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From zirconium to titanium: the effect of the metal in *t*-butylacrylate photoinitiated polymerisation

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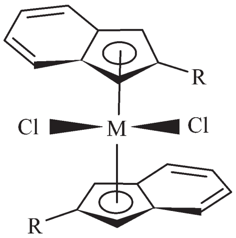
We report here the synthesis, photochemistry and photoinitiator activity of some titanocenes (**1**–**4**) and compare the results with those obtained for the corresponding zirconocenes (**5**–**8**). Analysis of the electronic spectra showed that the energy modulation of the lowest electronic transition, which appears to be LMCT in character, is driven both by the substituent on the cyclopentadienyl moiety and by the metal centre. Furthermore, the excited state resulting from irradiation of the complexes at the wavelength of the LMCT transition undergoes ligand-metal bond dissociation with formation of a radical pair, as evidenced by EPR spectroscopy coupled with spin trapping techniques. All the complexes were very active, compared with known organometallic photoinitiators, for the free-radical photopolymerisation of *t*-butylacrylate. The titanium complexes **1**–**4**, which can be used with visible light, were more active than the zirconium derivatives **5**–**8**. The better yields in photopolymerisation can be interpreted on the basis of the combined effect of two factors: (i) the photoreactivity of the complexes in solution and (ii) the high persistence of the Ti(III) radical species in solution, which guarantees high concentrations of initiators in the polymerisation process.

Introduction

Photochemical or photoinitiated polymerisations play a central role in several commercial technologies[1,2] and are largely employed today in the areas of surface coatings, photoresists, adhesives and holography. In the growing area of photoinitiators for use in pigmented coatings, compounds[3] showing absorption peaks at wavelengths higher than 350 nm are in particular required, since they can be used with the visible light produced by continuous wave lasers. Furthermore, since light can generate electronic excited states different from those achieved by thermal activation, it can be used as a clean, tunable and versatile "tool" to selectively activate a photoinitiator in the presence of organic solvents and chemical contaminants. While organic compounds still play a leading role among photoinitiators,[2,4] several classes of inorganic and organometallic complexes[5] are receiving increasing attention due to the possibility to tailor the polymer microstructure by a systematic and rational variation of their ligand structure and substitution pattern. The versatility of the chemistry of the cyclopentadienyl ligand makes the metallocene family particularly interesting from this point of view. Moreover, these complexes often leave low toxic and clear (or colourless) residues after exposure to argon lasers.

In the framework of our search for metallocenes suitable for use as photoinitiators in radical polymerisation processes, we have recently[6,7] started a systematic study of the photochemical behaviour and of the photopolymerisation activity of several mono- and bicyclic cyclopentadienyl group IV complexes. In particular, we have found that bicyclic cyclopentadienyl zirconium complexes containing saturated rings fused to the cyclopentadienyl unit gave better polymerisation yields and were more stable in solution compared with the corresponding unsaturated complexes.[6] With the substitution of the hydrogen by a phenyl in position 2 of the cyclopentadienyl ring[7] we achieved a significant increase in the absorption coefficients. In this way the light absorption efficiency was improved and, consequently, the polymerisation yields were almost doubled, probably due to a combined effect of a higher persistence of the radical in solution and/or an increased efficiency of the radical in initiating the polymerisation process. This kind of substitution, unfortunately, failed to shift the absorption maxima towards higher wavelengths in the visible area. As a further step we decided to synthesise, study and test analogous titanium complexes, since the metallocenes of this metal usually absorb in the visible region.

In this work, several titanium complexes were synthesised and studied: bis(η^5-indenyl)titanium dichloride [Ind_2TiCl_2] (**1**), bis[η^5-(4,5,6,7-tetrahydro-1*H*-indenyl)]titanium dichloride [$(C_6Cp)_2TiCl_2$] (**2**), bis[η^5-(2-phenylindenyl)]titanium dichloride [$(IndPh)_2TiCl_2$] (**3**) and bis[η^5-(2-phenyl-4,5,6,7-tetrahydro-1*H*-indenyl)titanium dichloride [$(C_6CpPh)_2TiCl_2$] (**4**). Their properties and activities were compared with those obtained using the corresponding zirconium metallocenes: bis(η^5-indenyl)zirconium dichloride [Ind_2ZrCl_2] (**5**), bis[η^5-(4,5,6,7-tetrahydro-1*H*-indenyl)zirconium dichloride [$(C_6Cp)_2ZrCl_2$] (**6**), bis[η^5-(2-phenylindenyl)]zirconium dichloride [$(IndPh)_2ZrCl_2$] (**7**) and bis[η^5-(2-phenyl-4,5,6,7-tetrahydro-1*H*-indenyl)]zirconium dichloride [$(C_6CpPh)_2ZrCl_2$] (**8**).



