Mononuclear Tungsten(VI) Phenylimido Phenoxide and Alkoxide Complexes with Intramolecular Amine Coordination: Molecular Structure of WCl₃(=NPh)[OC₆H₂(CH₂NMe₂)₂-2,6-Me-4]

Paul A. van der Schaaf,[†] Jaap Boersma,[†] Wilbert J. J. Smeets,[‡] Anthony L. Spek,[‡] and Gerard van Koten*,[†]

Debye Institute, Department of Metal-Mediated Synthesis, and Bijvoet Center for Biomolecular Research, Laboratory of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Mononuclear tungsten(VI) phenylimido phenoxide and alkoxide chlorides have been synthesized in which a potential intramolecularly coordinating amine donor atom is present. The selected ligands were phenoxides with one or two *ortho*-(dimethylamino)methyl groups, [OC₆H₄CH₂NMe₂-2] (**a**) and [OC₆H₂(CH₂NMe₂)₂-2,6-Me-4] (**b**), respectively, 8-quinolinolate (8-quin) (**c**) or α-substituted 2-pyridylmethoxides, *i.e.* 2,4-dimethyl-3-(2-pyridyl)-3-pentoxide (**d**) and diphenyl-2-pyridylmethoxide (**e**), respectively. They were attached to the metal center by reaction of their lithium or sodium salts with WCl₄(=NPh)(OEt₂) in diethyl ether. To establish the influence of a potentially intramolecular coordinating amine function, three methyl-substituted phenoxide complexes have been prepared in which a diethyl ether molecule instead of the tertiary amine function coordinates to tungsten. Variable-temperature NMR spectroscopy as well as cryoscopic molecular weight measurements in benzene indicate that these complexes are six-coordinate monomers in solution. The solid-state structure of WCl₃(=NPh)[OC₆H₂(CH₂NMe₂)₂-2,6-Me-4] (**2a**), a tungsten(VI) phenylimido phenoxide containing two potentially *ortho*-chelating (dimethylamino)methyl groups, has been determined. Crystals of **2a** are monoclinic, space-group *P*2₁/*c*, with unit-cell dimensions *a* = 6.893(1) Å, *b* = 15.415(2) Å, *c* = 21.334(2) Å, *β* = 94.53(1)°, and *V* = 2259.7 Å³, *Z* = 4, *R* = 0.0353, and *R*w = 0.0259 for 3544 observed reflections and 260 parameters. One of the *ortho*-CH₂NMe₂ substituents of the "pincer-phenolate" ligand intramolecularly coordinates to the tungsten center *trans* to the phenylimido group, whereas the second *ortho*-CH₂NMe₂ group is not coordinated. This octahedral geometry was also found for **2a** in solution, and even at elevated temperatures two resonance patterns were observed for two different *ortho*-CH₂NMe₂ substituents indicating that intramolecular exchange between the tertiary amine groups does not occur.

Introduction

During the last decade, tungsten(VI) phenoxides of the type WCl₆₋ₓ(OAr)ₓ (*x* = 0–4, 6) or W(O)Cl₄₋ᵧ(OAr)ᵧ, (*y* = 0–4) have been reported. They are known to be very active metathesis catalysts for linear as well as cyclic olefins. These complexes require the addition of a cocatalyst, *e.g.* RₓAlCl₃₋ₓ or an alkyltin hydride, to generate the active catalyst species *in situ*.[1-9] The phenoxide groups present in these tungsten catalysts increase the solubility and stability of the complexes, and more importantly, they are used to influence the steric and electronic properties of the reaction site.

Intramolecular amine coordination in high-valent (arylamine)-tungsten(VI) complexes greatly enhances their thermal stability.[10] For example, a solution of the aryltungsten(VI) oxo complex W[(*R*)-C₆H₄CH(Me)NMe₂-2]Cl₃(=O) (see i in Figure 1),
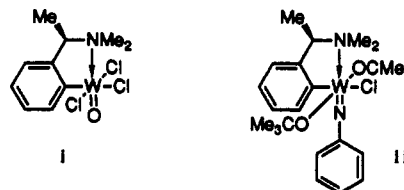

Figure 1. Examples of aryltungsten(VI) complexes stabilized by intramolecular amine coordination.

containing a chelating arylamine ligand, is stable up to at least 120 °C in an inert atmosphere. In addition, W[(*R*)-C₆H₄CH-(Me)NMe₂-2]Cl(=NPh)(OCMe₃)₂ (ii in Figure 1), an aryltungsten(VI) phenylimido complex which contains also two π-electron-donating *tert*-butoxide anions, can be melted in air (mp 138 °C) without decomposition.

Recently, we reported the synthesis of the novel tungsten(VI) alkylidene complex W(C₆H₄CH₂NMe₂-2)(=CHSiMe₃)(CH₂-SiMe₃)(=NPh) and its reactivity toward linear and cyclic olefins, ketones, and aldehydes.[11] The reactivity of this type of complex can be further tuned by the introduction of alkoxide or phenoxide ligands.[12-19] Because of the electronic flexibility of these ligands

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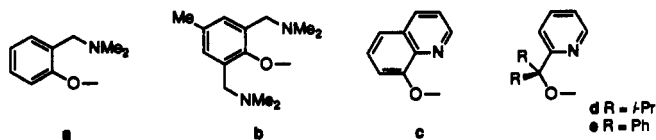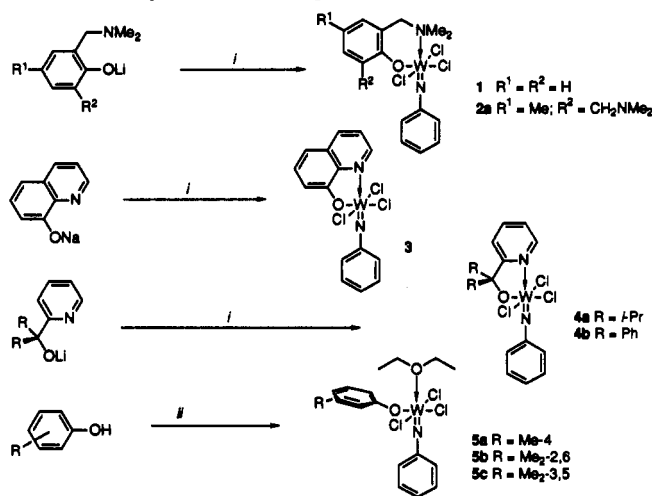(18) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986,** *108,* 2771.

