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Thermally Stable Aryltungsten(VI) Oxo and Phenylimido Complexes Containing Phenyl Ligands with *ortho*-Chelating Tertiary Amine Substituents: Molecular Structures of $W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}O)$ and $W(C_6H_4CH_2NMe_2\text{-}2)Cl_2({=}NPh)(OCMe_3)$

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

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

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Thermally stable aryltungsten(VI) oxo and phenylimido complexes have been synthesized using phenyl ligands with *ortho*-chelating CH_2NMe_2, $CH(Me)NMe_2$, and CH_2OMe substituents. By a combination of the stabilizing features of the *ortho*-chelating phenyl ligands with those of *tert*-butoxide ligands, aryltungsten(VI) phenylimido complexes have been obtained which are not only surprisingly thermally stable (up to at least 140 °C) but also stable toward air and water. The solid-state structures of two of these complexes, $W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}O)$ (**1b**) and $W(C_6H_4CH_2NMe_2\text{-}2)Cl2({=}NPh)(OCMe_3)$ (**5**) have been investigated. Crystals of **1b** are monoclinic, space group $P2_1$, with unit-cell dimensions $a = 8.182(1)$ Å, $b = 12.100(1)$ Å, $c = 13.885(1)$ Å, $\beta = 90.04(1)°$, $V = 1374.6(2)$ Å^3, $Z = 4$, final $R = 0.033$, and $R_w = 0.041$ for 4561 reflections with $I > 2.5\sigma(I)$ and 308 parameters. Crystals of **5** are monoclinic, space group $P2_1/n$, with unit-cell dimensions $a = 9.0035(5)$ Å, $b = 25.182(1)$ Å, $c = 9.3131(5)$ Å, $\beta = 97.621(4)°$, $V = 2092.9(2)$ Å^3, $Z = 4$, final $R = 0.047$, and $R_w = 0.040$ for 2785 reflections with $I > 2.5\sigma(I)$ and 228 parameters. Both complexes are monomeric, octahedral species which are six-coordinated as a result of intramolecular amine coordination (in a *trans* position relative to the oxo group in **1b** and the phenylimido group in **5**). These aryltungsten(VI) complexes are six-coordinate in solution both at ambient and at elevated temperatures.

Introduction

Recently, we published the synthesis of a series of thermally stable aryltantalum(V) complexes in which the strategy of using intramolecular coordination of tertiary amines was successfully applied.[1] The presence of a chelating arylamine ligand not only stabilizes the resulting organotantalum(V) complexes but is also responsible for an interesting intramolecular aminomethyl C–H activation reaction, which results in the formation of an alkane and an intramolecularly bonded tantala(V)azacyclopropane species. We were interested whether similar effects could occur in corresponding high-valent organotungsten complexes. Therefore, we set out to study the accessibility and stability of such aryltungsten(VI) complexes and to use the results in the design of tungsten(VI) alkylidene complexes for olefin metathesis and ring-opening metathesis polymerization reactions.[2]

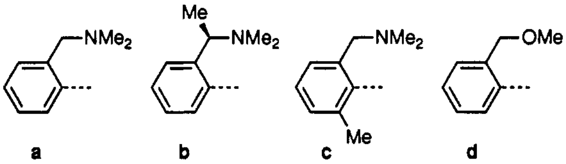

Figure 1. Selected bidentate, monoanionic aryl ligands.

We here report the synthesis and characterization of a series of stable, monomeric aryltungsten oxo and phenylimido complexes, containing potentially bidentate aryl ligands (cf. Figure 1).

The selected bidentate, monoanionic ligands possess an anionic *ipso*-carbon atom and either a tertiary amine (**a**–**c**) or an ether oxygen atom (**d**) as ligating sites. Ligand **b** contains a stereogenic benzylic center which provides a unique NMR probe[3,4] for the detection of W–N coordination. The *ortho*-methyl-containing ligand **c** is of interest because it lacks β-hydrogen atoms. Its methyl group may interfere, for example *via* γ-elimination reactions, with other ligands present in the tungsten coordination sphere. In ligand **d** the dimethylamino group is replaced by a more weakly donating methoxy group.

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[*] To whom correspondence should be addressed.

[†] Debye Institute.

[‡] Bijvoet Center for Biomolecular Research.

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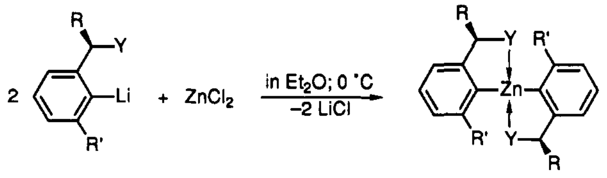
Scheme I



R = R' = H; Y = NMe$_2$
R = Me; R' = H; Y = NMe$_2$
R = H; R' = Me; Y = NMe$_2$
R = R' = H; Y = OMe

Finally, it is well-documented that improved stability toward intramolecular decomposition pathways, e.g. β-elimination, can be achieved by using more strongly π-electron-donating ligands, such as the phenylimido group instead of the oxo group, and by introducing hard alkoxide ligands.[5] Therefore, derivatives of W(C$_6$H$_4$CH$_2$NMe$_2$-2)-Cl$_3$(=NPh) (**3a**) have been prepared, and characterized, in which the chlorides are successively replaced by *tert*-butoxy groups.

Results

Synthesis and Stability of the Aryltungsten(VI) Complexes. The new aryltungsten(VI) oxo and phenylimido complexes **1**–**6** have been prepared *via* metalation of the starting tungsten chloride complex with the diarylzinc derivative (ZnAr$_2$) of the corresponding ligand. These diarylzinc compounds were prepared from the corresponding aryllithium compound and zinc dichloride (see Scheme I).