M = Ti
R = H, [Ind_2TiCl_2, **1**]
Ph, [$(IndPh)_2TiCl_2$, **3**]
M = Zr
R = H, [Ind_2ZrCl_2, **5**]
Ph, [$(IndPh)_2ZrCl_2$, **7**]

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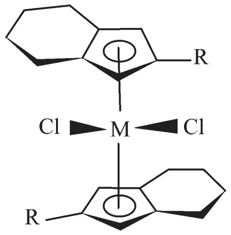
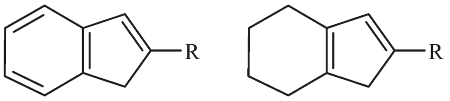


M = Ti
R = H, [$(C_6Cp)_2TiCl_2$, **2**]
Ph, [$(C_6CpPh)_2TiCl_2$, **4**]
M = Zr
R = H, [$(C_6Cp)_2ZrCl_2$, **6**]
Ph, [$(C_6CpPh)_2ZrCl_2$, **8**]

Results and discussion

Synthesis of complexes 1–4

The starting materials necessary for the synthesis of the ligands were the commercially available indene, **9**, and the dienes, **10**,[8] **11**,[9] and **12**,[7] prepared according to previously published procedures. The synthetic approach to the Ti complexes is similar for all complexes and it is described in the Experimental.



R = H (**9**), Ph (**11**)   R = H (**10**), Ph (**12**)

We have found that the synthesis by direct reaction of the lithium salts (a method that works well for the corresponding zirconium derivatives) of the dienes **9**–**12** with $TiCl_4$ in THF (or with $TiCl_3$, followed by oxidation with $PbCl_2$) gave poor yields of complexes extremely difficult to purify. This problem is due to the fact that the Ti complexes **1**–**4** are easily reduced, either by visible light in solution (in particular in THF) or by traces of alkyllithiums from the previous deprotonation step acting as reducing agents. This problem was overcome by converting the lithium salts into their corresponding air-stable trimethylsilyl derivatives and by carrying out the subsequent metallation reaction in CH_2Cl_2, taking care to protect the reaction vessel from light. The complexes were collected by elimination under vacuum of the solvent and of the $ClSiMe_3$ produced in the reaction and washing with petroleum ether. This two-step procedure gave higher yields of easy-to-purify complexes.

Photochemistry

UV/Vis spectra of the titanium complexes **1**–**4** have been recorded in benzene and compared with those obtained previously[7] for the zirconium complexes **5**–**8** (Table 1). As expected, we found the position of the absorption maxima to be remarkably shifted towards longer wavelengths (>400 nm). This feature fulfils the desired condition of requiring lower energies for the photochemical activation and it is in agreement with the fact that the energy of the lowest transition depends strongly on the nature of the metal, an effect that is particularly enhanced with titanium.[10]

Since the free ligand shows absorption bands at higher energies ($\lambda < 330$ nm), the observed shift supports the hypothesis of a prevalent ligand-to-metal charge transfer (LMCT) character for the electronic transition. Both the λ_{max} and the ε_{max} values (Table 1) strongly support the LMCT assignment and are in agreement with the most recent findings on the excitation states for similar metallocenes of group IV.[10,11] Then, the primary photochemical act should consist in the homolytic cleavage of the ligand-metal bond with formation of ligand- and metal-centred radicals upon electronic excitation.

Table 1 Spectroscopic properties of complexes **1**–**8** in benzene

Complex		λ_{max}/nm	ε_{max}/M^{-1} cm^{-1}
1	$(Ind)_2TiCl_2$	397	3240
		519	1820
2	$(C_6Cp)_2TiCl_2$	415	1700
		543	160
3	$(IndPh)_2TiCl_2$[a]	397	550
		503	1225
4	$(C_6CpPh)_2TiCl_2$	394	3275
		479	3400
5	$(Ind)_2ZrCl_2$	310	1475
		380	720
6	$(C_6Cp)_2ZrCl_2$	310	1600
		350	1100
7	$(IndPh)_2ZrCl_2$	310	60 500
		330	41 000
8	$(C_6CpPh)_2ZrCl_2$	320	23 400
		345	–

[a] In CH_2Cl_2 as **3** is not completely soluble in benzene.