Figure 2. Selected alkoxide and phenoxide ligands with a potentially *ortho*-chelating amine donor.

Scheme I. Synthesis of Complexes 1–5[a]

[a] **Key:** (i) Ligands added as their lithium or sodium salts to $WCl_4(=NPh)(OEt_2)$, in Et_2O at 0 °C; yields 86–92%; (ii) *via* alcoholysis, in Et_2O; yields 85–95%.

the degree of π-donation can be continuously adapted to the need of the metal atom, in particular during a reaction. An obvious next step is to combine intramolecular amine coordination with phenoxide and alkoxide ligands, leading to the preparation of mononuclear tungsten(VI) alkylidene complexes containing an intramolecularly coordinating alkoxide or phenoxide ligand. To this end, we started with the preparation and characterization of a series of tungsten(VI) phenylimido phenoxide and alkoxide chlorides containing a potentially coordinating amine donor. These complexes have been prepared to gather information about the stability of these complexes and their reactivity, for example toward intramolecular C–H activation, and to investigate their use as starting compounds for the synthesis of active tungsten-(VI) alkylidene species.

The ligands we used, depicted in Figure 2, are all monoanionic *O,N*-chelating ligands. The phenoxide ligands (**a**, **b**) will form a six-membered chelate ring upon W–N coordination, while the 8-quinolinolate (8-quin) (**c**) and 2-pyridylmethoxide ligands (**d**, **e**) will form a five-membered chelate ring. The "pincer-phenolate" ligand (**b**) differs from the other ligands because of the presence of two potentially *ortho*-chelating amine substituents.

To establish the influence of intramolecular W–N coordination on the stability and reactivity of these tungsten(VI) species, three substituted phenoxide (4-methyl-, 2,6-dimethyl-, and 3,5-dimethyl) tungsten(VI) phenylimido chlorides were prepared in which such a donor possibility is absent. In these complexes, the remaining sixth coordination site is occupied by a coordinating Et_2O molecule.

Results

Synthesis of the Complexes. The complexes 1–4 were prepared by reacting $WCl_4(=NPh)(OEt_2)$ with the lithium or sodium salts of the phenoxide, alkoxide, or 8-quinolinolate ligands (see Scheme I). The methyl-substituted phenoxide complexes, **5a–c**, were prepared *via* direct alcoholysis of $WCl_4(=NPh)(OEt_2)$ by the corresponding methyl-substituted phenols.

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Scheme II. Synthesis of **2a,b**[a]
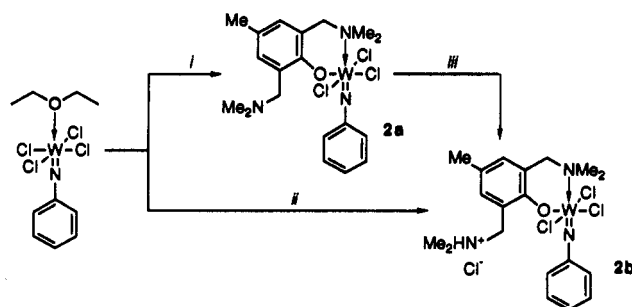
[a] Reaction in Et_2O. **Key:** (i) Addition of lithium phenoxide or *via* an alcoholysis reaction in the presence of NEt_3; (ii) alcoholysis reaction without NEt_3; (iii) 1:1 molar reaction with 1.5 M HCl solution in Et_2O.

The latter route is also a good alternative for the preparation of **2a**, provided that a nonnucleophilic base, such as triethylamine, is present to bind the HCl formed during the reaction. When this base is not added, the second *ortho*-CH_2NMe_2 substituent of the "pincer-phenolate" acts as the base and the HCl salt **2b** is obtained; see Scheme II.

These new complexes are intensely colored; *e.g.*, the aryloxides, **1**, **2a**, **3**, and **5a–c**, are deep-purple or black solids which gave deep-purple colored solutions (benzene), whereas the alkoxides, **4a,b**, are deep red, both as solids and in solution. The solid complexes are moisture sensitive but can be handled for short periods (<1 min) in air and can be stored for longer periods in an inert atmosphere.

In contrast with **2a**, complex **2b**, with one protonated *ortho*-CH_2NMe_2 substituent, is insoluble in aromatic solvents, such as toluene, and hydrocarbons and only slightly soluble in dichloromethane. Complex **2b** undergoes quantitative metathesis with, for example, acetone in a Wittig-type reaction to produce an *N*-phenyl imine and the corresponding tungsten(VI) oxo derivative (eq 1). Unfortunately, attempts to isolate the newly formed tungsten oxo phenoxide complexes were unsuccessful.

$$L_nM=N-Ph \ + \ Me_2CO \ \longrightarrow \ Me_2C=N-Ph \ + \ L_nM=O \qquad (1)$$

Solid-State structure of 2a. In order to establish the proposed *O,N*-bidentate bonding of the "pincer-phenolate" ligand in **2a**, its solid-state structure was determined by X-ray diffraction. The unit cell of **2a** comprises the packing of four discrete molecules. An ORTEP plot is given in Figure 3. The atomic coordinates and the selected bond distances and angles are given in Tables I and II, respectively.