Bis[2-(methoxymethyl)phenyl]zinc, the diarylzinc compound derived from **d**, is new, while the diarylzinc compounds derived from **a**–**c** have been reported before.[1f,6,7]

For 1–4, the synthesis was carried out using a diethyl ether suspension of tungsten oxo or phenylimido tetrachloride at low temperature. Complexes **5** and **6** were prepared in CH$_2$Cl$_2$ at 0 °C, using the anionic tungsten chloride complex [WCl$_{5-x}$(=NPh)(OCMe$_3$)$_x$][NEt$_4$] (x = 1 and 2, respectively). These anionic tungsten chlorides are easily accessible and are stable toward intramolecular decomposition.[8] The alkyl complexes **7a,b** were prepared by adding 1 equiv of LiCH$_2$SiMe$_3$ to a benzene solution of **6a,b**, respectively (see Scheme II).

Initial attempts to prepare the described aryltungsten(VI) complexes **1**–**6** involved reactions of the tungsten chlorides with the more easily accessible organolithium or Grignard reagents. None of these reactions afforded an isolable aryltungsten(VI) complex, but unidentifiable products were obtained, most probably due to the greater reactivity of lithium and magnesium compounds in substitution and reduction reactions of metal halides.

Complexes **1**–**4** were obtained as dark, moisture- and air-sensitive solids which decompose rapidly in air but are stable for several months under an inert atmosphere at ambient temperatures. Surprisingly, **1b** tolerated refluxing in toluene under a nitrogen atmosphere for at least 1 week, whereas **2** and **4** slowly decompose in solution under an inert atmosphere at 80 °C. Even **3c**, containing an *o*-Me group, does not decompose *via* a γ-elimination reaction, which is known to be a common decomposition pathway for *o*-Me-containing ligands in both early-[9] and late-transition-metal chemistry.[10] The stability of the aryltungsten(VI) complexes does not change significantly when the oxo group is replaced by a phenylimido group. However, when a *tert*-butoxy group, which is a good π donor, is attached to the tungsten center, as in **5**, the stability is enhanced dramatically. For example, **5** can be handled in air, and the data collection for an X-ray diffraction study (*vide infra*) could be performed in air without taking special precuations; however, for longer periods it is advisable to store **5** under an inert atmosphere. Complex **5** slowly decomposes upon heating in air (dec pt ~145 °C). Complexes **6a,b**, containing two *tert*-butoxy groups, are very air stable, even for longer periods. For example, **6b** can be melted in air without decomposition (mp 138 °C), and even addition of water to a solution of **6b**, at 300 K, in toluene-k_8 does not lead to decomposition. Solutions of **7a,b**, which, besides two *tert*-butoxy groups, contain a (trimethylsilyl)methyl group, are thermally stable under an inert atmosphere up to at least 80 °C but slowly decompose upon exposure to air.

Structures of the Aryltungsten(VI) Complexes 1–7 in the Solid State and in Solution. Solid-State Structures. To elucidate the stereochemistry of these complexes and to have direct proof for the intramolecular coordination of NMe$_2$ group, X-ray structure determinations were carried out on W[(*R*)-C$_6$H$_4$CH(Me)NMe$_2$-2]Cl$_3$(=O) (**1b**) and W(C$_6$H$_4$CH$_2$NMe$_2$-2)Cl$_2$(=NPh)-(OCMe$_3$) (**5**). Suitable crystals were obtained by cooling saturated hexane solutions of **1b** and **5** to −30 °C.

The asymmetric unit in the crystal structure of **1b** contains two independent molecules which are chemically identical but which differ slight, although not significantly, in structure. Figure 2 shows the ORTEP drawings of **1b** and **5** together with the adopted numbering schemes. The atomic coordinates for the molecules, as well as the selected bond distances and angles, are given in Tables I–IV.

The tungsten atoms in both complexes are six-coordinate. In **1b**, C$_{ipso}$ and the three chlorine atoms lie in one plane, and in **5**, the same is true for C$_{ipso}$, two chlorine atoms, and the *tert*-butoxide group. Intramolecular W–N coordination occurs in both complexes with the N atom *trans* to the oxo oxygen in **1b** and *trans* to the imido tungsten in **5**. The resulting W–C–C–C–N chelate rings are slightly puckered.

The W–N bond lengths in **1b** and **5** are different, i.e. 2.499(7) and 2.476(7) Å for both residues in **1b** (average 2.487(5) Å) and 2.420(8) Å in **5**, but both lie in the range of W–N,[2] Ta–N,[1] and Sn–N[4] bond lengths in complexes with this type of chelating ligand. They also are close to the bond lengths of a tungsten(VI) tmeda complex, which, to our knowledge, is the only example of a tertiary amine