The study of the photoreactivity in solution of the complexes **1**–**4** was performed by photolysis in benzene at $\lambda > 350$ nm. The nature of the complexes has a significant influence on their photoreactivity in solution: the change of metal, combined with the presence of the phenyl substituent, seems to accelerate the photoreactivity of the metallocenes. This effect is due to the fact that the orbitals are less stabilised with titanium than with zirconium because of a weaker metal-ligand interaction. Once irradiated, the titanium complexes decay more easily by nonradiative processes than the corresponding zirconium derivatives.[10] After 1 h irradiation the photodecomposition of the indenyl complexes **1** and **3** was almost complete, while only 20% of their tetrahydro counterparts, **2** and **4**, was degraded. In both cases the presence of the phenyl substituent increased the rate and the extent of the process.

An interesting feature common to the spectra of the titanium complexes **1**–**4** is the presence of an isobestic point at 570 nm and the concomitant growth upon irradiation of a new broad transition at around 635 nm, which can be attributed to a new Ti(III) species on the basis of the literature data (Fig. 1).[12]

EPR spin-trapping investigation

To study the nature of the species produced upon irradiation, EPR spin-trapping experiments have been carried out by direct irradiation of benzene solutions of the titanocenes inside the spectrometer cavity. The LMCT irradiation ($\lambda > 350$ nm) of

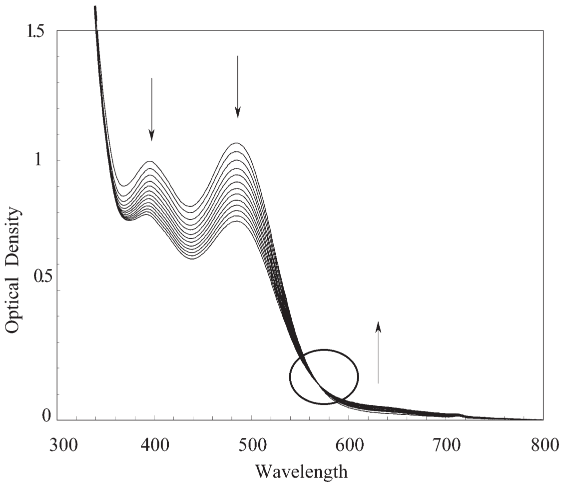


Fig. 1 $(C_6CpPh)_2TiCl_2$, **4**, irradiated in benzene ($\lambda > 350$ nm) at 20 °C under argon atmosphere. The spectra were recorded every 5 min.

complexes **1**–**4** in the presence of the spin trap *N-tert*-butyl-α-phenylnitrone (PBN) (metallocene:PBN molar ratio = 1:25) showed fairly intense EPR signals. We remarked two different patterns depending on the type of ligand (Table 2). In the case of the complexes **1** and **2** we observed only one signal, a triplet of doublets, stable during and after irradiation, that can be assigned to the spin adduct of the indenyl or tetrahydroindenyl radical with PBN (Scheme 1).[13,14] The a_N (14.5–14.6 G) and a_H (2.2–2.3 G) values are in good agreement with those observed during the photolysis of the corresponding zirconium metallocenes **5** and **6**.[7]

In the case of the spectra of the titanium complexes **3** and **4** (Fig. 2), besides the signals consistent with the presence of a radical on the cyclopentadienyl moiety,[13] we observed also the presence of another signal due to a species not trapped with PBN and characterised by a *g* value typical of a Ti(III) species (Table 2).[15] This result supports the attribution of the new absorption at 635 nm in the UV/Vis spectrum to a Ti(III) compound. In titanocenes **3** and **4**, the phenyl substituent on the cyclopentadienyl unit seems to provide an additional stabilisation that allows direct observation of the metal-centred radical, which was hardly visible in the spectra of the zirconium analogues and only at low temperature.[16]

We can conclude that the electronic spectral changes that occur during the irradiation of benzene solutions of the titanium complexes and the EPR findings are in agreement with the literature data reported for similar titanium complexes[17] and indicate that the first step in the photoprocess is the dissociation of the LMCT state to give ligand and metal-centred radicals (Scheme 2).