The tungsten center has a slightly distorted octahedral geometry, due to intramolecular coordination of the *ortho*-chelating CH_2NMe_2 group, which occupies an axial position. This NMe_2 group is bonded *trans* to the phenylimido group, whereas the phenoxide oxygen and the three remaining chloride atoms are in equatorial positions. The second *ortho*-(dimethylamino)methyl group is not coordinated to the metal center and is in a position that minimizes steric interaction with the other ligands. The $W-O-C_3-N$ six-membered chelate ring is puckered. The W–N(1) bond length of 2.451(4) Å is comparable with those found for tertiary amine dative bonds in tungsten(VI)[11] and tantalum(V) complexes.[20] As expected, the length of this bond by a tertiary amino group is significantly longer than lengths of those reported for aromatic heterocyclic sp^2-nitrogen dative bonds. For example, comparable tungsten complexes containing 8-quin-

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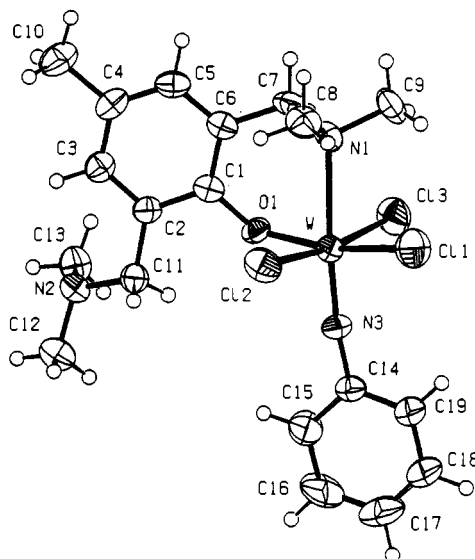
Figure 3. ORTEP drawing (50% probability level) of WCl₃-(=NPh)[OC₆H₂(CH₂NMe)₂-2,6-Me-4] (2a), with the adopted numbering scheme.

Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $WCl_3(=NPh)[OC_6H_2(CH_2NMe)_2-2,6-Me-4]$ (2a)

atom	x	y	z	$U_{eq},^a$ Å²
W	0.41822(3)	0.07236(1)	0.18508(1)	0.0354(1)
Cl(1)	0.6339(2)	0.06391(10)	0.10653(7)	0.0698(6)
Cl(2)	0.6189(2)	–0.02972(9)	0.24285(7)	0.0570(5)
Cl(3)	0.2496(2)	0.18958(9)	0.13599(7)	0.0600(6)
O(1)	0.3043(5)	0.09013(19)	0.26125(14)	0.0366(11)
N(1)	0.6413(6)	0.1868(2)	0.22543(18)	0.0409(17)
N(2)	0.0529(6)	–0.0249(3)	0.41239(18)	0.0378(16)
N(3)	0.2587(6)	–0.0035(3)	0.15136(18)	0.0410(14)
C(1)	0.3662(7)	0.1149(3)	0.3204(2)	0.0337(17)
C(2)	0.3046(7)	0.0681(3)	0.3707(2)	0.0351(17)
C(3)	0.3742(7)	0.0933(3)	0.4309(2)	0.0415(17)
C(4)	0.5003(8)	0.1630(3)	0.4417(2)	0.0433(19)
C(5)	0.5569(7)	0.2087(3)	0.3910(3)	0.0431(19)
C(6)	0.4920(7)	0.1858(3)	0.3298(2)	0.0360(17)
C(7)	0.5444(8)	0.2383(3)	0.2739(2)	0.0440(19)
C(8)	0.8287(7)	0.1529(3)	0.2542(3)	0.051(2)
C(9)	0.6906(10)	0.2505(4)	0.1769(3)	0.064(3)
C(10)	0.5708(9)	0.1878(4)	0.5086(2)	0.062(2)
C(11)	0.1691(7)	–0.0082(3)	0.3594(2)	0.0400(17)
C(12)	–0.0454(8)	–0.1090(3)	0.4057(3)	0.055(2)
C(13)	–0.0906(8)	0.0427(3)	0.4200(3)	0.052(2)
C(14)	0.1420(7)	–0.0616(3)	0.1166(2)	0.0370(17)
C(15)	0.0062(8)	–0.1107(4)	0.1454(3)	0.059(2)
C(16)	–0.1062(9)	–0.1686(4)	0.1081(3)	0.082(3)
C(17)	–0.0834(10)	–0.1761(4)	0.0449(3)	0.079(3)
C(18)	0.0480(10)	–0.1276(4)	0.0179(3)	0.064(3)
C(19)	0.1606(8)	–0.0708(3)	0.0528(2)	0.0508(19)

^{a} U(eq) = one-third of the trace of the orthogonalized U tensor.

Table II. Selected Geometrical Parameters
$WCl_3(=NPh)[OC_6H_2(CH_2NMe)_2-2,6-Me-4]$ (2a)

Bond Lengths (Å)			
W–N(1)	2.451(4)	W–Cl(1)	2.3299(15)
W–N(3)	1.723(4)	W–Cl(2)	2.3747(15)
W–O(1)	1.880(3)	W–Cl(3)	2.3496(15)
C(1)–O(1)	1.355(5)	N(3)–C(14)	1.380(6)

Bond Angles (deg)			
W–N(3)–C(14)	172.0(3)	N(1)–W–N(3)	175.53(16)
Cl(1)–W–O(1)	164.5(11)	N(1)–W–O(1)	83.38(13)
Cl(2)–W–Cl(3)	171.23(5)	W–O(1)–C(1)	136.4(3)

olinolate, or substituted derivatives, have W–N bond lengths in the range of 2.188–2.290 Å.[21–24] The W=N(3) bond length of 1.723(4) Å and the W=N(3)–C(14) bond angle of 172.0(3)°

are typical for arylimido ligands that are terminally bonded to electron-deficient early-transition-metal complexes.[25] These small bond lengths and large bond angles are the result of a strong nitrogen to metal π-donation.[25] The W–O(1) bond length of 1.880(3) Å is slightly longer than those in related tungsten(VI) phenoxides, *e.g.* cis-WCl₄(OC₆H₃Ph₂-2,6)₂ (1.824–1.855 Å),[26,27] WCl₃(OC₆H₃*i*-Pr₂-2,6)₃ (1.832–1.845 Å),[27] and trans-WCl₂-(OC₆H₅)₄[28] (average W–O = 1.82 Å).

