

but that acid catalysis leads to a significantly lower value. Presumably, this corresponds to an appreciably earlier transition state in the rate-limiting ionization due to the much better leaving group in the protonated substrate. This corresponds to a quite unusual sensitivity of the value of the α -KIE to the effectiveness of the leaving group bonded through a common element. It remains to identify conditions under which **1** reacts with rate-limiting ion pair separation and to determine the α -KIE for that process, whereupon the results of the enzymic reactions may be more confidently interpreted. It is clear from the present results, however, that the endocyclic oxygen of **1**, which facilitates the departure of the nucleofuge, does not significantly affect the α -KIE. Moreover, if the similarity in the isotope effects for uncatalysed hydrolysis of **1** and solvolysis of simple secondary alkyl arenesulfonates indicates a similar extent of C–O bond cleavage in the transition states, the nucleophilic assistance provided by the α -oxygen of the acetal must be compensating for the very considerable difference in leaving group abilities of arenesulfonate and *p*-nitrophenoxide as reflected by the pK_a values of their conjugate acids.

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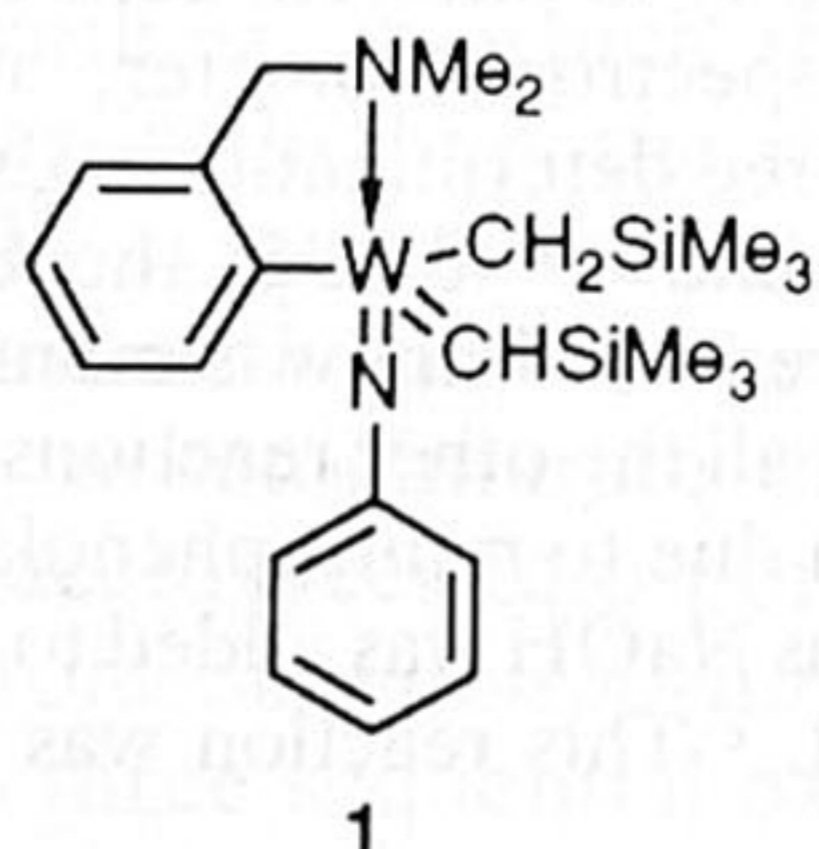
A New Type of Tungsten(VI) Phenylimido Alkylidene Complex and its Triorganotungsten Precursor with an *O,N*-Chelating Ligand; Molecular Structures of $[W(CH_2SiMe_3)_3(=NPh)\{OCPH_2(2-py)\}]$ and $[W(=CHSiMe_3)(CH_2SiMe_3)(=NPh)\{OCPH_2(2-py)\}]$ (py = pyridine)

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A new type of tungsten(VI) alkylidene complex has been prepared with $[OCPH_2(2-py)]$, a potentially bidentate *O,N*-chelating monoanionic ligand, and the corresponding triorganotungsten phenylimido alkoxide precursor complexes have been isolated; the new tungsten(VI) alkylidene complex $[W(=CHSiMe_3)(CH_2SiMe_3)(=NPh)\{OCPH_2(2-py)\}]$ **3** reacts with norbornene (70 °C) to provide selectively the *cis*-polymer in a ring-opening metathesis polymerization reaction.