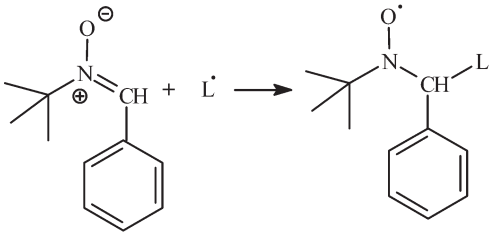
Polymerisation studies

Polymerisation tests were performed in benzene on *t*-butylacrylate (*t*-BA) and the results obtained have been compared with those obtained with the analogous zirconium derivatives (Table 3). Since this monomer is the least reactive in the acrylate series, a positive result obtained in *t*-BA polymerisation can be considered as proof of the high efficiency of a metallo-organic complex as a radical initiator. Since this monomer absorbs only at $\lambda < 300$ nm, we can exclude the possibility that the polymer obtained can be produced, in part or completely, from direct photochemical activation of the monomer.

In a typical experiment, a vigorously stirred 20% v/v solution of *t*-butylacrylate in benzene was irradiated at 20 °C for 1 h in the presence of 7 mg of the metallocene at $\lambda > 320$ nm for the zirconium complexes **5**–**8** and at $\lambda > 350$ nm for the titanium complexes **1**–**4**. In the absence of the catalysts, the irradiation in the same conditions of a reference solution of *t*-BA in benzene did not produce any polymeric material.

Table 2 Hyperfine coupling constants of the radical spin adducts with PBN in benzene (metallocene:PBN molar ratio = 1:25).

		Species I			Species II	
Complex		a_N/G	a_H/G	%	%	*g*
1	$(Ind)_2TiCl_2$	14.6	2.2	100	–	–
2	$(C_6Cp)_2TiCl_2$	14.5	2.2	100	–	–
3	$(IndPh)_2TiCl_2$	14.6	2.3	71	29	2.0113
4	$(C_6CpPh)_2TiCl_2$	14.6	2.3	63	37	2.0117



Scheme 1 Mechanism of action of PBN.

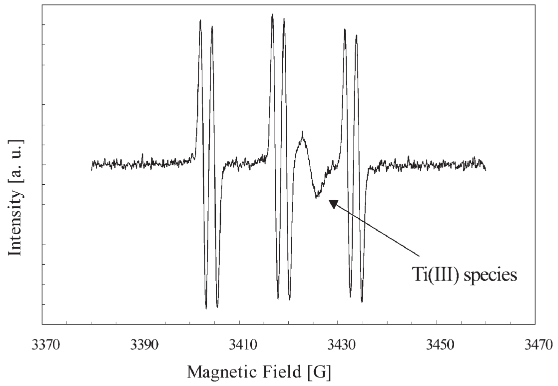
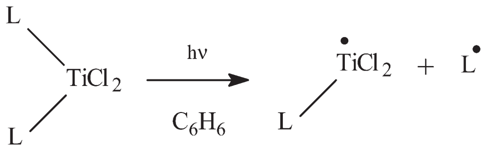


Fig. 2 $(IndPh)_2TiCl_2 + 0.1$ M PBN irradiated in benzene ($\lambda > 350$ nm).



Scheme 2 Primary photochemical act.

The polymer yields obtained with the titanium complexes **1**–**4** were all higher than those obtained with the corresponding zirconium metallocenes, **5**–**8**, and followed the same trend: the indenyl complexes, **1** and **3**, exhibited an increase of about the 15%, while the tetrahydroindenyl derivatives **2** and **4** showed an average increase of 21%. Also in this case the titanium complexes bearing a phenyl substituent on the cyclopentadienyl ring (**3** and **4**) gave polymerisation yields twice as high as those obtained with the unsubstituted complexes (**1** and **2**). This increase in the polymerisation outcome suggests the involvement of a Ti(III) radical species in the polymerisation process in addition to the species already detected with the zirconium complexes.

