dark the solution consisted of only TiNpCl$_3$. When the reaction was complete, the product was stored in the dark at − 196 °C.

The same procedure, using differing proportions of TiNp$_4$ and TiCl$_4$, was used to prepare TiNp$_3$Cl and TiNp$_2$Cl$_2$.

3.6. Reaction of ZrNp$_4$ with ZrCl$_4$, preparation of ZrNp$_3$Cl, ZrNp$_2$Cl$_2$ and ZrNpCl$_3$

A 5 mm NMR tube was loaded in the glovebox with a mixture of the solids, ZrNp$_4$ (0.05 g, 133 μmol) and ZrCl$_4$ (0.010 g, 44 μmol). The NMR tube was attached to the vacuum line, cooled to − 196 °C, and CDCl$_3$ was transferred by vacuum distillation. The tube was sealed under vacuum and allowed to slowly warm to room temperature forming a yellow solution. The reaction was monitored by ^{1}H NMR, and after 3 h at 20 °C the solution consisted of > 95% ZrNp$_3$Cl. The sample was stored at − 196 °C and slowly darkened over a week.

The same procedure was used to prepare a sample of ZrNp$_2$Cl$_2$. The preparation of the sparingly soluble ZrNpCl$_3$ requires the reaction of ZrNp$_4$ with 4.5 equiv. of ZrCl$_4$.

References

[1] J.A. Martinho Simoes, J.L. Beauchamp, Chem. Rev. 90 (1990) 629.
[2] G.J. Erskine, D.A. Wilson, J.D. McCowan, J. Organomet. Chem. 114 (1976) 119. G.J. Erskine, J. Hartgerink, E.L. Weinberg, J.D. McCowan, J. Organomet. Chem. 170 (1979) 51.
[3] M. Bottrill, P.D. Gavens, J.W. Kelland, J. McMeeking, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982, Chapter 22.4. M. Bochmann, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II

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[1] This preparation is based on those found in the literature for Me$_3$CCD$_2$MgBr [22] and (Me$_3$CCD$_2$)$_2$Mg [23].

—A Review of the Literature 1982–1994, vol. 4, Elsevier, Oxford, 1995, Chapter 5, pp. 280–288.

[4] M.T. Reetz, Titanium in organic synthesis, in: M. Schlosser (Ed.), Organometallics in Synthesis–A Manual, Wiley, Chichester, 1994.

[5] P.J. Davidson, M.F. Lappert, R. Pearce, J. Organomet. Chem. 57 (1973) 269.

[6] W. Mowat, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1973) 1120.

[7] J.H. Wengrovius, R.H. Schrock, J. Organomet. Chem. 205 (1981) 310.

[8] L.K. Hoyt, J.L. Pollitte, Z. Xue, Inorg. Chem. 33 (1994) 2497.

[9] I.Sh. Guzman, O.I. Adrov, G.N. Bondarenko, E.I. Tinyakova, B.A. Dologoplosk, Organomet. Chem. USSR 3 (1990) 694.

[10] M.Yu. Antipin, Yu.T. Struchkov, I.Sh. Guzman, O.I. Adrov, Organomet. Chem. USSR 3 (1990) 697.

[11] H. De Vries, Recl. Trav. Chim. 80 (1961) 866.

[12] M.L.H. Green, A.K. Hughes, J. Chem. Soc. Chem. Commun. (1991) 1231.

[13] P. Briant, J. Green, A. Haaland, H. Møllendal, K. Rypdal, J. Tremmel, J. Am. Chem. Soc. 111 (1988) 3434.

[14] M.Yu. Antipin, S.I. Troyanov, Yu.T. Struchkov, L.S. Bresler, Metalloorg. Khim. (Organometallic Chem. USSR) 1 (1988) 111.

[15] Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa, K. Prout, A.J. Schultz, J.M. Williams, T.F. Koetzle, J. Chem. Soc. Dalton Trans. (1986) 1629.

[16] O. Eisenstein, Y. Jean, J. Am. Chem. Soc. 107 (1985) 1177.

[17] R.G. Weiss, E.I. Snyder, J. Org. Chem. 36 (1971) 403.

[18] B. Stephenson, G. Solladie, H.S. Mosher, J. Am. Chem. Soc. 94 (1972) 4184.

[19] S. Berger, W. Bock, G. Frenking, V. Jonas, F. Müller, J. Am. Chem. Soc. 117 (1995) 3820.

[20] M. Brookhart, M.L.H. Green, L.-L. Wong, Prog. Inorg. Chem. 36 (1988) 1.

[21] R.R. Schrock, J.D. Fellmann, J. Am. Chem. Soc. 100 (1978) 3359.

[22] K.G. Caulton, M.H. Chisholm, W.E. Streib, Z. Xue, J. Am. Chem. Soc. 113 (1991) 6082.

[23] P. Legzdins, S.J. Rettig, J.E. Veltheer, R.J. Batchelor, F.W.B. Einstein, Organometallics 12 (1993) 3575.