Tungsten(VI) alkylidene complexes are important species in various olefin metathesis reactions,¹ and their reactivity strongly depends on the other ligands present.² We have recently shown that a five-coordinate tungsten(VI) alkylidene complex $[W\{C_6H_4(CH_2NMe_2)-2\}(=CHSiMe_3)(CH_2SiMe_3)(=NPh)]$ **1** containing a *C,N*-chelating ligand, is easily accessible, and that **1** is a very active catalyst in the ring-opening metathesis polymerization of norbornene.³



In order to tune the reactivity and stability of this new type of alkylidene complex with chelating ligands, we have investigated the use of other potentially bidentate monoanionic ligands. We chose to combine our strategy of intramolecular amine coordination with the electronic flexibility of alkoxide ligands, and now report the first results of the use of monoanionic, potentially *O,N*-chelating α -substituted 2-pyridylmethoxide ligands, $[OCR^1R^2(2-py)]^-$, in early-transition-metal chemistry. The *O,N*-chelating ligand $[OCPH_2(2-py)]^-$ allows successful preparation and characterization of a six-coordinate triorganotungsten(VI) phenylimido alkoxide, **2**, which undergoes an internal H_α -abstraction to afford the five-coordinate alkylidene complex **3** (see Scheme 1).

Addition of a suspension of $[Li\{OCPH_2(2-py)\}]$ (1.43 g, 5.19 mmol) in 30 ml of tetrahydrofuran (THF) to a solution of $[W(CH_2SiMe_3)_3Cl(=NPh)]^+$ (2.95 g, 5.16 mmol) in 40 ml of THF gave, after reflux for 1 h, a clear, red solution.

Evaporation of the volatiles *in vacuo* and extraction of the residue with hexane (2 × 60 ml) gave a light-brown solid. Recrystallization from a saturated pentane solution at -30 °C afforded [W(=CHSiMe₃)(CH₂SiMe₃)(=NPh){OCPH₂(2-py)}] **3** as analytically pure, orange crystals (isolated yield: 91%).

A ¹H NMR spectrum† of **3** in C₆D₆ shows the complex to exist as a mixture of two isomers in a ratio of approximately 10:1. There are two alkylidene resonances, for the minor and major isomer at δ 11.96 (²J_{WH} not obs.) and δ 10.67 (²J_{WH} 11.4 Hz), respectively. Based on literature data, these two species can be ascribed to the *anti*- and *syn*-alkylidene rotamers, respectively.⁵ The chemical shift for 6-H of the 2-pyridyl fragment [Δδ_(py-6H) = 0.30 with respect to the free alcohol] is good evidence for the coordination of the pyridyl nitrogen atom to the tungsten centre, with the consequence that complex **3** is a five-coordinate species. To elucidate the geometry of this alkylidene complex and have further proof for the intramolecular pyridyl coordination an X-ray structure determination was carried out.‡

Suitable crystals were grown from a hexane solution at -30 °C. The molecular structure of **3**, with the adopted numbering scheme is depicted in Fig. 1.