The tacticity of the polymer formed was estimated by deconvolution of the methine peaks of poly(*t*-BA) at about 42 ppm in the ^{13}C-NMR spectra. As we could expect, the stereochemical outcome of the polymerisation reaction was quite independent of the metallocene used and the data were quite similar to those reported for the zirconium complexes, with a content of

Table 3 *tert*-Butylacrylate polymerisation[a] data

Complex		Yield[b]	M_w[c] /g mol^{-1}	PDI[d]	η[e] /dL g^{-1}
1	$(Ind)_2TiCl_2$	30	1825 482	3.0	3.95
2	$(C_6Cp)_2TiCl_2$	31	787 203	4.5	1.02
3	$(IndPh)_2TiCl_2$	65	2077 649	2.8	4.33
4	$(C_6CpPh)_2TiCl_2$	58	889 753	3.4	1.43
5	$(Ind)_2ZrCl_2$	25	1299 118	2.5	2.36
6	$(C_6Cp)_2ZrCl_2$	24	395 451	2.3	0.92
7	$(IndPh)_2ZrCl_2$	56	1316 731	2.3	2.94
8	$(C_6CpPh)_2ZrCl_2$	46	425 691	2.3	1.01

[a] Polymerisation conditions: a vigorously stirred 20% v/v monomer solution in benzene in a 4 ml cuvette was irradiated for 1 h in the presence of 7 mg of the metallocene. [b] Polymerisation degree = (weight of polymer obtained/weight of starting monomer) × 100. [c] Average molecular weight by GPC based on polystyrene standards. [d] Polydispersity index = M_w/M_n [e] Intrinsic viscosity measured in $CHCl_3$ at 35 °C.

syndiotactic triads, [rr], ranging from 30% to 35% and of isotactic triads, [mm], ranging from 5% to 10%. This result is consistent with the radical nature of the process.

The polymers obtained have been also characterised by gel permeation chromatography (GPC) and viscosity measurements (Table 3).

The polymer analysis showed that we can obtain quite a wide range of high molecular weight *tert*-butylacrylates through small changes in the structure of the photoinitiator. If we try to draw a correlation between the structure of the complexes and the polymerisation data, we can remark that:

(i) the indenyl complexes **1**, **3**, **5** and **7** gave polymers with average molecular weights (M_w) and intrinsic viscosities (η) higher than those prepared with the tetrahydroindenyl complexes **2**, **4**, **6** and **8**, and the titanocenes always gave higher values than the corresponding zirconocenes in both series.

(ii) The phenyl-substituted complexes **3**, **4**, **7** and **8** always gave higher polymerisation yields than the related unsubstituted compounds **1**, **2**, **5** and **6** and the indenyl derivatives also gave polymers with higher M_w.

(iii) The complexes **2**, **4**, **6** and **8**, which decompose more slowly in solution under irradiation than the corresponding unsaturated analogues **1**, **3**, **5** and **7**, gave polymers with lower M_w. Since the polymerisation yields were quite similar when compared pairwise, this fact suggests the hypothesis that, in the presence of more long-lived radical species, it is easier to build a new polymer chain than to add a monomer to an already existing one.

(iv) The Ti complexes **1–4** produced polymers with polydispersities higher than those obtained with the Zr derivatives **5–8** and the highest values were obtained with the most photochemically stable complexes in solution. The zirconium complexes did not show significant differences in this regard. Interestingly, the polydispersity index (PDI) is in all cases much higher than that expected for a typical radical reaction (usually around 2). The broader polydispersity can be attributed to the fact that more than one initiator is produced upon irradiation. This hypothesis is confirmed by the fact that in the case of titanium complexes **1–4** we always obtain PDI values higher than with the corresponding zirconium derivatives **5–8**, a fact that is consistent with the UV/Vis and EPR findings (*vide supra*).

Conclusions

We have reported here the synthesis, photochemistry and photoinitiator activity for the polymerisation of acrylates of a series of titanocenes (**1–4**) and we have compared the results with those obtained with the corresponding zirconocenes (**5–8**). The analysis of the electronic spectra showed that the change of metal shifts (as expected) the absorption maxima of the complexes into the visible region of the spectrum, thus expanding the wavelengths available for the photoinitiation process.

The radical species involved in the photoinduced cleavage of the metal-ligand bond have been identified and *t*-butylacrylate polymerisation has been studied in detail. All the complexes are highly active compared with similar photoinitiators[18] in the polymerisation of *t*-BA. The better yields in photopolymerisation can be interpreted on the basis of the combined effect of two factors: (i) the photoreactivity of the complexes in solution and (ii) the higher persistence of the Ti(III) radical species in solution (with respect to the corresponding zirconium analogues) that guarantees higher concentrations of initiators in the polymerisation process.