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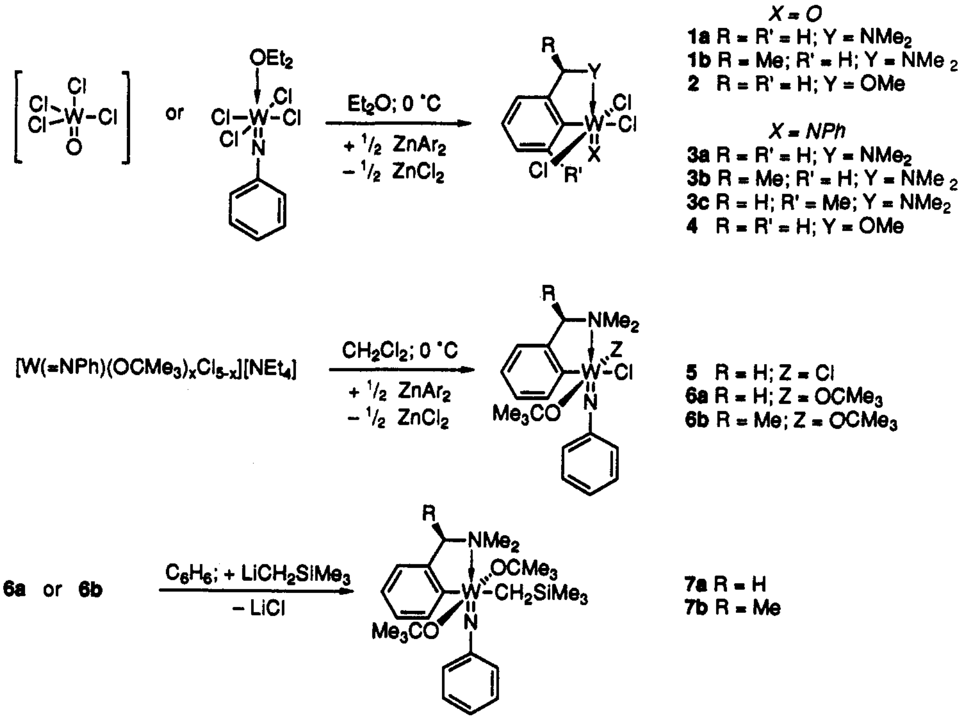
Scheme II



coordinating to a tungsten(VI) center.[11] The *R* configuration of the benzylic carbon atom in **1b** could be unambiguously established and is in accord with the configuration of the starting (*R*)-α-methylbenzylamine.

Structures in Solution. The aryltungsten(VI) complexes **1**–**7** can be either five- or six-coordinate depending on whether intramolecular coordination of the amino group, for ligands **a**–**c**, or methoxy group, for ligand **d**, occurs. Some relevant ^{1}H and ^{13}C NMR data are given in Tables V and VI, respectively.

The possibility of detecting W–N or W–O dative bonding in solution by NMR spectroscopy depends on the ligand arrangement in the complexes. When the molecule contains a plane of symmetry that also contains the benzylic carbon center and/or the amine nitrogen center, W–N coordination cannot be established. Although the chemical shifts of the NMe_2 and OMe groups in these complexes do not allow conclusions to be drawn about the presence of W–N and W–O coordination, they do suggest that all resonances are shifted significantly to lower field with respect to those in the free ligand ($\Delta\delta \approx 0.75$ for the NMe_2 group and $\Delta\delta \approx 0.85$ for the OMe group relative to the free ligands in the same solvent). Moreover, the resonance of the NMe_2 group shifts to higher field when the chlorine atoms in the aryltungsten phenylimido complexes are successively replaced by *tert*-butoxy groups ($\Delta\delta \approx 0.1$ per $OCMe_3$ group). This substituent effect on the NMe_2 chemical shift does suggest that W–N coordination occurs in these complexes. A similar trend is observed for **2** and **4**, derived from ligand **d**. With ligand **b**, containing a chiral benzylic carbon atom, a stereogenic center is introduced. All complexes containing this ligand show diastereotopicity for the NMe_2 groups, which unambiguously demonstrates that also in solution W–N coordination is present (on the NMR time scale).[3]

Discussion

The present results show that stable aryltungsten(VI) complexes are easily accessible when phenyl ligands are used which contain a potentially coordinating group. With these types of ligands even simple aryltungsten(VI) oxo and phenylimido trichlorides show very good thermal stability, when compared with most of the earlier reported aryltungsten complexes.[12] The first examples of aryltungsten(II) complexes with intramolecular coordination were reported recently, viz. divalent complexes prepared by oxidative-addition reactions of benzylideneamines with zerovalent tungsten complexes.[13] To our knowledge, just one thermally stable aryltungsten(VI) complex has been reported (which is stabilized by a terdentate tris(3,5-dimethylpyrazolyl)borate ligand).[14]

As expected, the stability of aryltungsten phenylimido trichlorides can be further enhanced by replacing the chloride anions by strong π-electron-donor substituents, such as *tert*-butoxides, which render the metal center less electron deficient. The π-electron-donating capacity of the *tert*-butoxide ligand is reflected in the NMR data for complexes **5** and **6**. When in these complexes the chemical shift of C_{ipso} of the chelating ligand is compared with those of complexes **3**, in which *tert*-butoxy groups are absent, the resonance for C_{ipso} is shifted to higher field (see Table