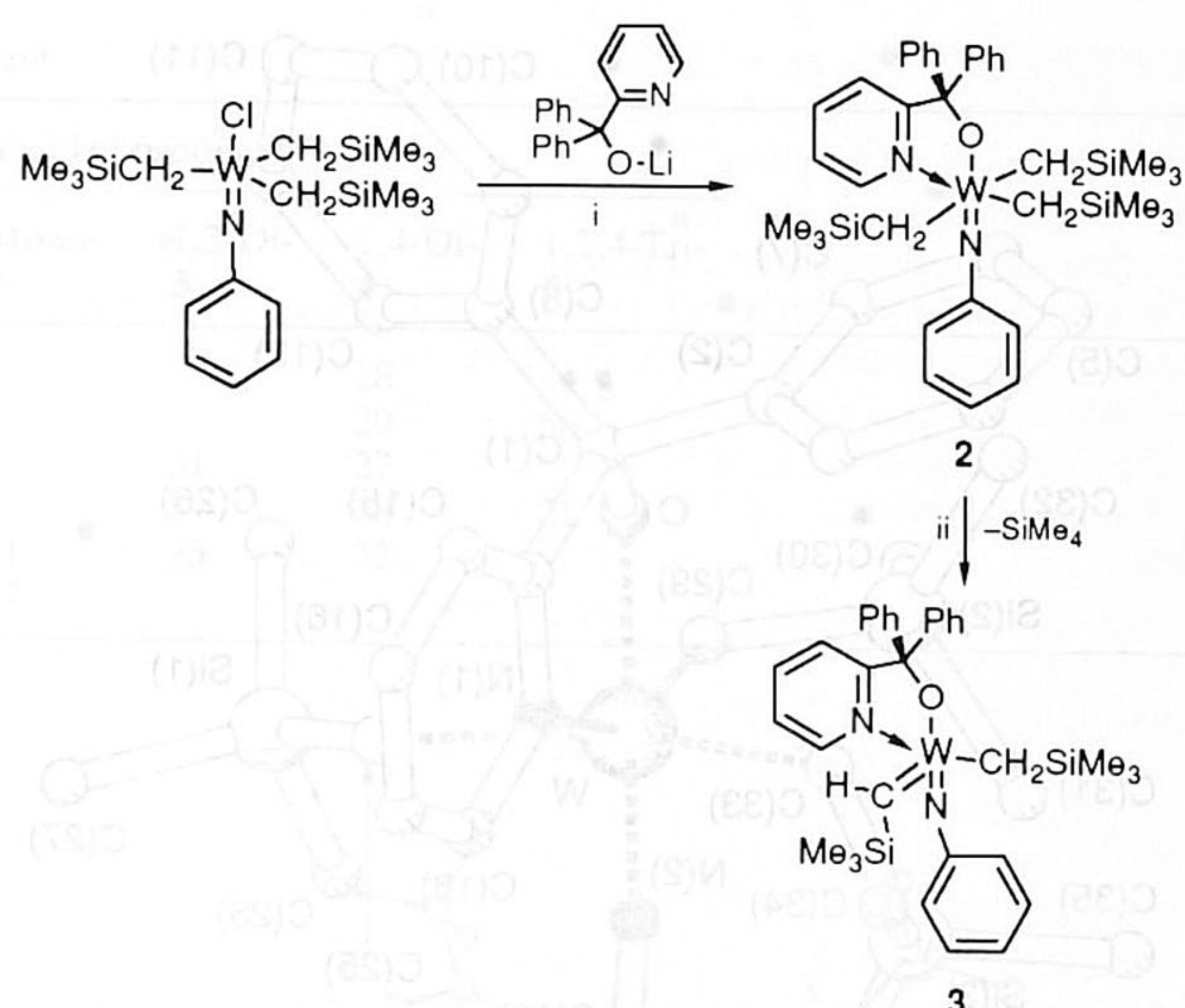
The geometry of **3** can be described as a distorted square pyramid in which the C(23)-bonded alkylidene function

† Selected spectroscopic data of **3** (NMR data of the *syn*-rotamer only are given) ¹H NMR (300 MHz, C₆D₆, 300 K): δ 10.67 (s, 1H, ²J_{HW} 11.4 Hz, H_α), 8.48 (d, 1H, 6-H-py), 7.49–6.88 (m, 16H, Ar-H), 6.57 (t, 1H, *p*-H NPh), 6.04 (t, 1H, H-py), 1.10 (d, 1H, ²J_{H_AH_B} 12.7 Hz, CH_AH_BSi), 0.99 (d, 1H, ²J_{H_BH_A} 12.7 Hz, CH_AH_BSi), 0.43, 0.32 (2s, 18H, SiMe₃). ¹³C NMR (75 MHz, C₆D₆, 300 K): δ 247.7 (*J*_{CW} 137.2 Hz, *J*_{CH} = 115.1 Hz, CHSi), 168.9 (C-2-py); 157.1 (*C*_{ipso}-NPh), 150.6, 147.6, 146.7, 138.4, 138.0, 128.9–123.0 (Ar-C); 98.6 (OC), 33.3 (*J*_{CW} 103.5 Hz, CH₂Si), 2.6, 2.3 (2 SiMe₃). Satisfactory elemental analyses were obtained. Residual signals of **2** observed in a ¹H NMR spectrum of crude **3**: δ 8.11 (d, 1H, 6-H-py), 1.40 (s, 6H, CH₂Si); 0.11 (s, 27H, SiMe₃).