Complexes in Solution. Association measurements in benzene show that WCl₃(=NPh)(OC₆H₄CH₂NMe₂-2) (1), WCl₃-(=NPh)[OC₆H₂(CH₂NMe₂)₂-2,6-Me-4] (2a), and WCl₃-(=NPh)[OC-*i*-Pr₂(2-Py)] (4a) are monomeric species in solution (see Experimental Section).

The NMR spectra of 1 and 2a have comparable resonance patterns, indicating that the structures of these complexes in solution are related (see Table III and experimental data). Both complexes show broadened signals for the NMe₂ and CH₂N hydrogens at ambient temperature, and in 2a the second (dimethylamino)methyl group appears as two sharp singlets, one for the CH₂N and one for the NMe₂ hydrogens. This suggests that the structure of 2a in solution is similar to that found in the solid state, *i.e.* a structure with one coordinating and one free (dimethylamino)methyl group (*vide supra*). Therefore, the single *ortho*-CH₂NMe₂ substituent in 1 most probably occupies the sixth coordination site, in analogy with the solid-state structure of 2a. The broadened ¹H NMR signals for the CH₂NMe₂ hydrogens in complexes 1 and 2a at room temperature sharpen upon raising of the temperature to 80 °C. For 2a, two sets of resonances remain for both *ortho*-CH₂NMe₂ substituents, indicating that also at elevated temperatures W–N coordination is rigid on the NMR time scale and, moreover, that intramolecular exchange between *ortho*-CH₂NMe₂ substituents does not occur. Lowering the temperature to –40 °C gives rise to decoalescence of the broadened signals observed at room temperature: the CH₂N hydrogens appear as an AB-pattern, while two distinct singlets were observed for the NMe₂ methyl groups. It must be noted that both 1 and 2a have a molecular symmetry plane containing the phenoxide ligand. This implies that the observed diastereotopicity of the CH₂N hydrogens and the NMe₂ methyl groups must arise from a different cause, *i.e.* the puckering of the six-membered W–O–C₃–N chelate ring in which the three carbon atoms are in one plane (see molecular structure of 2a). When inversion of the puckered conformation becomes slow on the NMR time scale, the apparent molecular symmetry plane disappears. The puckered conformation then is a stereogenic element which renders the CH₂N hydrogens and the NMe₂ methyl groups diastereotopic. An example of such a process has been found in, for example, triorganotin halides containing a six-membered chelate ring.[29] Figure 5 shows the two ring conformers, δ and λ, in 1, which are in fast exchange at ambient temperature. Upon lowering of the temperature, this ring-flipping process is slowed down until finally the slow-exchange limit is reached ($\Delta G^* \approx 47$ kJ mol⁻¹ for both 1 and 2a).

It is more difficult to deduct the structure of the complexes WCl₃(=NPh)(8-quin) (3) and WCl₃(=NPh)[OR₂(2-Py)] (R

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Table III. Selected ^{1}H and ^{13}C NMR Data for the Tungsten(IV) Complexes 1–5[a]

no.	complex	C_{ipso}–O	C_{ipso}–NPh	p-H NPh
1	WCl$_3$(=NPh)(OC$_6$H$_4$CH$_2$NMe$_2$-2)	160.5	151.3	6.36
2a	WCl$_3$(=NPh)[OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]	157.4	151.6	6.47
3	WCl$_3$(=NPh)(8-quinolinolate)[b]	158.6	149.4	7.12
4a	WCl$_3$(=NPh)[OCi-Pr$_2$([2]-Py)]	168.3	151.5	6.48
4b	WCl$_3$(=NPh)[OCPh$_2$([2]-Py)]	164.7	151.2	6.44
5a	WCl$_3$(=NPh)(OC$_6$H$_4$Me-4)(OEt$_2$)	163.6	150.8	6.38
5b	WCl$_3$(=NPh)(OC$_6$H$_3$Me$_2$-2,6)(OEt$_2$)	163.7	151.1	6.36
5c	WCl$_3$(=NPh)(OC$_6$H$_3$Me$_2$-3,5)(OEt$_2$)	165.6	150.8	6.36

[a] All values are in δ relative to SiMe$_4$; benzene-d_6 solvent, at 300 K. [b] In chloroform-d_1.
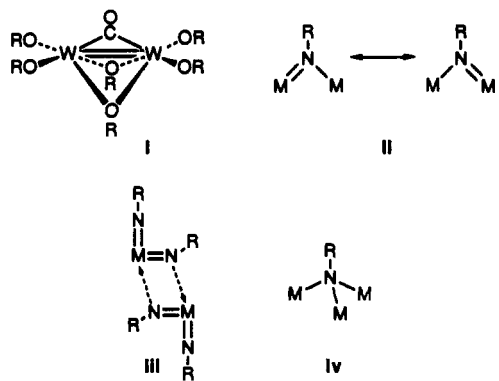

Figure 4. Schematic representation of examples of bridging alkoxide and imido ligands in early-transition-metal complexes.

= i-Pr, **4a**; R = Ph, **4b**) from their NMR data, since stereogenic elements are absent. However, the chemical shift of the proton at the *ortho*-C in the heterocyclic ring (H^2 for 8-quin and H^6 for the pyridine groups) can be used as a very efficient indicator for the absence or presence of W–N coordination. In the latter case this hydrogen atom is forced into the proximity of a W^{VI}–halogen bond and a typical downfield shift is observed. For complexes **3** and **4a,b** these chemical shift differences are 1.19, 1.34, and 1.33 ppm, respectively, with respect to the chemical shift of the corresponding hydrogen atom in the free ligand (alcohols). These shift differences indicate that W–N coordination occurs and that, consequently, the W-center in **3** and **4a,b** is six-coordinated as a result of intramolecular coordination of the amino group.