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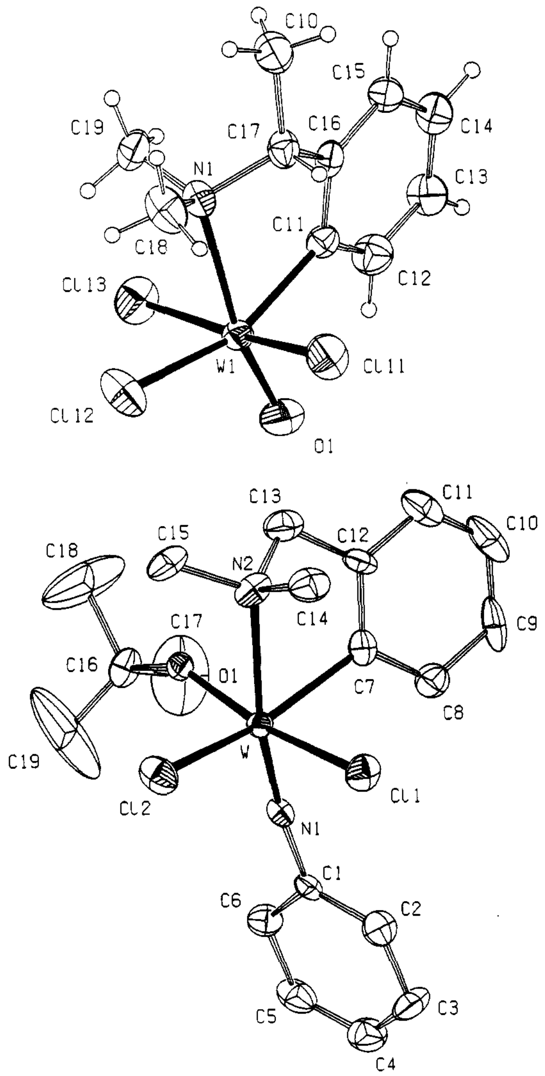

Figure 2. ORTEP drawings (30% probability level) of **1b** (top; one residue is shown) and **5** (bottom; H atoms are omitted for clarity) with the adopted numbering schemes.

Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parametes for W[(*R*)-$C_6H_4CH(Me)NMe_2$-2]Cl_3(=O) (1b)

atom	*x*	*y*	*z*	U_{eq}, Å^2
W(1)	0.20102(4)	1.0031(3)	0.01249(2)	0.0403(1)
O(1)	0.0288(10)	0.9411(7)	0.0530(5)	0.080(3)
N(1)	0.4665(9)	1.0520(6)	−0.0642(5)	0.050(3)
C(10)	0.6742(13)	0.9560(10)	−0.1732(9)	0.078(5)
C(11)	0.2348(11)	0.8855(8)	−0.0983(6)	0.045(3)
C(12)	0.1149(13)	0.8168(10)	−0.1268(8)	0.069(4)
C(13)	0.1334(13)	0.7424(10)	−0.1990(7)	0.064(4)
C(14)	0.2822(14)	0.7352(10)	−0.2468(7)	0.060(4)
C(15)	0.4107(12)	0.8024(9)	−0.2207(6)	0.050(3)
C(16)	0.3909(12)	0.8784(8)	−0.1461(7)	0.046(3)
C(17)	0.5305(11)	0.9439(8)	−0.1034(7)	0.051(3)
C(18)	0.5897(13)	1.1015(10)	−0.0005(9)	0.073(4)
C(19)	0.4331(13)	1.1290(8)	−0.1461(8)	0.066(4)
Cl(11)	0.3686(5)	0.8981(3)	0.1123(2)	0.0792(10)
Cl(12)	0.2555(4)	1.1533(3)	0.1082(3)	0.0864(11)
Cl(13)	0.0684(3)	1.1181(3)	−0.0921(2)	0.0765(10)
W(2)	0.28348(4)	0.14603(4)	0.49399(3)	0.0491(2)
O(2)	0.4840(9)	0.1589(9)	0.4787(8)	0.108(4)
N(2)	−0.0069(9)	0.1493(7)	0.5440(6)	0.055(3)
C(20)	−0.1748(13)	0.2144(12)	0.6861(8)	0.075(4)
C(21)	0.2579(12)	0.2655(10)	0.5999(8)	0.056(4)
C(22)	0.3908(12)	0.3437(10)	0.6169(8)	0.062(4)
C(23)	0.3765(14)	0.4216(11)	0.6886(8)	0.076(5)
C(24)	0.2378(14)	0.4231(11)	0.7456(7)	0.077(5)
C(25)	0.1180(15)	0.3482(10)	0.7347(7)	0.070(4)
C(26)	0.1264(11)	0.2705(9)	0.6605(7)	0.048(3)
C(27)	−0.0069(12)	0.1817(8)	0.6462(7)	0.061(3)
C(28)	−0.0964(16)	0.0417(11)	0.5363(10)	0.088(5)
C(29)	−0.0998(13)	0.2342(9)	0.4867(7)	0.067(4)
Cl(21)	0.2952(5)	0.0019(3)	0.6025(3)	0.1003(13)
Cl(22)	0.1935(5)	0.0235(3)	0.3754(2)	0.0868(13)
Cl(23)	0.2304(5)	0.2843(3)	0.3844(2)	0.0848(11)

Table II. Selected Geometrical Data for W[(*R*)-$C_6H_4CH(Me)NMe_2$-2]Cl_3(=O) (1b)

residue 1		residue 2	
	Bond Lengths (Å)		
W(1)–C(11)	2.091(9)	W(2)–C(21)	2.073(12)
W(1)–Cl(11)	2.308(4)	W(2)–Cl(21)	2.307(4)
W(1)–Cl(12)	2.322(4)	W(2)–Cl(22)	2.334(3)
W(1)–Cl(13)	2.305(3)	W(2)–Cl(23)	2.307(3)
W(1)–O(1)	1.678(8)	W(2)–O(2)	1.662(7)
W(1)–N(1)	2.499(7)	W(2)–N(2)	2.476(7)
	Bond Angles (deg)		
N(1)–W(1)–O(1)	168.5(3)	N(2)–W(2)–O(2)	169.1(4)
N(1)–W(1)–C(11)	74.8(3)	N(2)–W(2)–C(21)	72.1(3)
C(11)–W(1)–Cl(12)	157.7(3)	C(21)–W(2)–Cl(22)	155.7(3)
Cl(11)–W(1)–Cl(13)	171.33(12)	Cl(21)–W(2)–Cl(23)	171.43(14)
C(11)–W(1)–O(1)	93.9(3)	C(21)–W(2)–O(2)	96.5(4)

VI). We also note that $^1J_{WC}$ increases with increasing numbers of *tert*-butoxy groups. This increase suggests that the W–C_{ipso} bond acquires a larger s-orbital contribution. However this effect is not reflected in the W–C_{ipso} bond lengths for the two aryl groups in the solid-state structures; 2.091(9) and 2.073(2) Å for **1b** and 2.137(11) Å for **5**, which differ less than the sum of their 3σ values.

