New Ring-opening Metathesis Polymerization Catalyst based on a Five-coordinate Tungsten(VI) Alkylidene Complex Containing an *ortho*-Chelating Arylamine Ligand; X-Ray Structure of [W{$C_6H_4(CH_2NMe_2)$-2}(=NPh)(=$CHSiMe_3$)(CH_2SiMe_3)]

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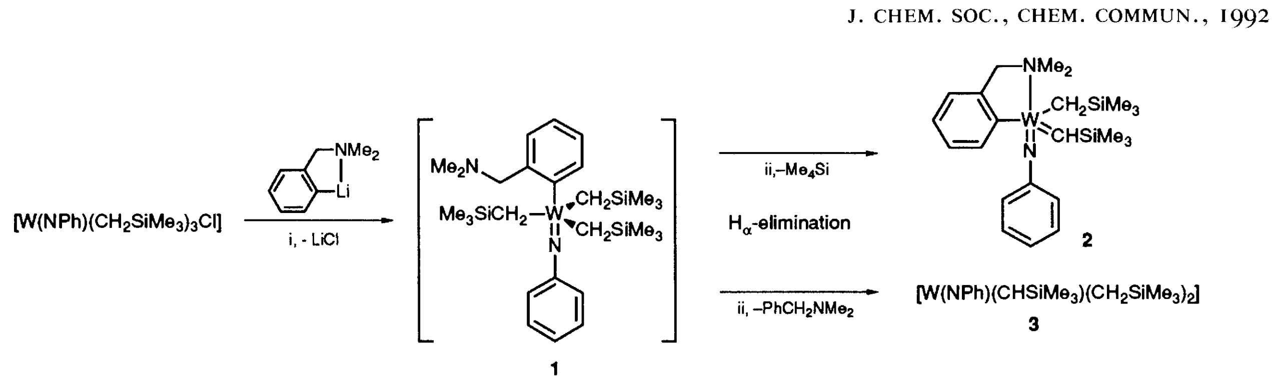
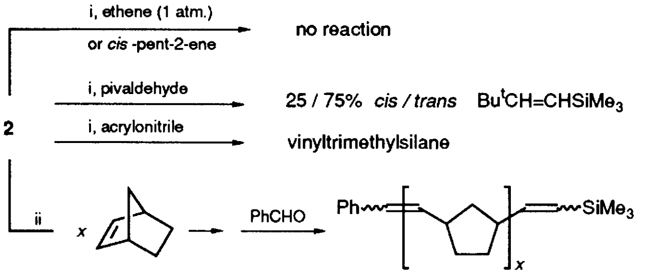
At −78 °C [W(=NPh)(CH_2SiMe_3)$_3$Cl] reacts with 2-[(dimethylamino)methyl]phenyllithium in diethyl ether to produce a tetra-organotungsten(VI) complex which decomposes by an H_α-elimination reaction generating a novel tungsten(VI) alkylidene with intramolecular coordination of an amine function; this complex reacts with norbornene to provide a *cis*-polymer that is the result of a selective ring-opening metathesis.

Cyclometallated organometallic complexes are of great interest because (*i*) they are generally more stable than the complexes having an equivalent number of monodentate ligands and (*ii*) the reactivity of the metal centre in these complexes is strongly influenced by the intramolecular co-ordination.[1,2] Recently we became interested in the use of potentially *ortho*-chelating arylamine ligands, for example 2-[(dimethylamino)methyl]phenyl, as an appropriate ligand for controlling tungsten(VI) alkylidene reactivity. Some well-characterized, four-coordinate, tungsten(VI) alkylidene complexes are known to be good catalysts in, for example, alkene metathesis reactions[3] and ring-opening metathesis polymerization reactions that produce polymers having a very narrow distribution of molecular weights.[4] Five-coordinate tungsten(VI) alkylidene complexes, containing besides the alkylidene group only monoanionic ligands, are known to be selective Wittig reagents.[5] To date the concept of intramolecular coordination has not been explored in this field. We now report the synthesis, structural aspects and reactivity towards linear alkenes as well as cyclic alkenes of a novel type of five-coordinate tungsten(VI) alkylidene complex possessing intramolecular coordination of a tertiary amine donor.



