

Fig. 1 Light image formation on PAn/TiO<sub>2</sub> film immersed in 0.5 mol dm<sup>-3</sup> phosphate buffer (pH 7) containing 20 wt% methanol by projecting the positive image on the PAn/TiO<sub>2</sub> film with illumination by a 500 W xenon lamp for 1 min

not successful for producing light images. The reduced area was steadily spread over the entire film with increased illumination time, because the oxidized form of polyaniline possesses high conductivity, which allows easy diffusion of photogenerated electrons beyond the periphery of the illuminated area.

It is well known<sup>6</sup> that the conductivity of a polyaniline film can be remarkably decreased by immersing it in aqueous neutral solutions; as a result of deprotonation. The film changes from green to blue in that case. Illumination of the PAn/TiO<sub>2</sub> film in 0.5 mol dm<sup>-3</sup> phosphate buffer solution (pH 7) containing 20 vol% of methanol caused a change from blue to yellow in the illuminated area alone, and light images could be produced as shown in Fig. 1. The polarization of the film at 0.5 V vs. SCE was again enough to erase the light image and turn it blue again. The light image was produced by projecting the positive image on the PAn/TiO<sub>2</sub> film for 1 min using the

500 W xenon lamp as a light source and an enlarger for printing photographs. The shade of the obtained picture resulted from difference in the degree of reduction of polyaniline, which depended on the intensity of irradiated photons. The produced images were very stable and no change in their contrast was noticed for at least 2 weeks if the film was kept under open circuit in the N<sub>2</sub>-purged solution. Considering that deprotonated polyaniline films have no redox activity,<sup>1,7</sup> it is unlikely that polyaniline films in the deprotonated state were photoreduced to give the light images. It is more likely that deprotonated films were converted into the protonated form only in the illuminated area with the mechanism that protons which are released from methanol on its oxidation with involvement of photogenerated positive holes attach to the deprotonated polyaniline at the place where the proton-release occurs, resulting in photoreduction of the film as observed. The 'write-erase' cycle was successfully repeated for more than 100 cycles, though gradual oxidative degradation of polyaniline was noticed from changes in its absorption spectrum.

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## 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<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}(=NPh)(=CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)]