The π-donating properties of the phenylimido and *tert*-butoxy groups **1b** and **5** are reflected in the opening of the W–N–C and W–O–C angles around the imido nitrogen to 170.4° and around the *tert*-butoxy oxygen to 145.4°. Surprisingly, the W–N bond in the phenylimido complex **5** is significantly shorter than this bond in the oxo complex **1b**, with lengths of 2.420(8) and 2.487(7) Å, respectively. If this shortening is discussed in terms of trans influence of the oxo and imido ligands, it would mean that the oxo ligand is a better electron donor than the phenylimido group, in contrast with claims in the literature.[5b] However, it must be noted that substitution of a chloride by a *tert*-butoxy group in an equatorial position may also influence, both sterically and electronically, the bond lengths of the ligands in the apical positions.

Interestingly, the substituent effect of the number of *tert*-butoxy groups is also observed for other resonances in the ^{1}H NMR data for compounds **3**–**7** (see Table V). For example, the absorption of the *ortho* proton of the aryl ligand shifts to higher field when the electron density on the metal center is increased.

The trend in the values of $^1J_{WC}$ observed in the compounds of types **3**–**6** is not continued in the compounds of type **7**. We believe that this is caused by the introduction of an alkyl substituent. However, using the other substituent effects on the chemical shift in type **7** compounds, the structure of **7a,b** in solution can be unambiguously established. The *ortho* H chemical shift seems to be an excellent indicator, being close to the imido nitrogen atom, as are the same protons in **3**, **5**, and **6**, and shows the same substituent effect. On the basis of this effect, we propose a structure for **7a,b** in which the NMe_2 group coordinates to the metal center *trans* with respect to the phenylimido group. The change in the trend of $^1J_{WC}$ would then be caused by the presence of a *trans* CH_2SiMe_3 substituent in **7** as compared with chloride substituents in **3**–**6**.

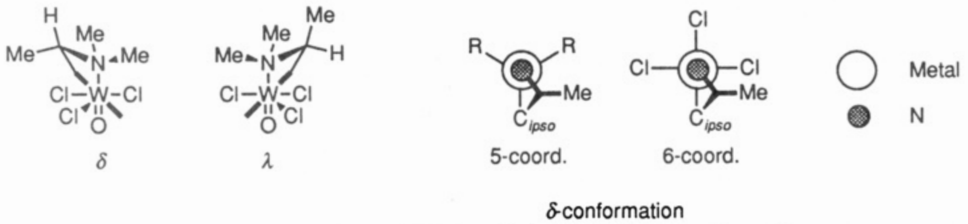

Figure 3. Schematic representation of the structures of **1b** in which the chelate ring has either a δ or λ conformation, together with two Newman projections along the N–metal axis of the trigonal-bipyramidal complex **8** and the octahedral complex **1b** showing the increased steric α-Me/equatorial ligand interaction, *i.e.* Me/R for **8** and Me/Cl for **1b**, *when* the chelate ring is in the δ conformation.

Table III. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $W(C_6H_4CH_2NMe_2\text{-}2)Cl_2({=}NPh)(OCMe_3)$ (5)

atom	x	y	z	U_{eq},[a] Å^2
W	0.64126(5)	0.13486(2)	0.21765(5)	0.0300(1)
Cl(1)	0.8961(3)	0.14008(14)	0.3426(3)	0.0511(10)
Cl(2)	0.5868(4)	0.18701(12)	0.4202(3)	0.0579(12)
O(1)	0.4610(7)	0.1477(2)	0.1122(7)	0.035(3)
N(1)	0.6256(9)	0.0705(3)	0.2730(9)	0.033(3)
N(2)	0.6851(10)	0.2191(3)	0.1056(11)	0.044(3)
C(1)	0.6388(11)	0.0181(4)	0.3257(11)	0.033(3)
C(2)	0.7775(12)	–0.0002(5)	0.3838(14)	0.052(5)
C(3)	0.7964(16)	–0.0528(5)	0.4382(14)	0.066(6)
C(4)	0.6733(17)	–0.0842(5)	0.4343(14)	0.061(5)
C(5)	0.5346(16)	–0.0672(5)	0.3784(14)	0.058(5)
C(6)	0.5142(13)	–0.0151(5)	0.3227(12)	0.047(4)
C(7)	0.7453(11)	0.1167(4)	0.0302(13)	0.040(4)
C(8)	0.8131(12)	0.0680(5)	0.0066(13)	0.050(4)
C(9)	0.8721(13)	0.0593(6)	–0.1236(16)	0.067(6)
C(10)	0.8647(17)	0.0968(7)	–0.2275(16)	0.081(7)
C(11)	0.8037(13)	0.1443(6)	–0.2026(14)	0.065(6)
C(12)	0.7443(12)	0.1542(5)	–0.0756(12)	0.044(4)
C(13)	0.6679(14)	0.2072(5)	–0.0520(13)	0.058(5)
C(14)	0.8365(12)	0.2414(5)	0.1468(14)	0.057(5)
C(15)	0.5765(13)	0.2612(4)	0.1257(14)	0.060(5)
C(16)	0.3098(11)	0.1263(5)	0.0638(13)	0.046(4)
C(17)	0.3283(19)	0.0776(8)	–0.013(2)	0.159(11)
C(18)	0.236(2)	0.1654(8)	–0.041(3)	0.213(13)
C(19)	0.2343(18)	0.1200(11)	0.183(2)	0.26(2)

[a] U(eq) = one-third of the trace of the orthorgonalized **U**.