Scheme 1 *Conditions*: i, in Et_2O, −78 °C; ii, in Et_2O, 20 °C



Scheme 2 *Conditions*: i, in C_6D_6, 20 °C; ii, **2** (50 μmol), norbornene (2.5 mmol), x = 500, in C_6H_6 (20 ml), 20 °C

The reaction of $[W(=NPh)(CH_2SiMe_3)_3Cl]$[6] with 2-[(dimethylamino)methyl]phenyllithium[7] in a 1 : 1 molar ratio at −78 °C in Et_2O affords a tetra-organotungsten(VI) complex **1**. Warming the reaction mixture to 20 °C and stirring for 2 h, removal of the precipitate (LiCl, by centrifugation) and evaporation of the solvent provides a mixture of two tungsten(VI) alkylidene complexes **2** and **3** (see Scheme 1). After recrystallization from a saturated pentane solution at low temperature the five-coordinate tungsten(VI) alkylidene complex $[W\{C_6H_4(CH_2NMe_2)\text{-}2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$ **2** was obtained pure in 70% yield.

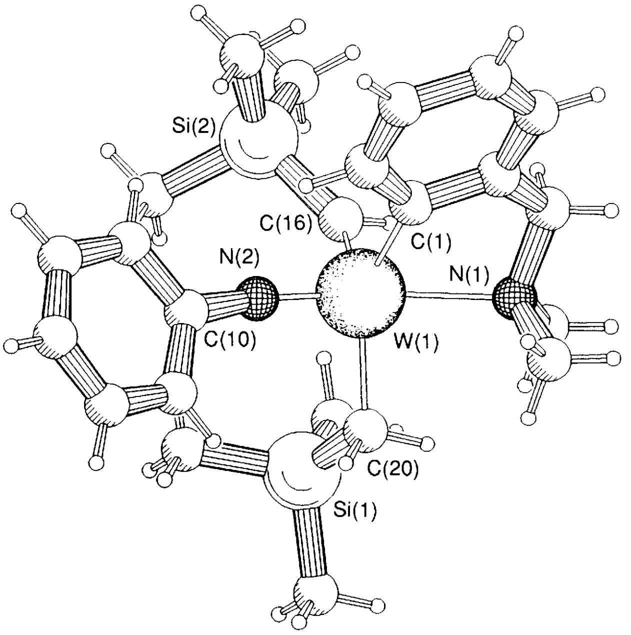


Fig. 1 Molecular structure of $[W\{C_6H_4(CH_2NMe_2)\text{-}2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$ **2** with the adopted numbering scheme. Only one of the two nearly identical molecules of the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): W(1)–C(1), 2.15(2); W(1)–C(20), 2.18(2); W(1)–C(16), 1.87(2); W(1)–N(1), 2.37(2); W(1)–N(2), 1.75(1). W(1)–C(16)–Si(2), 138.5(11); W(1)–C(20)–Si(1), 119.9(10); W(1)–N(2)–C(10), 162.6(13); N(1)–W(1)–C(1) 72.8(6).

Complex **2** can be safely handled under an inert atmosphere at 20 °C and can be stored so for months. However, as a solid **2** decomposes on contact with air or water and in solution (toluene) it slowly decomposes at temperatures of ⩾80 °C. The stereochemistry of **2** and proof for the intramolecular nitrogen coordination was obtained from an X-ray structure determination.† The asymmetric unit contains two independent, nearly identical molecules. Fig. 1 shows the molecular geometry of **2** that can be described as a distorted square-pyramidal structure [29 and 33% distortion along the Berry pseudorotation coordinate towards a trigonal bipyramid for W(1) and W(2), respectively]. The alkylidene function is bonded at the apical position of the square pyramid with the phenylimido, *ortho*-chelate bonded arylamine ligand and the (trimethylsilyl)methyl group at the basal positions. The W(1)–N(1) and W(2)–N(3) distances of 2.37(2) Å, and the N(1)–W(1)–C(1) and N(3)–W(2)–C(24) angles of 72.8(6) and 73.3(7)° are comparable with those found for mono- and bis-*ortho*-chelated arylamine tantalum(V) complexes.[8]

An important aspect for understanding the reactivity of **2** is the nature of the intramolecular W–N coordination in solution. ^1H NMR (C_6D_6, 298 K)‡ data show that **2** is a

