1-Azadiene Complexes of Zirconocene

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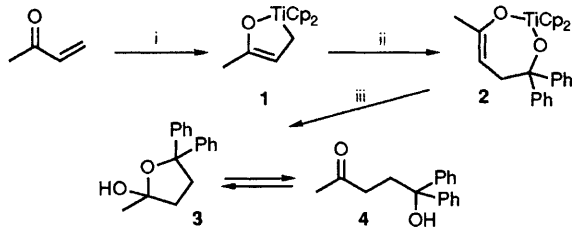
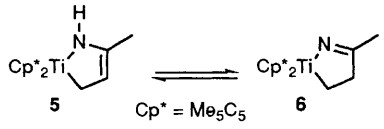
1-Azadiene complexes of zirconocene were prepared by ligand exchange between zirconocene butene and the 1-azadiene, and by a C–H activation route from allylic amines; they are best described as 1-zircona-2-azacyclopent-3-enes and 5-unsubstituted examples are fluxional.

We recently discovered that reaction between $TiCp_2(PMe_3)_2$ (Cp = C_5H_5) and methyl vinyl ketone gave the 1-oxadiene titanocene complex **1** which inserted diphenylketone to afford the 1-titana-2,7-dioxahept-3-ene **2**. On aqueous work-up this gave the 1,4-dioxygenated compounds **3** and **4** in good yield (Scheme 1).[1] The intermediate metallacycles proved difficult to isolate and characterise in a pure state so we report here the formation and properties of a series of stable 1-azadiene complexes of zirconocene.

Diene complexes of zirconium have been investigated by several groups,[2] and 1,4-diaza-, 1,4-dioxa- and 1,4-dithiono-diene complexes are also known[3] but we are only aware of one



Scheme 1 *Reagents and conditions*: i, $TiCp_2(PMe_3)_2$, hexane, −40–20 °C; ii, Ph_2CO, benzene, room temp., 5 min; iii, HCl aq., room temp.



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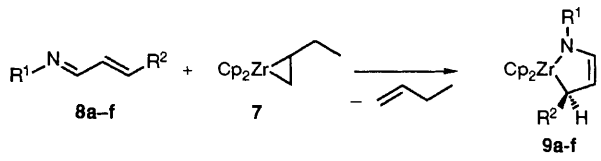
report of a group 4 1-heterodiene complex, the azadiene complex **5** seen as part of an equilibrating mixture with **6**.[4] A niobium azadiene complex has been proposed as an intermediate in the coupling of 1-azadienes with esters reported recently.[5]

The most direct route to the required complexes would be by complexation of a 1-azadiene to zirconocene ($ZrCp_2$). Zirconocene itself is not a viable intermediate and its phosphine stabilised form $ZrCp_2(PMe_3)_2$ is inconvenient. Fortunately the zirconocene equivalent prepared from $ZrCp_2Cl_2$ and two equivalents of BuLi introduced by Negishi[6] and shown to be zirconocene butene **7**[6,7] underwent a clean ligand exchange with 1-azadienes **8a–f** to form the required complexes **9a–f**. Thus to a solution of $ZrCp_2Cl_2$ (0.292 g, 1 mmol) in tetrahydrofuran (THF) (10 ml) at −78 °C was added butyllithium (0.8 ml of 2.5 mol dm^{-3} solution in hexanes, 2 mmol). After stirring at this temperature for 1 h, *N*-benzyl-4-phenyl-1-azabuta-1,3-diene **8a** (0.221 g, 1 mmol) in THF (10 ml) was added. After warming to room temperature over 2 h, removal of solvent, extraction into toluene, filtration, and final removal of solvent afforded **9a** as an orange solid, >90% pure by NMR spectroscopy, in near quantitative yield. Recrystallisation from toluene–hexane afforded the pure complex as orange crystals in 72% overall yield.† The NMR spectrum of **9a** indicates that the 1-azadiene complex is best described as a 1-zircona-2-azacyclopent-3-ene, rather than the alternative fomulation as an η^4-azadiene complex **10**, in particular C-5 (δ_C 68.0) and the proton on the carbon (δ_H 1.43) show chemical shifts typical of those for alkyl carbons next to zirconium. The 1-azadiene has thus formally been reduced in this reaction.