Table IV. Selected Geometrical Data for $W(C_6H_4CH_2NMe_2\text{-}2)Cl_2({=}NPh)(OCMe_3)$ (5)

Bond Lengths (Å)			
W–C(7)	2.137(11)	W–O(1)	1.811(6)
W–Cl(1)	2.435(3)	W–Cl(2)	2.402(3)
W–N(1)	1.712(8)	W–N(2)	2.420(8)
N(1)–C(1)	1.407(13)		
Bond Angles (deg)			
N(2)–W–N(1)	169.9(4)	N(2)–W–C(7)	73.8(4)
C(7)–W–Cl(2)	156.3(3)	O(1)–W–C(1)	165.80(18)
W–O(1)–C(16)	145.4(6)	W–N(1)–C(1)	170.4(7)

Finally, the molecular structure of **1b** shows a peculiar bonding mode of the α-Me group which so far has not been encountered for this ligand in other organometallic complexes. In **1b** the five-membered chelate ring is slightly puckered, and the α-Me group can thus be bonded either axially or equatorially. In **1b** it is equatorial, whereas in all other organometallic complexes containing ligand **b**, the α-Me group is an axial position. For example, the α-Me group in $SnBr[C_6H_4CH(Me)NMe_2\text{-}2]MePh$ (**8**)[4] favors the axial position (perpendicular to the aryl ring), *i.e* the δ conformation. In the alternative λ conformation the α-Me group is bonded in the equatorial position (*i.e* in the plane of the aryl ring). This latter conformation seems less favorable because some steric repulsion may occur with the *meta* H on the aryl ring.[4] The fact that in **1b** this α-Me group is in the λ conformation (see Figure 3) is the result of the octahedral stereochemistry of these tungsten complexes (triorganotin bromide **8** has a trigonal-bipyramidal geometry). If the chelate ring in **1b** had the δ conformation, then one of the meridionally bonded *cis*-chlorine atoms would form a considerable steric constraint for the α-Me group. This is clearly illustrated by the Newman projections in Figure 3.

Conclusions

Our results show that aryltungsten(VI) complexes with an intramolecularly coordinating donor atom are readily accessible. The intramolecular coordinating donor atom is always bonded in the *trans* position with respect to the oxo or phenylimido ligand present in the molecule. Also in solution these donor atoms form strong dative bonds, especially the nitrogen atom in tertiary amine groups, as no W–N dissociation processes could be observed by ^1H NMR spectroscopy in toluene-d_8 at elevated temperature. We believe that these W–N bonds are the main reason for the high thermal stability of the aryltungsten(VI) complexes. The introduction of *tert*-butoxide ligands enhances this thermal stability even more, and air-stable complexes could be obtained.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. All solvents were dried and distilled from sodium–benzophenone ketyl prior to use. Commercially available reagents were used as supplied (WCl_6 from Strem Chemicals and n-BuLi from Aldrich Chemical Co.), while others, $WCl_4({=}O)$,[16] $WCl_4({=}NPh)(OEt_2)$,[8] $[WCl_{5-x}({=}NPh)(OCMe_3)_x][NEt_4]$ ($x = 1$, 2),[8] $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$,[6] $Zn(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}6)_2$,[1f] and $LiCH_2SiMe_3$,[15] were prepared by standard literature methods. $Zn(CH_2SiMe_3)_2$ was prepared from $LiCH_2SiMe_3$ and anhydrous $ZnCl_2$ in a 2:1 ratio in Et_2O. Enantiomerically pure (R)-$C_6H_5CH(Me)NMe_2$ was synthesized *via* a conventional Eschweiler–Clarke procedure starting from commercially available (R)-$C_6H_5CH(Me)NH_2$ (Aldrich, ee 96%). The preparation of the corresponding diorganozinc compound was similar to that of $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$. ^1H and ^{13}C NMR spectra of the compounds dissolved in benzene-d_6 were recorded, at room temperature, on a Bruker AC 200 or AC 300 spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry TNO, Zeist, The Netherlands, or by the Mikroanalytisches Laboratorium Dornis and Kolbe, Mülheim a.d. Ruhr, Germany.

$Zn(C_6H_4CH_2OMe)_2$. n-BuLi (0.13 mol, 90 mL of a 1.5 M solution in hexane) was added dropwise to a cooled solution (–78 °C) of 1 equiv of 2z-bromobenzyl methyl ether (prepared from 2-bromobenzyl bromide with potassium methanolate in MeOH at 0 °C) (27.1 g, 0.13 mol) in Et_2O (75 mL). The reaction mixture was warmed to room temperature and was stirred for another 1

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[16] Sommer, L. H.; Mitch, F. A.; Goldberg, G. M. *J. Am. Chem. Soc.* **1949**, *71*, 2746.