‡ Crystal data for **2**: [W(CH₂SiMe₃)₃(=NPh){OCPH₂(2-py)}], C₃₆H₅₂N₂O₂Si₃W, *M* = 796.93, yellow crystal mounted in Lindemann glass capillary, monoclinic, spacegroup *P*2₁/*c*, with *a* = 10.974(1), *b* = 18.531(3), *c* = 20.307(2) Å, β = 106.47(1), *V* = 3960.2(9) Å³, *Z* = 4, *D*_c = 1.337 g cm⁻³, *F*(000) = 1624, μ(Mo-Kα) = 30.9 cm⁻¹; 7686 reflections scanned, 7035 unique (θ < 25.4°; ω/2θ - scan, Δω = 1.08 + 0.35tgθ°; *T* = 298 K) were measured on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz-polarization-effects, a linear decay of 11% and absorption/extinction (DIFABS; correction range 0.68–1.18). The structure was solved with DIRDIF-92 and refined on *F* by full-matrix least-squares (SHELX76). Final *R* = 0.063, *R*_w = 0.053, w⁻¹ = σ²(*F*) + 0.000256*F*², for 2644 reflections with *I* ≥ 2.5σ(*I*) and 415 parameters. Hydrogen atoms were included at calculated positions. One of the Si(CH₃)₃ groups is disordered. A final difference map showed no density outside -1.28 and 1.26 e Å⁻³ (near W).

For **3**: [W(=CHSiMe₃)(CH₂SiMe₃)(=NPh){OCPH₂(2-py)}], C₃₂H₄₀N₂O₂Si₂W, *M* = 708.70, orange, rod-shaped crystal mounted in Lindemann glass capillary, triclinic, spacegroup *P*1̄, with *a* = 9.4359(10), *b* = 10.8887(10), *c* = 16.611(2) Å, α = 81.60(1), β = 88.37(1), γ = 79.19(1)°, *V* = 1658.4(3) Å³, *Z* = 2, *D*_c = 1.419 g cm⁻³, *F*(000) = 712, μ(Mo-Kα) = 36.5 cm⁻¹; 9647 reflections scanned, 9122 unique (θ < 30.2°; ω/2θ, Δω = 0.94 + 0.35tanθ°; *T* = 298 K) were measured on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz-polarization effects, a linear decay of 11% and absorption/extinction (DIFABS; correction range 0.80–1.18). The structure was solved with SHELXS86/PATT and refined on *F* with SHELX76. Final *R* = 0.042, *R*_w = 0.026 for 5879 reflections with *I* ≥ 2.5σ(*I*) and 348 parameters. All hydrogen atoms were taken into account at calculated positions except for the hydrogen atom on C(23) that was located from a difference map and refined, weights based on counting statistics were used. A final difference Fourier showed no residual density outside -1.27 and 0.72 e Å⁻³ (near W).

For both structures, 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.