Unlike the titanium analogue this complex proved quite inert towards the insertion of carbonyl compounds, or even isocyanides, and could survive brief exposure to air. In a similar way the substituted azadiene complexes **9b–f** were prepared and characterised (Table 1), in each case the crude yield being near quantitative. They were purified by either recrystallisation from toluene–hexane or filtration of toluene solutions through a short column of grade 1 neutral alumina under argon. When the chiral azadiene **8e** derived from α-methylbenzylamine was used there was little stereocontrol in the complexation, a 60:40 mixture of diastereoisomers being obtained.[8] Hydrazones can also be successfully used as shown by the formation of **9f**, though those derived from phenylhydrazine, with a residual NH proton, are not substrates.

Postulating that the unreactivity of **9a–f** was due to the presence of a substituent at the 5-position blocking approach of the incoming electrophile we sought to prepare the analogous terminally unsubstituted azadiene complexes. We could not prepare the required 1-azadienes in the required state of purity, however, the *N,N*-dimethyl hydrazone of methacrolein could be so prepared and was successfully complexed to zirconocene to form the 5-unsubstituted azadiene complex **11** in 56% yield after filtration of a toluene solution through neutral alumina. At room temperature this complex showed a single very broad Cp peak in both the ^1H and ^{13}C NMR spectra. The other ^{13}C signals were all sharp. In the ^1H NMR the signals for H-5 and H-5′ appeared to be absent, though the remainder of the spectrum was as expected. Variable temperature NMR spectroscopy confirmed that this unusual behaviour was caused by rapid

† All zirconocycles were characterised by ^1H and ^{13}C NMR, mass and IR spectrometry.



8a–f 7 9a–f

Table 1 Selected NMR data for complexes **9a–f**

				δ_H(ppm)			δ_C(ppm)
	R^1	R^2	Yield (%)	H-3	H-4	H-5	C-5
a	$PhCH_2$	Ph	72[a]	5.85	5.36	1.63	68.0
b	Ph	Ph	74[a]	6.03	5.58	1.74	68.8
c	$PhCH_2$	Me	47[b]	5.82	4.56	0.18	60.5
d	Me_3C	Me	54[b]	5.75	4.39	−0.05	62.6
e	PhCH(Me)	Ph	62[b]	6.12	5.40	1.52	68.0
f	Me_2N	Ph	67[a]	6.37	5.34	1.44	69.6

[a] Purified by recrystallisation from toluene–hexane. [b] Purified by filtration of a toluene solution through neutral alumina.

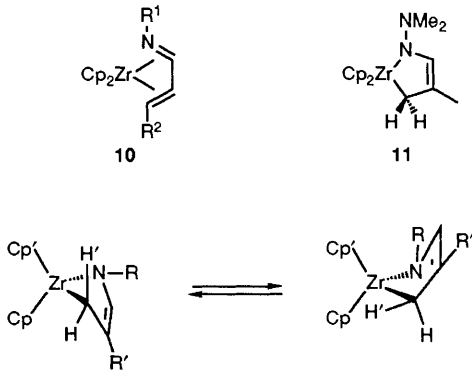


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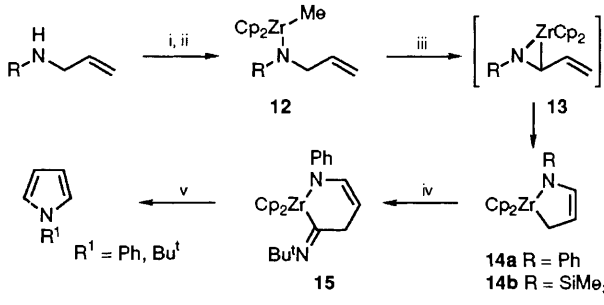
Fig. 1 Ring flipping of 1-zircona-2-azacyclopent-3-enes



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Scheme 2 *Reagents and conditions*: i, BuLi, −78 °C, THF; ii, $ZrCp_2MeCl$, −78–20 °C; iii, benzene, 60 °C, 1.5 h; iv, Bu^tNC, 20 °C, 1 h; v, MeOH, room temp.