Table V. Relevant ^1H NMR Data[a] for Aryltungsten Oxo and Phenylimido Complexes 1–7

complex	*o*-H[b]	*p*-H NPh[c]	$CH_2/CH(Me)$[d]	NMe_2
$W(C_6H_4CH_2NMe_2\text{-}2)Cl_3({=}O)$ (**1**)	9.20		3.50	2.45
$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}O)$ (**1b**)	9.40		4.15 (0.70)	2.70, 2.10
$W(C_6H_4CH_2OMe\text{-}2)Cl_3({=}O)$ (**2**)	9.00		*e*	*f*
$W(C_6H_4CH_2NMe_2\text{-}2)Cl_3({=}NPh)$ (**3a**)	8.70	6.35	3.70	2.80
$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}NPh)$ (**3b**)	8.85	6.50	4.55 (0.90)	3.15, 2.55
$W(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}6)Cl_3({=}NPh)$ (**3c**)	*g*	6.45	4.00	2.85
$W(C_6H_4CH_2OMe\text{-}2)Cl_3({=}NPh)$ (**4**)	8.65	6.50	*h*	*i*
$W(C_6H_4CH_2NMe_2\text{-}2)Cl_2({=}NPh)(OCMe_3)$ (**5**)	8.36	6.67	4.19, 3.53[j]	2.93, 2.53
$W(C_6H_4CH_2NMe_2\text{-}2)Cl({=}NPh)(OCMe_3)_2$ (**6a**)	8.43	6.68	3.72	2.62
$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl({=}NPh)(OCMe_3)_2$ (**6b**)	8.47	6.69	4.48 (1.12)	3.03, 2.19
$W(C_6H_4CH_2NMe_2\text{-}2)Ns({=}NPh)(OCMe_3)_2$[k] (**7a**)	8.30	6.72	3.73	2.32
$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Ns({=}NPh)(OCMe_3)_2$[k] (**7b**)	8.33	6.73	4.34 (1.17)	2.60, 2.06

[a] All values are in δ relative to $SiMe_4$ (indirectly referenced using solvent signals): solvent, benzene-d_6; temperature, 25 °C. [b] Doublet with $^3J_{HH}$ = 8 Hz. [c] $^3J_{HH}$ = 7 Hz. [d] CH and Me as quartet and doublet, respectively, with $^3J_{HH}$ = 7 Hz. [e] 4.45 (CH_2O). [f] 3.55 (OMe). [g] 2.83 (Me-6). [h] 4.65 (CH_2O). [i] 3.95 (OMe). [j] Double doublet: $^2J_{HH}$ = 13.9 Hz. [k] Ns = CH_2SiMe_3.

Table VI. Relevant ^{13}C NMR Data[a] for Aryltungsten Oxo and Phenylimido Complexes 1–7

complex	C_{ipso} aryl	$^1J_{CW}$[b]	$C_{ips}d_o$ NPh	CH_2 or CH(Me)	NMe_2
1a	214.5	90.5[c]		71.5	52.0
1b	2196.0	*d*		68.5 (9.6)	48.0, 44.9
2	217.0	*d*		*e*	*f*
3a	214.0	104.5	150.0	72.0	52.0
3b	216.0	103.0	150.0	69.0 (10.0)	47.0, 45.0
3c	217.0	103.0	151.0	72.0[g]	52.0
4	212.0	104.5	150.0	*h*	*i*
5	192.5	120.4	151.9	71.7	51.3, 51.2
6a	184.7	140.6	153.9	71.0	50.3
6b	185.9	139.5	153.8	67.2 (9.7)	46.9 42.0
7a	185.3	95.4	155.7	73.5	49.6
7b	187.2	94.8	155.6	68.3 (9.8)	46.2, 41.2

[a] All values are in δ relative to $SiMe_4$ (indirectly referenced using solvent signals): solvent, benzene-d_6; temperature, 25 °C. *b* $^1J_{CW}$ in Hz. [c] In chloroform-d_1. [d] Not observed. [e] 82.5 (CH_2O). [f] 63.5 (OMe). [g] 29.5 (Me-6). [h] 84.0 (CH_2O0. [i] 64.0 (OMe).

h. Subsequently, the solvent was removed *in vacuo*, leaving a yellow solid, which was washed with hexane (2 × 50 mL). The product, an off-white powder, gave a quantitative yield of 2-deuteriobenzyl methyl ether after hydrolysis with D_2O.

Solid, anhydrous $ZnCl_2$ (6.65 g, 48.8 mmol) was added to a cooled solution (−78 °C) of 2-lithiobenzyl methyl ether (12.5 g, 97.6 mmol) in 80 mL of Et_2O. The resulting reaction mixture was slowly warmed to room temperature and then stirred for an additional 1 h. The ethereal solution was separated from a white precipitate (LiCl) by centrifugation. The solvent was removed *in vacuo*, leaving a light yellow solid, which was washed with cold pentane (50 mL). The product (12.8 g, 85%) was an off-white solid. ^1H NMR (δ): 7.95 (d, 2, *o*-H); 7.35–6.90 (m, 6, Ar H); 4.25 (s, 4, CH_2O); 2.95 (s, 6, OMe). ^{13}C NMR (δ): 149, 146, 139, 127, 126, 123 (Ar C); 76 (CH_2O); 58 (OMe).