Scheme 1 Reagents and conditions: i, THF; ii, THF heated at reflux for 1 h

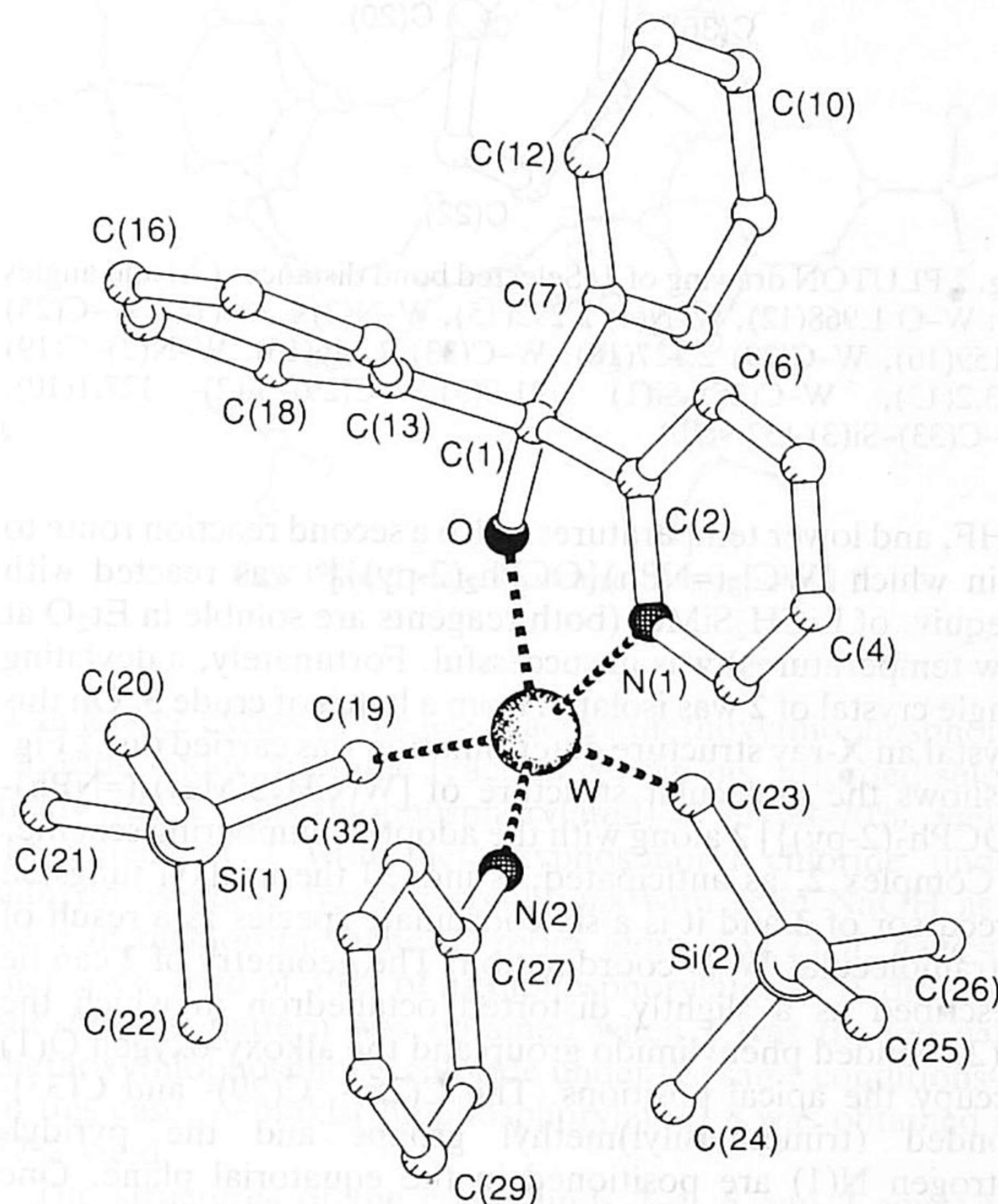


Fig. 1 PLUTON drawing of **3** (*syn*-rotamer). Selected bond distances (Å) and angles (°): W–O 1.945(3), W–N(1) 2.233(4), W–N(2) 1.758(4); W–C(19) 2.163(6), W–C(23) 1.876(5); W–N(2)–C(27) 159.3(3), W–C(19)–Si(1) 118.2(5), W–C(23)–Si(2) 136.4(3)

occupies the apical position. The metal atom is slightly above the basal plane defined by the alkoxy-oxygen O(1) and 2-pyridyl-nitrogen N(1) of the chelating ligand, together with the N(2)-bonded phenylimido and C(19)-bonded alkyl group. The molecular structure shown in Fig. 1 corresponds to the *syn*-rotamer (major isomer), *i.e.* the trimethylsilyl group of the alkylidene function points towards the phenylimido group.