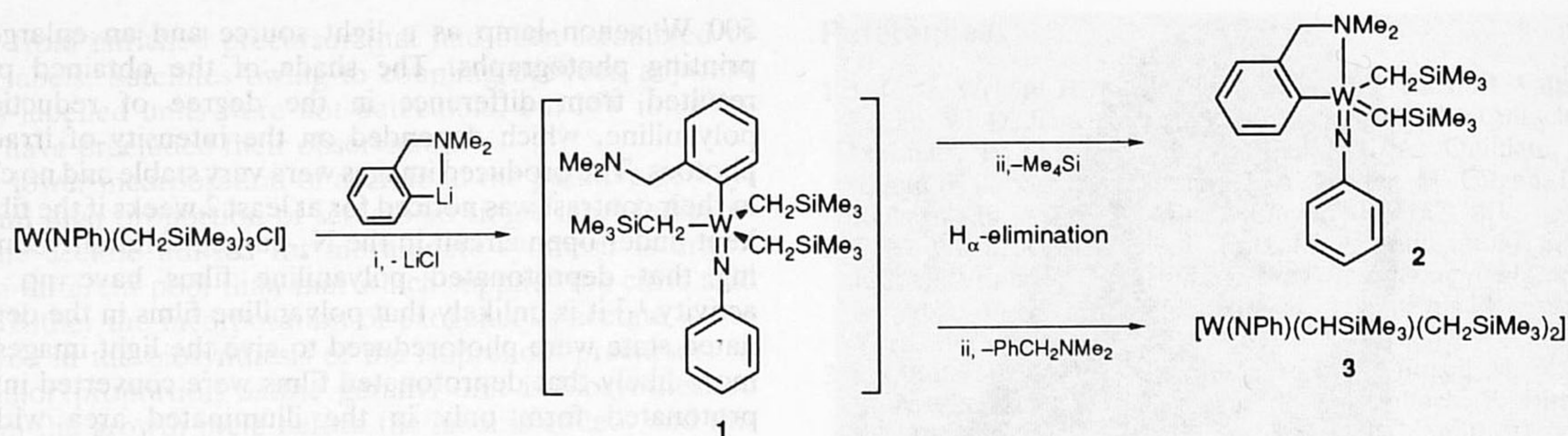
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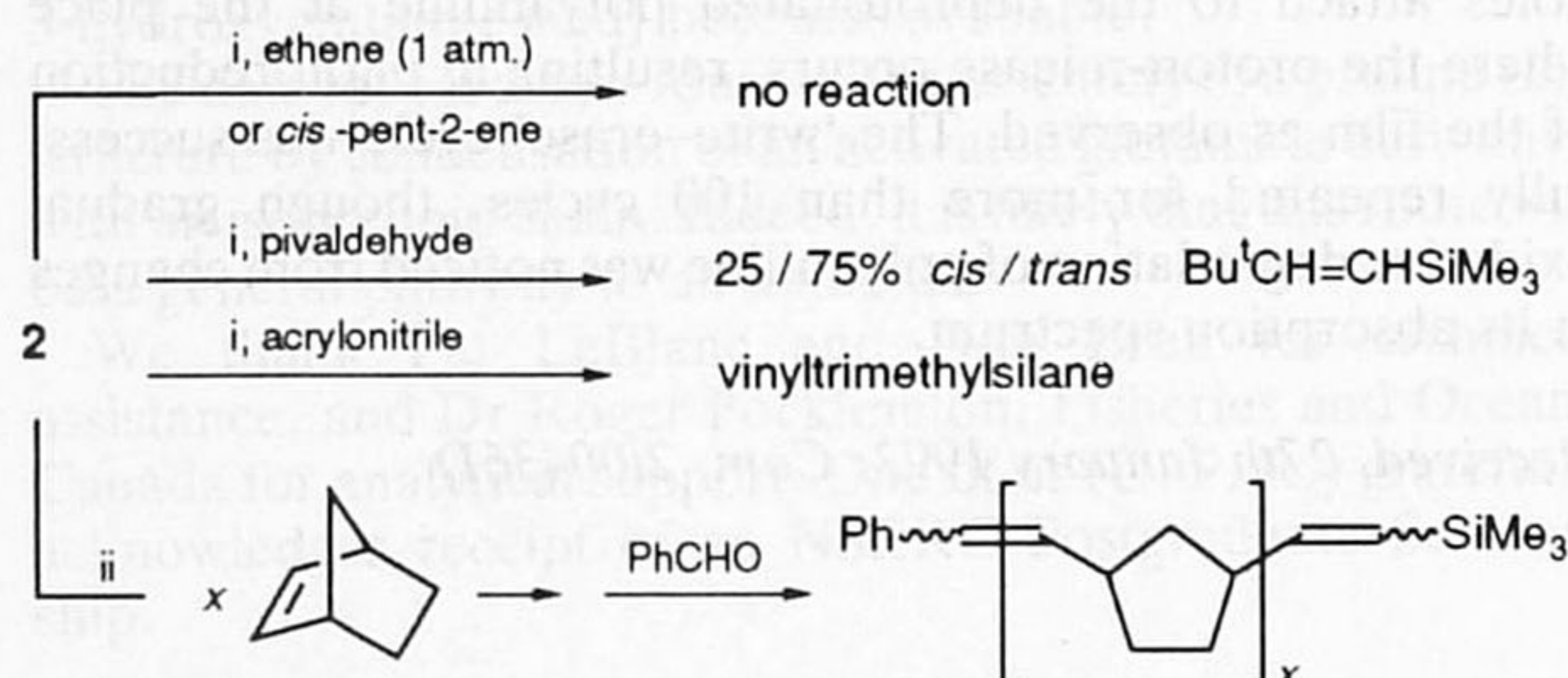
At -78 °C [W(=NPh)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>Cl] reacts with 2-[(dimethylamino)methyl]phenyllithium in diethyl ether to produce a tetra-organotungsten(vi) complex which decomposes by an H<sub>α</sub>-elimination reaction generating a novel tungsten(vi) alkylidene with intramolecular 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 coordination.<sup>1,2</sup> 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<sup>3</sup> and ring-opening metathesis polymerization reactions that produce polymers having a very narrow distribution of molecular weights.<sup>4</sup> Five-coordinate tungsten(vi) alkylidene complexes, containing besides the alkylidene group only monoanionic ligands, are known to be selective Wittig reagents.<sup>5</sup> 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<sub>2</sub>O, -78 °C; ii, in Et<sub>2</sub>O, 20 °C