As to the future, in order to determine which structural modifications in the catalysts are necessary to improve their performance in the photoinitiated polymerisation of acrylates, a deeper understanding of the details of the polymerisation mechanism is needed.

Experimental

General remarks

All manipulations of air- and/or moisture-sensitive compounds were carried out under inert atmosphere using a dual vacuum/argon line and standard Schlenk techniques. All solvents were thoroughly dehydrated and deoxygenated under argon before use. They were dried and purified by refluxing under argon over a suitable drying agent (petroleum ether, diethyl ether, benzene, toluene and THF over Na/benzophenone ketyl or potassium; C_6D_6 over K; CH_2Cl_2 and $CDCl_3$ over CaH_2) followed by distillation and storage under argon in Young's ampoules. Solvents and solutions were transferred, using a positive pressure of argon, through stainless-steel cannulae (diameter 0.5–2.0 mm) and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass-fibre filter disks (Whatman GFC). Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich and Fluka) and used without further purification. Indene, **9**, was purchased from Fluka and distilled under reduced pressure before use; the dienes **10**,[8] **11**,[9] and **12**,[7] were prepared as described in the literature.

Elemental analyses were performed using a Carlo Erba 1106 Elemental Analysis apparatus. ^1H (200.13 MHz) and ^{13}C (50.32 MHz) nuclear magnetic resonance spectra were recorded at room temperature with a Bruker AC200 spectrometer.

Measurements

EPR studies. The spin trap PBN was purchased from Sigma-Aldrich Chemical Co. and used without further purification. The EPR and spin trapping experiments were performed on a Bruker EMX spectrometer, operating in the X band (microwave frequency = 9.74 GHz, microwave power = 20 mW, magnetic field modulation frequency = 100 KHz, magnetic field modulation amplitude = 1 G). Sample solutions were freeze-pump-thaw degassed and then irradiated with a 350 W medium pressure Hg lamp directly in the EPR spectrometer cavity (Bruker ER-4104OR, TE102). Hyperfine coupling constants have been calculated by best fit simulation of experimental spectra using NIEHS WinSim software.[19]

Photochemical experiments. Irradiation was performed using an Oriel 500 W high pressure Hg lamp equipped with cut-off filters for wavelength selection and a water filter to exclude thermal processes. The experiments were carried at 20 °C under argon atmosphere in a 4 ml cuvette equipped with a Young stopper. UV/Vis spectra were recorded on a Perkin Elmer Lambda 40 double beam spectrophotometer.

Polymerisation tests. *t*-Butylacrylate was dried with CaH_2 and vacuum distilled immediately before sample preparation.

In a typical experiment a vigorously stirred 20% v/v monomer solution in benzene in a 4 ml cuvette was irradiated at 20 °C for 1 h ($\lambda > 320$ nm for the zirconium complexes **5–8** and $\lambda > 350$ nm for the titanium complexes **1–4**) in the presence of 7 mg of the metallocene. The reaction was quenched by addition of a small amount of aqueous hydrochloric acid and the polymer was precipitated by pouring a solution of CH_3OH–HCl (1:1) into the reaction cuvette. The polymer was collected by removal of the solvent under reduced pressure, redissolved in acetone, air dried and collected as a thin film.

GPC measurements. The molecular mass distribution (MMD) was measured using a Waters GPCV 2000 high temperature GPC, equipped with a refractive index (RI) detector and a viscosity detector (differential viscometer). The column set was composed of three TSKGMHXL-HT columns.

Measurements were carried out in chloroform at 35 °C at a flow rate of 0.8 mL min^{-1}. Universal calibration with 18 PS narrow standards ranging from 162 to 5.5×10^6 g mol^{-1} was applied. Sample concentration was about 2 mg mL^{-1}, injection volume 218 mL.

Synthesis of the Ti complexes: general procedure

The dienes (10 mmol) were dissolved in 30 mL petroleum ether (**9**, **10** and **12**) or diethyl ether (**11**) and cooled to -10 °C; *n*-butyllithium (13 mmol) was added dropwise and the solution was allowed to reach room temperature and stirred overnight. The lithium salts of **9**, **10** and **12** separated from the solution as dusty solids, which were filtered *via* a cannula, washed twice with petroleum ether, then the residual solvent was pumped off. In the case of the diene **11** a dark solution was obtained. The solvent was removed under reduced pressure and the dark solid obtained was washed twice with petroleum ether to remove excess *n*-butyllithium, then the residual solvent was pumped off.