The NMR data of WCl$_3$(=NPh)(OAr)(OEt$_2$) (OAr = OC$_6$H$_4$Me-4 (**5a**), OC$_6$H$_3$Me$_2$-2,6 (**5b**), OC$_6$H$_3$Me$_2$-3,5 (**5c**)) show a very strong resemblance with those of the above mentioned complexes containing an intramolecularly coordinating amino group; see Table III. It is well-known that the chemical shift of a carbon atom bonded to the imido nitrogen[25] or the phenoxide oxygen[30] is strongly influenced by the electronic properties of the metal atom. Because of the fact that these values for **5** are very similar to those for **1–4**, it is likely that in complexes **5a–c** the phenoxide ligand is also bonded at an equatorial position and that the coordinating Et$_2$O molecule is bonded *trans* to the phenylimido ligand. The large downfield shift for the CH$_2$O hydrogens of the coordinating Et$_2$O molecule in **5** ($\Delta\delta$ = 1.0 for **5a–c**) indicates that it is bound to the metal center *via* a very strong dative bond: it appeared to be impossible to remove the ether molecule in **5c** at 50 °C *in vacuo* (10^{-3} mmHg).

In order to compare the thermal stabilities of **1** and **2a** (containing intramolecular coordination) with that of **5**, the decomposition temperatures were determined by thermographimetric analysis (TGA). It appeared that **1** and **2a** start to decompose at temperatures around 350 °C, whereas **5b** already decomposes at 150 °C.

Discussion

The present study shows that a new class of monophenoxide and monoalkoxide tungsten(VI) phenylimido complexes, with
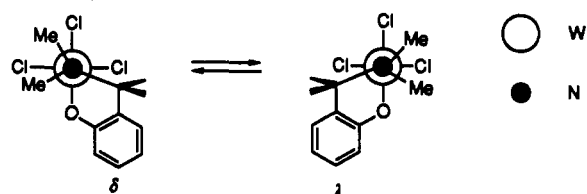

Figure 5. Newman projections along the N–W axis of **1** in which the interconversion between ring conformers, δ and λ, in a six-membered chelate ring is represented.

intramolecular W–N coordination, is easily accessible. These complexes are monomeric in the solid state (cf. molecular structure of **2a**), as well as in solution, and are six-coordinate due to intramolecular W–N coordination.

It is well established in early-transition-metal chemistry that alkoxide and phenoxide ligands may occupy either terminal or bridging positions; see Figure 4i.[19,31] Likewise, imido ligands can bridge either two and even three metal atoms, ii–iv, while the metal–nitrogen bonds may be symmetric, ii, or asymmetric, iii.[32] Examples of each type of complexes are (t-BuO)$_2$W(μ-O-t-Bu)$_2$-(μ-CO)W(O-t-Bu)$_2$[33] or W$_2$(CO)$_6$(μ-OPh)$_3$$^{(3-)}$[34] for i, (Me$_2$N)$_2$-Zr($\mu$-N-$t$-Bu)Zr(NMe$_2$)$_2$[35] for ii, [Mo(O-$t$-Bu)$_2$(N-$p$-tolyl)($\mu$-N-$p$-tolyl)]$_2$[32] for iii, and Fe$_3$($\mu$-NMe)$_2(CO)_9$[32] for iv. The molecular structure of [WCl$_4$(N-p-tolyl)]$_2$ demonstrates that even the chloride atoms present in a tungsten(VI) imido complex can bridge between two metal centers.[36]

The complexes **1–4**, however, all contain intramolecular W–N coordination that obviously is very effective in blocking the sixth coordination site. In **5** this sixth coordination site is occupied by a coordinating diethyl ether molecule. In addition, these phenoxide and alkoxide complexes are all monomeric species, even when imido as well as phenoxide or alkoxide ligands are present.

The influence of intramolecular W–N coordination on the properties of these tungsten(VI) phenoxide and alkoxide complexes appears from the high thermal stability, *i.e.* the absence of intramolecular decomposition pathways (compare: T_{dec} of **5b** = 150 °C, and T_{dec} of **1** and **2a** = 350 °C).

The strong influence of intramolecular W–N coordination was recently also found in a series of aryltungsten(VI) oxo and phenylimido chloride complexes in which a chelating arylamine ligand is present.[10] These complexes also were shown to be thermally very stable, and even at elevated temperatures no W–N dissociation processes were observed. However, in related aryltantalum(V) complexes such intramolecular amine coordination is significantly weaker, and at higher temperature Ta–N

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dissociation occurred, followed by intramolecular aminomethyl C–H activation and subsequent formation of an alkane and an intramolecularly bonded tantala(V)azacyclopropane species.[20]

To our knowledge, there is just one other reported example of a tungsten phenoxide complex in which a stabilizing chelating group is present, *viz.* low-valent tungsten 2,6-diphenylphenoxide complexes, prepared by Rothwell *et al.*, in which one of the *ortho*-phenyl substituents forms an η^6-arene bond or can give rise to a C–H activation with the subsequent formation of a σ-aryl bond.[37–42]

Compound **2a** has one strongly bonded *ortho*-CH$_2$NMe$_2$ substituent, while the second *ortho*-CH$_2$NMe$_2$ substituent is free. It is remarkable that even at elevated temperatures no exchange between these amine substituents occurs. It moreover suggests that six-coordinate tungsten centers are not capable of activating a C–H bond in an alkyl group which is held in the coordination sphere of the metal center. Finally, it is surprising that protonation of this free *ortho*-CH$_2$NMe$_2$ substituent, as in **2b**, is possible without W–O or W≡N bond cleavage. The inertness of this second amine substituent of the "pincer-phenolate" ligand may lead to interesting reactivities of its metal complexes, since a Lewis base, which is unable to coordinate, is always present in the coordination sphere of the metal center.