Scheme 2 Conditions: i, in C<sub>6</sub>D<sub>6</sub>, 20 °C; ii, 2 (50 μmol), norbornene (2.5 mmol), x = 500, in C<sub>6</sub>H<sub>6</sub> (20 ml), 20 °C

The reaction of  $[W(=NPh)(CH_2SiMe_3)_3Cl]$ <sup>6</sup> with 2-[(dimethylamino)methyl]phenyllithium<sup>7</sup> in a 1:1 molar ratio at -78 °C in Et<sub>2</sub>O 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  $[W\{C_6H_4(CH_2NMe_2)_2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$  **2** was obtained pure in 70% yield.

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.<sup>†</sup> 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-

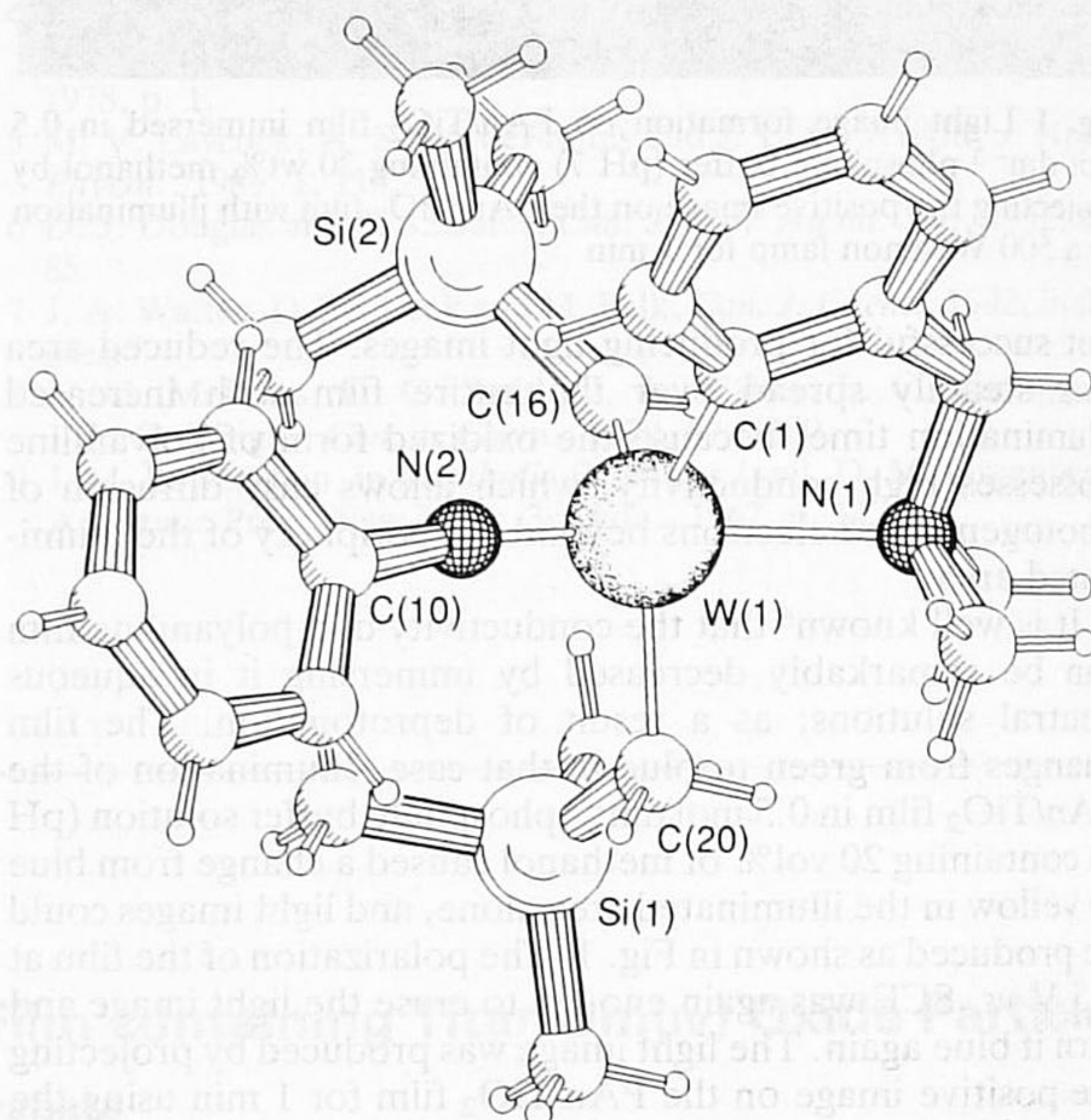


Fig. 1 Molecular structure of  $[W\{C_6H_4(CH_2NMe_2)_2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$  **2** with the adopted numbering scheme. Only one of the two nearly identical molecules of the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): W(1)–C(1), 2.15(2); W(1)–C(20), 2.18(2); W(1)–C(16), 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).

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.<sup>8</sup>

An important aspect for understanding the reactivity of **2** is the nature of the intramolecular W–N coordination in solution. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K)<sup>‡</sup> data show that **2** is a

<sup>†</sup> Crystal data for **2**:  $[W\{C_6H_4(CH_2NMe_2)_2\}(=NPh)(=CHSiMe_3)(CH_2SiMe_3)]$ , C<sub>23</sub>H<sub>38</sub>N<sub>2</sub>Si<sub>2</sub>W, *M* = 582.59, block-shaped crystal (0.50 × 0.25 × 0.12 mm), monoclinic, space group *P*2<sub>1</sub>/*a*, with *a* = 17.950(3), *b* = 16.633(4), *c* = 19.472(4) Å, β = 115.48(2)°, *V* = 5248(2) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.475 g cm<sup>-3</sup>, *F*(000) = 2336, μ(Mo-Kα) = 46.0 cm<sup>-1</sup>; 12011 independent reflections (1.16 < θ < 27.5°; ω/2θ-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*<sub>w</sub> = 0.065, *w*<sup>-1</sup> = [σ<sup>2</sup>(*F*)] for 5981 reflections with *I* ≥ 2.5 σ(*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.