In the ¹H NMR spectrum of a crude reaction mixture of **3**, which has been heated at reflux for only a few minutes, some resonances of a second compound, **2**, could be observed.† From these resonances it appears that **2** contains one alkoxy ligand and three equivalent alkyl groups and can, therefore, be considered as the precursor of **3**. Several unsuccessful attempts have been made to synthesize **2** under different conditions using different solvents, like in pyridine instead of

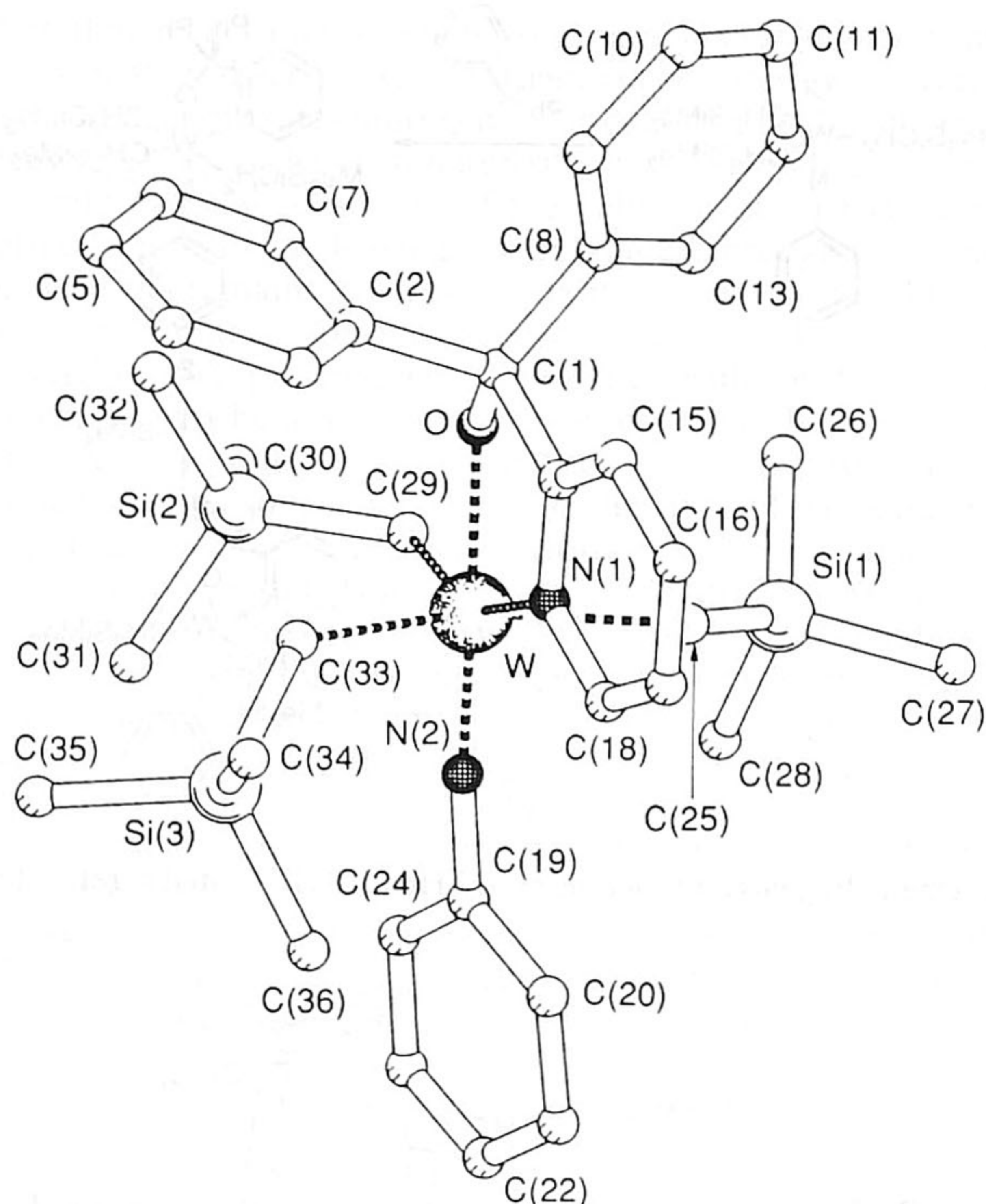


Fig. 2 PLUTON drawing of **2**. Selected bond distances (Å) and angles (°): W–O 1.968(12), W–N(1) 2.292(15), W–N(2) 1.736(14), W–C(25) 2.159(16), W–C(29) 2.127(18), W–C(33) 2.146(16), W–N(2)–C(19) 173.2(13), W–C(25)–Si(1) 121.0(9), W–C(29)–Si(2) 127.1(10), W–C(33)–Si(3) 132.9(10).