Conclusions

Tungsten(VI) phenylimido monophenoxide and alkoxide complexes containing chelating phenoxide or alkoxide ligands are easily accessible. They are monomeric in the solid state as well as in solution as a result of intramolecular W–N coordination. This W–N coordination is very strong as W–N dissociation processes were not observed, even at elevated temperatures. When a potentially coordinating group is absent within the molecule, coordination of a solvent molecule (diethyl ether in this case) occurs. The complexes containing intramolecular W–N coordination are thermally much more stable than the diethyl ether adducts. The "pincer-phenolate" ligand is bidentate bonded with one free *ortho*-CH$_2$NMe$_2$ substituent, and intramolecular exchange between the two amino groups does not occur. The properties of these phenoxide and alkoxide complexes are promising with respect to the planned synthesis of tungsten(VI) alkylidene complexes containing this type of ligands. The strong intramolecular W–N coordination may lead to very stable alkylidene complexes having interesting reactivities toward olefins.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of dry, deoxygenated N$_2$, using standard Schlenk techniques. All solvents were dried and distilled from sodium under nitrogen, prior to use. Commercially available reagents were used as supplied whereas WCl$_4$-(≡NPh)(OEt$_2$),[16] 2-{(dimethylamino)methyl}phenol,[44] and 2,6-bis-{(dimethylamino)methyl}-4-methylphenol[23] were synthesized by following literature procedures. Li(OC$_6$H$_4$CH$_2$NMe$_2$-2), and Li[OC$_6$H$_2$(CH$_2$-NMe$_2$)$_2$-2,6-Me-4] were prepared by reacting the phenols with *n*-BuLi

in a 1:1 ratio in hexane at –78 °C.[45] Na 8-quinolinolate was prepared from 8-hydroxyquinoline and sodium hydride in THF. Diphenyl-2-pyridylmethanol and 2,4-dimethyl-3-(2-pyridyl)pentan-3-ol were prepared *via* a modified literature procedure[46] from 2-pyridyllithium[47] and the appropriate ketone, followed by hydrolysis. The corresponding lithium alkoxides were prepared as mentioned above for the lithium phenoxides. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 or AC 300 spectrometers in benzene-d_6, at room temperature, unless noted otherwise. Thermographimetric analyses were performed on a Perkin-Elmer TGS-2 thermographic system. Cryoscopic measurements were performed in benzene in an inert atmosphere. Elemental analyses were carried out at the Institute for Applied Chemistry TNO, Zeist, The Netherlands, or by the Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr, Germany.

WCl$_3$(≡NPh)(OC$_6$H$_4$CH$_2$NMe$_2$-2) (1). Li(OC$_6$H$_4$CH$_2$NMe$_2$-2) (0.51 g, 3.24 mmol) was added as a solid to a solution of WCl$_4$(≡NPh)(OEt$_2$) (1.59 g, 3.24 mmol) in Et$_2$O (50 mL) at 0 °C. After the addition was completed, the reaction mixture was warmed to room temperature. This was accompanied by a color change of the reaction mixture from green to brick-red. The reaction mixture was stirred for 3 h, followed by removal of the volatiles *in vacuo*, and the product was extracted with CH$_2$Cl$_2$ (40 mL) and then dried *in vacuo* leaving a purple solid, which was washed with pentane (2 × 40 mL). The product was dried *in vacuo*. Yield: 2.98 g (92%, T_{dec} = 350 °C). The complex can be crystallized by cooling a toluene solution to –30 °C. ^{1}H NMR (δ): 7.23–6.60 (m, 7, aryl-H); 6.36 (t, 1, *p*-H NPh); 3.60 (br s, 2, CH$_2$N); 2.68 (s, 6, NMe$_2$). ^{13}C NMR (δ): 160.5 (C_{ipso}); 151.3 (C_{ipso} NPh); 131.8, 130.4, 130.1, 130.0–126.3, 119.1 (aryl-C); 62.8 (CH$_2$N); 50.8 (NMe$_2$). Anal. Calcd for C$_{15}$H$_{17}$Cl$_3$N$_2$OW: C, 33.90; H, 3.22; N, 5.27. Found: C, 33.84; H, 3.29; N, 5.26. Molecular weight determination by cryoscopy (0.21 g in 20.03 g of C$_6$H$_6$, 0.018 M): Calcd, 531.5; found, 515.

WCl$_3$(≡NPh)[OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4](2a). This product was synthesized *via* a procedure similar to that of **1**. Reaction of 1.42 g of Li[OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4] (6.22 mmol) with WCl$_4$(≡NPh)-(OEt$_2$) in a 1:1 molar ratio afforded 3.49 g of a dark purple solid (93%, T_{dec} = 350 °C). The product was crystallized from a saturated benzene solution layered with an equivalent amount of pentane.

Alternative synthesis *via* alcoholysis: A solution of 2,6-bis[(dimethylamino)methyl]-4-methylphenol (1.06 g, 4.77 mmol) in Et$_2$O (25 mL) was added dropwise to a mixture of WCl$_4$(≡NPh)(OEt$_2$) (2.27 g, 4.62 mmol) and NEt$_3$ (12 mmol) in Et$_2$O (50 mL). Upon addition the color of the reaction mixture immediately turned to dark red. After addition, the reaction mixture was stirred for 1 h. The solvent was removed *in vacuo* leaving a deep purple solid. The reaction product was extracted with CH$_2$Cl$_2$ (2 × 50 mL), and its ^{1}H NMR showed no impurities. Yield: 2.36 g (85%). ^{1}H NMR (δ): 7.43 (s, 1, *m*-H); 7.31 (d, 2, *o*-H NPh); 7.04 (t, 2, *m*-H NPh); 6.47 (t, 1, *p*-H NPh); 6.44 (s, 1, *m*-H); 3.61 (s, 2, CH$_2$NMe$_2$-free); 3.6 (br, 2, CH$_2$NMe$_2$-coord); 2.73 (br s, 6, CH$_2$NMe$_2$-coord); 2.21 (s, 3, *p*-Me); 2.14 (s, 6, CH$_2$NMe$_2$-free). ^{13}C NMR (δ): 157.4 (C_{ipso}); 151.6 C_{ipso} NPh); 136.4, 131.8, 131.0, 130.2, 130.1, 129.5–127.1 (aryl-C); 62.8 (CH$_2$N-coord); 57.3 (CH$_2$N-free); 50.8 (NMe$_2$-coord); 45.9 (NMe$_2$-free); 20.9 (*p*-Me). Anal. Calcd for C$_{19}$H$_{26}$Cl$_3$N$_3$OW: C, 37.87; H, 4.35; N, 6.97. Found: C, 37.61; H, 4.25; N, 6.97. Molecular weight determination by cryoscopy (0.27 g in 18.60 g of C$_6$H$_6$, 0.021 M): Calcd, 602.7; found, 618.