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† *Crystal data* for **2**: $[W\{C_6H_4(CH_2NMe_2)\text{-}2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$, $C_{23}H_{38}N_2Si_2W$, M = 582.59, block-shaped crystal (0.50 × 0.25 × 0.12 mm), monoclinic, space group $P2_1/a$, with a = 17.950(3), b = 16.633(4), c = 19.472(4) Å, β = 115.48(2)°, V = 5248(2) Å^3, Z = 8, D_c = 1.475 g cm^{-3}, $F(000)$ = 2336, μ(Mo-Kα) = 46.0 cm^{-1}; 12011 independent reflections ($1.16 < \theta < 27.5°$; $\omega/2\theta$-scan; T = 100 K) were measured on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-Kα radiation (λ = 0.71073 Å). The crystal was of rather poor quality, as indicated by broad reflection profiles. Data were corrected for Lorentz–polarization effects, for a small linear decay (3%) of the intensity control reflections and for absorption (DIFABS; correction range 0.789–1.214). The structure was solved by Patterson (SHELXS86) and difference Fourier techniques and refined by full-matrix least squares (SHELX76) to a R-value of 0.066, R_w = 0.065, $w^{-1} = [\sigma^2(F)]$ for 5981 reflections with $I \geqslant 2.5\,\sigma(I)$ and 276 parameters. H Atoms were introduced at calculated positions and refined riding on their carrier atoms. W, Si, N atoms were refined with anisotropic thermal parameters, C atoms were refined isotropically in view of the poor quality of the crystal. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ ^1H NMR data (C_6D_6, 300 MHz, 298 K): δ 8.41 (m, 1H, *o*-H); 8.25 (s, 1H, $^2J_{HW}$ = 10.3 Hz, Hα); 7.56–7.07 (m, 7H, Ar–H); 6.94 (t, 1H, *p*-H of NPh); 3.98 (d, 1 H, $^2J_{HAHB}$ = 12.6 Hz, CH_AH_BN); 3.32 (d, 1H, $^2J_{HBHA}$ = 12.6 Hz, CH_AH_BN); 2.45 and 1.59 (2s, 6 H, NMe); 0.57 (d, 1H, $^2J_{HAHB}$ = 11.9 Hz, $^2J_{HW}$ = 8.0 Hz, CH_AH_BSi); 0.33 and 0.27 (2s, 18H, $SiMe_3$); 0.02 (d, 1H, $^2J_{HBHA}$ = 11.9 Hz, $^2J_{HW}$ = 8.0 Hz, CH_AH_BSi). ^{13}C NMR data (C_6D_6, 75 MHz, 298 K): 236.1 (C_α, $^1J_{CW}$ = 133.0 Hz, $^1J_{CH}$ = 109.6 Hz); 190.0 (C_{ipso}, $^1J_{CW}$ = 109.3 Hz); 156.6 (C_{ipso} NPh); 149.1, 144.0, 128.8–123.2 (aromatic C), 75.1 (CH_2N), 49.3 (NMe); 49.1 (CH_2Si, $^1J_{CW}$ = 70.1 Hz); 45.8 (NMe); 3.0 and 2.7 ($SiMe_3$). Satisfactory elemental analyses were obtained.

mononuclear five-coordinate species as found in the solid state. The NMe groups and the CH_2 protons of both the 2-(dimethylamino)methyl and the (trimethylsilyl)methyl group are diastereotopic up to 80 °C indicating that up to this temperature the tungsten centre is stereogenic. Above 80 °C the two resonances of the NMe_2 group coalesce indicating that above this temperature a process involving W–N dissociation–association becomes operative on the NMR time-scale.

Complex **2** is inert towards simple linear alkenes like ethene and *cis*-pent-2-ene that can probably not compete with the intramolecular amine coordination. However, acrylonitrile reacts with **2** and, most probably through anchimeric assistance of the cyano group, leads to quantitative formation of vinyltrimethylsilane. Complex **2** reacts at 20 °C with pivaldehyde instantaneously yielding a 25 : 75 *cis–trans*-mixture of 1-*tert*-butyl-2-(trimethylsilyl)ethene in a Wittig-like reaction.

Surprisingly, a fast ring-opening metathesis polymerization occurs when **2** reacts with 200 equivalents of norbornene in benzene at 20 °C (see Scheme 2). The polymer formed, after quenching the reaction mixture with a little benzaldehyde and evaporating the solvent, was obtained as a colourless elastic film and is currently being fully characterized. Initial ^1H NMR studies show that more than 90% of the double bonds in the polymer are in the *cis*-configuration.

These preliminary results show that tungsten(VI) alkylidene complexes with an intramolecularly coordinating *N*-donor ligand site are readily accessible and are reactive. Tuning the reactivity of the alkylidene function with other related ligands is currently being studied.

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