The lithium salts were dissolved in 30 mL anhydrous THF and ClSiMe$_3$ (30 mmol) diluted in 10 mL of THF was added dropwise. The resulting cloudy solution was stirred 6 h at room temperature, then cooled to 0 °C; a saturated solution of NH$_4$Cl was slowly added until separation of two phases occurred. After separation, the aqueous solution was washed three times with diethyl ether. The collected organic fractions were dried over anhydrous magnesium sulfate, filtered and the solvent was removed with a rotary evaporator.

The trimethylsilyl derivatives were transferred into a Schlenk flask, degassed, protected from light and dissolved in about 30 mL of CH$_2$Cl$_2$; a solution of TiCl$_4$ (4.8 mmol) in 5 mL CH$_2$Cl$_2$ was added dropwise. The reaction mixture was stirred overnight. The solvent was then removed under vacuum, the residue washed with petroleum ether, filtered, and dried under reduced pressure to give a dusty solid.

Although the first synthesis of complexes **1** and **2** has been previously reported,[20] we report here the NMR characterisation, which was not reported in that paper. Furthermore, with our procedure the yields have been significantly improved.

Bis(η^5-indenyl)titanium dichloride (1). Purple volatile solid. Yield 70% (from indene; 4 steps; average yield per step: 88%). Anal. calcd for C$_{18}$H$_{14}$Cl$_2$Ti (349.08): C, 61.9; H, 4.0; Cl, 20.3; found C, 61.5; H, 4.2; Cl, 19.8. ^{1}H-NMR (CDCl$_3$): δ 7.10–7.18 (m, 2H, –C*H*–Cp), 7.22–7.30 (m, 4H, –C*H*–Cp), 7.42–7.65 (m, 4H, –Ar*H*), 7.63–7.88 (m, 4H, –Ar*H*).

Bis[η^5-(4,5,6,7-tetrahydro-1*H*-indenyl)titanium dichloride (2). Red-brown solid. Yield 48% (from bicyclo[4.3.0]non-6-en-8-one; 5 steps; average yield per step: 88%). Anal. calcd for C$_{18}$H$_{22}$Cl$_2$Ti (357.14): C, 60.5; H, 6.2; Cl, 19.8; found C, 60.7; H, 6.4; Cl, 19.4. ^{1}H-NMR (CDCl$_3$): δ 1.60–1.85 (m, 4H), 1.85–2.00 (m, 4H), 2.60–2.90 (m, 4H), 3.10–3.30 (m, 4H), 6.65 (d, J = 3.0 Hz, 4H), 7.05 (t, J = 3.0 Hz, 2H).

Bis[η^5-(2-phenylindenyl)]titanium dichloride (3). Purple solid. Yield 60% (from 2-indanone; 5 steps; average yield per step: 90%). Anal. calcd for C$_{30}$H$_{22}$Cl$_2$Ti (501.27): C, 71.9; H, 4.4; Cl, 14.2; found C, 71.5; H, 4.2; Cl, 14.8. ^{1}H-NMR (CDCl$_3$): δ 7.1–7.5 (m, 4H), 7.6–7.7 (m, 18H).

Bis[η^5-(2-phenyl-4,5,6,7-tetrahydro-1*H*-indenyl)]titanium dichloride (4). Red-brown solid. Yield 52% (from bicyclo-[4.3.0]non-6-en-8-one; 5 steps; average yield per step: 87%). Anal. calcd for C$_{30}$H$_{30}$Cl$_2$Ti (509.33): C, 70.7; H, 5.9; Cl, 13.9; found C, 70.8; H, 6.1; Cl, 13.4. ^{1}H-NMR (CDCl$_3$): δ 1.50–1.90 (m, 4H, C–CH$_2$–C*H*$_2$–), 1.90–2.20 (m, 4H, C–CH$_2$–C*H*$_2$–), 2.90–3.20 (m, 8H, –C–C*H*$_2$–CH$_2$–), 7.15 (s, 4H, –C*H*–Cp), 7.30–7.50 (m, 6H, –Ar*H*), 7.60–7.80 (m, 4H, –Ar*H*).

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