WCl$_3$(≡NPh)[OC$_6$H$_2$(CH$_2$NMe$_2$-2)(Me-4)(CH$_2$NHMe$_2$Cl-6)](2b). This complex was prepared *via* the alcoholysis reaction described above for **2a**. However, the alcoholysis was carried out in the absence of NEt$_3$. Complex **2b** was also prepared by a titration of a solution **2a** in Et$_2$O with a 1.8 M HCl solution in Et$_2$O. Both reactions gave **2b** as a red solid quantitatively. ^{1}H NMR (in CDCl$_3$) (δ): 12.6 (br s, 1, NH); 7.9–7.0 (m, 7, Ar-H); 4.21 (d, 2, CH$_2$NHMe$_2$); 4.11 (s, 2, CH$_2$NMe$_2$); 2.96 (s, 6, CH$_2$NMe$_2$); 2.72 (d, 6, CH$_2$NHMe$_2$); 2.50 (s, 3, *p*-Me). Anal. Calcd for C$_{19}$H$_{27}$Cl$_4$N$_3$OW: C, 35.71; H, 4.26; N, 6.57. Found: C, 35.47; H, 4.62; N, 6.35.

WCl$_3$(≡NPh)(8-quinolinolate) (3). This product was prepared from WCl$_4$(≡NPh)(OEt$_2$) (4.82 g, 9.83 mmol) and Na 8-quinolinolate (1.65 g, 9.87 mmol) by a procedure (12 h of stirring) similar to that described above for **1**. Crystalline, deep-purple **3** was obtained by cooling a saturated

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CH$_2$Cl$_2$ solution to –30 °C. Yield: 4.81 g (87%). ^{1}H NMR (in CDCl$_3$) (δ): 9.58 (d, 1, H^2); 8.59 (d, 1, H^7); 7.90–7.25 (m, 8, aryl-H); 7.12 (t, 1, p-H NPh). ^{13}C NMR (δ): 158.6 (C$_{ipso}$ OAr); 149.9 (C$_{ipso}$ NPh); 140.1, 140.0, 132.2, 130.5, 129.6, 129.2, 127.6, 124.6, 123.6 118.4 (aryl-C). Anal. Calcd for C$_{15}$H$_{11}$Cl$_3$N$_2$OW: C, 34.29; H, 2.11; N, 5.33. Found: C, 34.34; H, 2.19; N, 5.26.

WCl$_3$(=NPh)[OC-i-Pr$_2$(2-Py)] (4a). This complex was prepared *via* a procedure similar to the one given for **1**. Reaction of Li[OC-i-Pr$_2$-(2-Py)] (3.21 g, 16.11 mmol) with 1 equiv of WCl$_4$(=NPh)(OEt$_2$) in Et$_2$O (80 mL) yields 8.31 g of **4a** as a red solid (90%). ^{1}H NMR (δ): 9.56 (d, 1, H^6); 7.28 (d, 2), 6.99 M, 3), 6.68 (d, 1), 6.55 (t, 1) (aryl-H); 6.48 (t, 1, p-H NPh); 2.27 (dq, 2, –CHMe$_2$); 0.99, 0.97 (2d, 12, –CHMe$_2$). ^{13}C NMR (δ): 168.3 (C$_{ipso}$ Py); 151.5 (C$_{ipso}$ NPh); 149.4, 139.8, 131.1, 129.9, 124.7, 121.3 (aryl-C); 105.3 (CO); 36.5 (–CHMe$_2$); 20.1, 17.8 (–CHMe$_2$). Anal. Calcd for C$_{18}$H$_{23}$Cl$_3$N$_2$OW·0.5C$_6$H$_6$: C, 41.17; H, 4.28; N, 4.57. Found: C, 40.98; H, 4.24; N, 5.53. Molecular weight determination by cryoscopy (0.14 g in 16.45 g of C$_6$H$_6$, 0.013 M): Calcd, 573.6; found, 565.

WCl$_3$(=NPh){OCPh$_2$(2-Py)} (4b). This complex was prepared in THF (reflux, 3 h), using the workup procedure described for **1**. Starting with Li[OCPh$_2$(2-Py)] (1.23 g, 4.60 mmol) yields 2.54 g of **4b** as a red solid (86%). ^{1}H NMR (δ): 9.51 (d, 1, H^6 Py); 7.36–6.82 (m, 16, aryl-H); 6.56 (t, 1, H^5 Py); 6.44 (t, 1, p-H NPh). ^{13}C NMR (δ): 164.7 (C$_{ipso}$ Py); 151.2 (C$_{ipso}$ NPh); 148.8, 142.5, 139.5, 131.3, 129.9, 129.0, 128.9, 128.9, 127.7, 125.1 (aryl-C); 103.7 (CO). Anal. Calcd for C$_{24}$H$_{19}$Cl$_3$N$_2$OW: C, 44.93; H, 2.98; N, 4.37. Found: C, 45,00; H, 3.06; N, 4.43.