THF, and lower temperatures. Also a second reaction route to **2** in which $[\text{WCl}_3(=\text{NPh})\{\text{OCPh}_2(2\text{-py})\}]^6$ was reacted with 3 equiv. of $\text{LiCH}_2\text{SiMe}_3$ (both reagents are soluble in Et_2O at low temperatures) was unsuccessful. Fortunately, a deviating single crystal of **2** was isolated from a batch of crude **3**. On this crystal an X-ray structure determination was carried out.† Fig. 2 shows the molecular structure of $[\text{W}(\text{CH}_2\text{SiMe}_3)_3(=\text{NPh})\{\text{OCPh}_2(2\text{-py})\}]$ **2** along with the adopted numbering scheme.

Complex **2**, as anticipated, is indeed the trialkyl tungsten precursor of **3** and it is a six-coordinate species as a result of intramolecular W–N coordination. The geometry of **2** can be described as a slightly distorted octahedron in which the N(2)-bonded phenylimido group and the alkoxy-oxygen O(1) occupy the apical positions. The C(25)-, C(29)- and C(33)-bonded (trimethylsilyl)methyl groups and the pyridyl-nitrogen N(1) are positioned in the equatorial plane. One

noteworthy aspect is that both the W–N_{imido}–C_{Ph} angle [173.2(13)°] and one of the W–C_{alkyl}–Si angles [W–C(33)–Si(3) = 132.9(10)°] are significantly bigger than expected. Furthermore, there is an interesting difference between the W–N_{imido}–C_{Ph} bond angles in **2** [173.2(13)°] and in **3** [159.3(3)°]. With these two molecular structures one clearly sees the electronic advantage gained by a d⁰-metal centre when an alkylidene group is formed from two alkyl groups. On forming the alkylidene complex the electron deficiency decreases, and therefore, the donative bond of the imido-nitrogen to the tungsten centre weakens; this is reflected in a decrease of the bond angle around the imido nitrogen.

Preliminary experiments demonstrate that **3** is an active catalyst in the ring-opening metathesis polymerization of norbornene. The polymerization of norbornene at 20 °C in C_6H_6 with 0.4 mol% **3** is not complete after 12 h. However, when the same reaction is performed at 70 °C then 250 equiv. of norbornene polymerize within 5 min. In contrast, complex **3** does not react with linear olefins, such as Z-pent-2-ene.

Further studies on **3** and its derivatives are being directed towards their reactivity with linear as well as cyclic olefins and aldehydes. The promising potential of tuning the steric and electronic properties of the new chelating $[\text{OCR}^1\text{R}^2(2\text{-py})]$ -ligand in the field of early-transition-metal chemistry is currently being studied.

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Selective Phosphorylation of *p*-tert-Butylcalix[6]arene

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The synthesis of selectively phosphorylated and thiophosphorylated *p*-tert-butylcalix[6]arenes is described; the solid-state structure of the 1,4-bis(thiophosphorylated) *p*-tert-butylcalix[6]arene is elucidated by X-ray crystallography.

In addition to calix[4]arenes, the calix[6]arenes may become a versatile class of molecular building blocks for the construction of synthetic receptors. However, calix[6]arenes have an increased flexibility compared with calix[4]arenes, because of the two additional aryl moieties. So far, hexafunctionalized

calix[6]arenes have been used for the complexation of neutral molecules¹ and cations.² In order to make calix[6]arenes available as molecular building blocks, we have investigated possible synthetic routes towards selectively functionalized calix[6]arenes, as well as the conformational preferences of