<sup>‡</sup> <sup>1</sup>H NMR data (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K): δ 8.41 (m, 1H, *o*-H); 8.25 (s, 1H, <sup>2</sup>*J*<sub>HW</sub> = 10.3 Hz, H<sub>α</sub>); 7.56–7.07 (m, 7H, Ar-H); 6.94 (t, 1H, *p*-H of NPh); 3.98 (d, 1H, <sup>2</sup>*J*<sub>H<sub>A</sub>H<sub>B</sub></sub> = 12.6 Hz, CH<sub>A</sub>H<sub>B</sub>N); 3.32 (d, 1H, <sup>2</sup>*J*<sub>H<sub>B</sub>H<sub>A</sub></sub> = 12.6 Hz, CH<sub>A</sub>H<sub>B</sub>N); 2.45 and 1.59 (2s, 6H, NMe); 0.57 (d, 1H, <sup>2</sup>*J*<sub>H<sub>A</sub>H<sub>B</sub></sub> = 11.9 Hz, <sup>2</sup>*J*<sub>HW</sub> = 8.0 Hz, CH<sub>A</sub>H<sub>B</sub>Si); 0.33 and 0.27 (2s, 18H, SiMe<sub>3</sub>); 0.02 (d, 1H, <sup>2</sup>*J*<sub>H<sub>B</sub>H<sub>A</sub></sub> = 11.9 Hz, <sup>2</sup>*J*<sub>HW</sub> = 8.0 Hz, CH<sub>A</sub>H<sub>B</sub>Si). <sup>13</sup>C NMR data (C<sub>6</sub>D<sub>6</sub>, 75 MHz, 298 K): 236.1 (C<sub>α</sub>, <sup>1</sup>*J*<sub>CW</sub> = 133.0 Hz, <sup>1</sup>*J*<sub>CH</sub> = 109.6 Hz); 190.0 (C<sub>ipso</sub>, <sup>1</sup>*J*<sub>CW</sub> = 109.3 Hz); 156.6 (C<sub>ipso</sub> NPh); 149.1, 144.0, 128.8–123.2 (aromatic C), 75.1 (CH<sub>2</sub>N), 49.3 (NMe); 49.1 (CH<sub>2</sub>Si, <sup>1</sup>*J*<sub>CW</sub> = 70.1 Hz); 45.8 (NMe); 3.0 and 2.7 (SiMe<sub>3</sub>). Satisfactory elemental analyses were obtained.

mononuclear five-coordinate species as found in the solid state. The NMe groups and the CH<sub>2</sub> 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<sub>2</sub> 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 <sup>1</sup>H 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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## An Authentic *ortho*-Quinodimethane Radical Anion

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Photolysis of  $\alpha, \alpha'$ -dilithio- $\alpha, \alpha'$ -bis(trimethylsilyl)-*o*-xylene leads to an ESR spectrum assigned to the  $\alpha, \alpha'$ -bis(trimethylsilyl)-*o*-quinodimethane radical anion, the first representative of this class of radical anions to have been observed in solution.

The  $8\pi$ -electron *o*-quinodimethane system is a well known intermediate in organic chemistry,<sup>1,2</sup> but the  $9\pi$ -electron quinodimethane radical anion and its derivatives have remained elusive. Although resonance-energy calculations<sup>3</sup> suggest that the *o*-quinodimethane radical anion **1** should be well stabilised, it has eluded unequivocal experimental observation.<sup>2,4,5</sup> Michl *et al.*<sup>2</sup> speculated on the possible detection of **1** in a low temperature matrix. Bauld *et al.*<sup>4</sup> have implicated derivatives of **1** in reductive ring-openings of benzocyclobutenes, but a species reported<sup>5</sup> to be **1** was later shown<sup>6,7</sup> to be a benzocyclobutene radical anion in which ion-pairing effects gave rise to the unsymmetrical ESR spectrum. We now report the ESR spectrum of the bis-trimethylsilyl **2** derivative of **1** in solution at low temperature. As far as we are aware,

this is the first direct experimental observation of an *o*-quinodimethane radical anion.

The most promising method for producing radical anions of antiaromatic neutral precursors is one-electron oxidation of the corresponding dianion.<sup>8</sup> We were, for instance, able to observe the ESR spectrum of the pentalene radical anion by photolysing the dilithium salt of the dianion.<sup>8</sup> *o*-Quinodimethane dianions are readily accessible from the double deprotonation of *o*-xylenes,<sup>9</sup> and the X-ray structures of some derivatives are available.<sup>10,11</sup> We chose the bis-trimethylsilyl derivative **3a**<sup>10</sup> as a suitable precursor to **2**. Photolysis of **3a** in 2-methyltetrahydrofuran (2-MTHF) at –120 °C with a high-pressure mercury lamp (500 W) led to a strong ESR signal ( $g = 2.0029$ ) that showed hyperfine splittings of 0.698 mT (2H) and