Synthesis of the Methyl-Substituted Phenoxide Tungsten(VI) Phenylimido Chlorides. One equivalent of 4-methyl-, 2,6-dimethyl-, or 3,5-dimethylphenol was added as a solid to a solution of WCl$_4$(=NPh)(OEt$_2$) (10 mmol) in Et$_2$O (60 mL) over a period of 15 min. During the reaction the reaction flask was flushed with a flow of N$_2$. When the evolution of HCl had ceased (generally after 2 h), the crude reaction mixture was concentrated to 10 mL *in vacuo* and then cooled to 0 °C. The product was separated from the Et$_2$O layer by centrifugation and dried *in vacuo*. The isolated yields of the products, which are moisture-sensitive, deep-purple solids, are generally between 85 and 95%.

WCl$_3$(=NPh)(OC$_6$H$_4$Me-4)(OEt$_2$) (5a). ^{1}H NMR (δ): 7.03–6.79 (m, 8, aryl-H); 6.38 (t, 1, p-H NPh); 4.31 (q, 4, OCH$_2$CH$_3$), 2.08 (s, 3, Me-4); 1.14 (t, 6, OCH$_2$CH$_3$). ^{13}C NMR (δ): 163.6 (C$_{ipso}$ OAr); 150.8 (C$_{ipso}$ NPh); 136.1, 132.0, 130.0, 129.9, 127.7, 118.1 (aryl-C); 66.2 (OCH$_2$-CH$_3$); 20.6 (Me-4); 13.3 (OCH$_2$CH$_3$). Anal. Calcd for C$_{17}$H$_{22}$Cl$_3$-NO$_2$W: C, 36.29; H, 3.94; N, 2.49. Found: C, 36.18; H, 3.88; N, 2.54.

WCl$_3$(=NPh)(OC$_6$H$_4$Me$_2$-2,6)(OEt$_2$) (5b). T$_{dec}$ = 150 °C. ^{1}H NMR (δ): 6.96–6.82 (m, 6, aryl-H); 6.69 (t, 1, p-H OAr); 6.36 (t, 1, p-H NPh); 4.27 (q, 4, OCH$_2$CH$_3$); 2.52 (s, 6, Me-2,6); 1.12 (t, 4, OCH$_2$CH$_3$. ^{13}C NMR (δ): 163.7 (C$_{ipso}$ OAr); 151.1 (C$_{ipso}$ NPh); 136.0, 132.0, 129.7, 129.3, 127.7, 125.9 (aryl-C); 65.7 (OCH$_2$CH$_3$); 17.9 (Me-2,6); 13.3 (OCH$_2$CH$_3$). Anal. Calcd for C$_{18}$H$_{24}$Cl$_3$NO$_2$W: C, 37.50; H, 4.20; N, 2.43. Found: C, 37.42; H, 4.30; N, 2.47.

WCl$_3$(=NPh)(OC$_6$H$_4$Me$_2$-3,5)(OEt$_2$) (5c). ^{1}H NMR (δ): 7.01–6.8 (m, 6, aryl-H); 6.45 (s, 1, p-H OAr); 6.36 (t, 1, p-H NPh); 4.33 (q, 4, OCH$_2$CH$_3$), 1.92 (s, 6, Me-2,6); 1.16 (t, 4, OCH$_2$CH$_3$). ^{13}C NMR (δ): 165.6 (C$_{ipso}$ OAr); 150.8 (C$_{ipso}$ NPh); 139.4, 131.9, 130.0, 128.3, 116.0 (aryl-C); 66.2 (OCH$_2$CH$_3$); 21.1 (Me-3,5); 13.3 (OCH$_2$CH$_3$). Anal. Calcd for C$_{18}$H$_{24}$Cl$_3$NO$_2$W: C, 37.50; H, 4.20; N, 2.43. Found: C, 37.36; H, 4.22; N, 2.49.

X-ray Structure Determination and Refinement of Complex 2a. A dark-red block-shaped crystal was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD4T diffractometer (rotating anode, 50 kV, 200 mA, graphite-monochromated Mo Kα radiation) for data

Table IV. Crystal Data and Details of the Structure Determination of Complex **2a**

formula	WC$_{19}$H$_{26}$Cl$_3$N$_3$O
mol wt	602.64
space group	P2$_1$/c (No. 14)
a–c, Å	6.893(1), 15.415(2), 21.334(2)
β, deg	94.53(1)
V, Å^3	2259.7(5)
Z	4
D$_{calc}$, g cm^{-3}	1.772
μ, cm^{-1}	55.9
radiation (λ, Å)	Mo Kα (graphite-monochromated) (0.710 73)
final R, and R$_w$, S	0.0353, 0.0259, 1.96
min, max resd dens, e/Å^3	–0.84, 0.71 (near W)

collection. Unit-cell parameters were determined from a least-squares treatment of the SET4 settings angles of 25 reflections with 11.3 < θ < 14.2°. Unit-cell parameters were checked for the presence of higher lattice symmetry.[48] Data were corrected for Lp and for absorption (DIFABS;[49] correction range 0.818–1.216) and for linear decay (61%) observed in the intensity control reflections during the 36 h of X-ray exposure time. The structure was solved with direct methods (SHELXS86)[50] and subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques. H-atoms were introduced at calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, and H-atoms with one common isotropic thermal parameter (U = 0.071(3) Å^2). Weights were introduced in the final refinement cycles; convergence was reached at R = 0.0353 and R$_w$ = 0.0259, with w = 1/[σ^2(F)]. Crystal data and the numerical details of the structure determination are given in Table IV. Final atomic coordinates and the equivalent thermal parameters are listed in Table I. Neutral-atom scattering factors were taken from Cromer and Mann[51] and corrected for anomalous dispersion.[52] All calculations were performed with SHELX76[53] and PLATON[54] (geometrical calculations and illustrations) on a DEC 5000 system.

Supplementary Material Available: Tables of anisotropic thermal parameters, all H atoms parameters, bond lengths and angles, and crystallographic details for **2a** (5 pages). Ordering information is given on any current masthead page.

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