flipping between two degenerate conformers (Fig. 1) (which can also be viewed as the migration of the metal from one face of the diene ligand to the other). At −60 °C the protons H-5 and H-5′ appeared at δ_H 2.92 and −0.20 (a remarkably wide range for geminal protons!), and the Cp peaks appeared as two singlets at δ_H 5.55 and 5.05. Warming to 300 K gave a singlet for the Cp protons and a signal for H-5 and H-5′ appeared as a broad singlet at δ_H 1.36. This is an important result in that it confirms that the 1-azadiene complexes exist in an envelope conformation (as recently confirmed by X-ray studies for diene and 1,4-azadiene complexes[2,3]). The coalescence temperature for the Cp peaks gives a free energy of activation ($\Delta G^{\ddagger}$) for the ring flip of 54.5 kJ mol^{-1} at 280 K. In the ring flip most of the carbons and protons do not change

their environments hence the very selective broadening observed.

We required a better route to these complexes which avoided the need to form unstable 1-azadienes and found it in a C–H activation route from allylic amines. Buchwald[9] and ourselves[10] have recently shown that η^2-imine complexes of zirconium can be generated from amines *via* loss of methane from methylzirconocene amides. Applying this to allylic amines should generate the required 1-azadiene complexes **14** by rearrangement of the first formed η^2-imine complexes **13** (Scheme 2). Thus to a solution of *N*-allyl aniline (0.266 g, 2 mmol) in THF (5 ml) under argon at −78 °C was added Bu^{n}Li (2 mmol, 0.8 ml of 2.5 mol dm^{-3} solution in hexanes). After warming to room temperature the resulting solution was added to a solution of zirconocene methyl chloride (0.544 g, 2 mmol) in THF (5 ml) at −78 °C under argon. The reaction mixture was allowed to warm to room temperature over 10 min then stirred at this temperature for a further 1 h. Solvent was removed *in vacuo*, the orange residue taken up in benzene (10 ml), filtered through a sinter, then heated at reflux for 1.5 h. Removal of benzene *in vacuo* gave 1-zircona-2-phenyl-2-azacyclopent-3-ene **14a** as an orange solid (0.65 g, 92%). This could be further purified by recrystallisation from toluene–hexane to give orange crystals in 51% overall yield. As with the hydrazone complex **11** described above **14a** was fluxional. In the room temperature NMR spectra the cyclopentadienyl protons appeared as a fairly sharp singlet at δ_H 5.4, and the C-5 protons as a broad singlet at δ_H 1.5. Cooling to −60 °C gave the Cp signals at δ_H 5.06 and 5.62, and the C-5 protons at δ_H 3.053 and −0.15, again a remarkably wide range. A coalescence temperature of 242 ± 2 K for the Cp signals gives a $\Delta G^{\ddagger}$ of 46.8 kJ mol^{-1} for the ring flip at this temperature. This is notably less than for the hydrazone derived complex above and may be due to a flattening of the nitrogen atom by interaction of a lone pair with the phenyl π-system. Attempts to obtain a crystal structure for this compound have been thwarted by its rapid decomposition on exposure to X-rays. The *N*-trimethylsilyl analogue **14b** was prepared by a similar procedure (87% yield of >95% pure material), though elimination of methane occurs at room temperature, and showed similar fluxional properties with a comparable $\Delta G^{\ddagger}$.

Our hopes for greater reactivity for the C-5 unsubstituted azadiene complex were confirmed by the insertion of *tert*-butyl isocyanide into **14a** to give **15** which afforded a mixture of *N*-phenylpyrrole and *N-tert*-butylpyrrole (5 : 1) on work-up with methanol, the former being isolated in 22% yield. The complex was, however, still completely inert to reaction with diphenylketone, acetone and benzaldehyde.

In conclusion we have developed two routes to zirconocene 1-azadiene complexes, shown that these are best represented as 1-zircona-2-azacyclopent-3-enes, and that 5-unsubstituted examples are fluxional confirming a bent conformation. They are unreactive species though insertion of isocyanide into 5-unsubstituted examples produces pyrroles on aqueous work-up. This conversion of an allylic amine into a pyrrole by incorporation of an extra carbon may be of synthetic interest.

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