$W(C_6H_4CH_2NMe_2\text{-}2)Cl_3({=}O)$ (1a). A solution of $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$ (1.02 g, 3.04 mmol) in Et_2O (25 mL) was added over *ca.* 15 min to a cooled suspension (0 °C) of $WCl_4({=}O)$ (2.08 g, 6.08 mmol) in Et_2O (50 mL). At the first addition of the zinc compound the color of the reaction mixture changed immediately from orange to purple. After the addition of the zinc compound had been completed, the reaction mixture was warmed to room temperature, at which temperature it was stirred for another 1 h. The solvent was removed *in vacuo*. The resulting deep purple residue was extracted with benzene (100 mL). An off-white precipitate ($ZnCl_2$) was separated by centrifugation and subsequent decantation of the benzene. The benzene was removed *in vacuo*, leaving a deep purple sponge. Addition of hexane (30 mL) afforded, after centrifugation, a deep purple powder as the product (2.08 g, 78%). ^1H NMR (δ): 9.20 (d, 1, *o*-H); 7.30–6.80 (m, 3, Ar H); 3.50 (s, 2, CH_2N); 2.45 (s, 6, NMe_2). ^{13}C NMR (δ): 222 (C_{ipso}, $^1J_{WC}$ = 90.5 Hz, measured in $CDCl_3$); 148–125 (Ar C); 71 (CH_2N); 52 (NMe_2). Anal. Calcd for $C_9H_{12}Cl_3NOW$: C, 24.55; H, 2.75; N, 3.18. Found: C, 24.68; H, 2.70; N, 2.98.

$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}O)$ (1b). This enantiomerically pure product was prepared from $WCl_4({=}O)$ (1.45 g, 4.24 mmol) with $Zn[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]_2$ (0.77 g, 2.12 mmol) by a procedure similar to that described above for **1a**. Yield: 1.58 g (82%). Suitable crystals for an X-ray diffraction study were obtained by cooling a saturated hexane solution to −30 °C. ^1H NMR (δ): 9.40 (d, 1, *o*-H); 7.00–6.80 (m, 3, Ar H); 4.15 (q, 1, *CH*(Me)N); 2.70, 2.10 (s, 6, NMe_2); 0.70 (d, 3, CH(*Me*)N). ^{13}C NMR (δ): 224 (C_{ipso}, $^1J_{WC}$ not observed); 150–152 (Ar C); 68.5 (*C*H(Me)N); 48.0, 44.9 (NMe_2); 9.6 (CH(*Me*)N). Anal. Calcd for $C_{10}H_{14}Cl_3NOW$: C, 26.41; H, 3.11; N, 3.08. Found: C, 26.23; H, 3.17, N, 3.02.

$W(C_6H_4CH_2OMe\text{-}2)Cl_3({=}O)$ (2). A suspension of $WCl_4({=}O)$ (0.83 g, 2.43 mmol) in 25 mL of Et_2O was cooled to −78 °C. An ethereal solution (25 mL) of $Zn(C_6H_4CH_2OMe\text{-}2)_2$ (0.37 g, 1.22 mmol) was added dropwise over 0.5 h; a slow change of color, from orange to purple, was observed. The reaction mixture was warmed to room temperature and stirred for 4 h. The Et_2O was removed *in vacuo*, and the residue was extracted with 75 mL of benzene. After centrifugation the purple solution was decanted and the benzene was removed *in vacuo*, leaving a deep purple solid, which was washed with 50 mL of pentane. Yield: 0.79 g (76%). ^1H NMR (δ): 9.00 (d, 1, *o*-H); 7.15–6.45 (m, 3, Ar H); 4.45 (s, 2, CH_2O); 3.55 (s, 3, O*Me*). ^{13}C NMR (δ): 220 (C_{ipso}, $^1J_{WC}$ not observed); 147–121 (Ar C); 82 (CH_2O); 63 (OMe). Anal. Calcd for $C_8H_9Cl_3O_2W$: C, 22.48; H, 2.12. Found: C, 22.66; H, 2.07.

$W(C_6H_4CH_2NMe\text{-}2)Cl_3({=}NPh)$ (3a). $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$ (2.14 g, 6.4 mmol) in Et_2O (25 mL) was added over 0.5 h to a solution of $WCl_4({=}NPh)(OEt_2)$ (6.30 g, 12.8 mmol) in 30 mL of Et_2O at −78 °C. After addition of the zinc compound the reaction mixture was warmed to room temperature and stirred for an additional 2 h. The solvent was removed *in vacuo*, and the reddish brown residue was extracted with benzene (2 × 50 mL). The benzene fractions were combined, and the solvent was removed *in vacuo*, leaving a sponge. This sponge gave after washing with 25 mL of pentane a reddish brown solid as the product (5.0 g, 76%). ^1H NMR (δ): 8.70 (d, 1, *o*-H); 7.20–6.80 (m, 7, Ar H); 6.35 (t, 1, *p*-H NPh); 3.70 (s, 2, CH_2N); 2.80 (s, 6, NMe_2). ^{13}C NMR (δ): 214 (C_{ipso}, $^1J_{WC}$ = 104 Hz); 150 (C_{ipso} NPh); 144–125 (Ar C); 72 (CH_2N); 52 (NMe_2). Anal. Calcd for $C_{15}H_{17}Cl_3N_2W$: C, 34.95; H, 3.32; N, 5.43. Found: C, 33.95; H, 3.41; N, 5.04. The somewhat low value found for C corresponds to a C:H ratio of 15:17.95.

$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl_3({=}NPh)$ (3b). This enantiomerically pure product was prepared from $WCl_4({=}NPh)(OEt_2)$ (3.01 g, 6.13 mmol) and $Zn[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]_2$ (1.11 g, 3.07 mmol) by a procedure similar to that described for **3a**, yielding a reddish brown solid (2.34 g, 72%). ^1H NMR (δ): 8.85 (d, 1, *o*-H); 7.35–6.90 (m, 7, Ar H); 6.50 (t, 1, *p*-H NPh); 4.55 (q, 1, *CH*(Me)N); 3.15, 2.55 (2, s, 6, NMe_2); 0.90 (d, 3, CH(*Me*)N). ^{13}C NMR (δ): 216 (C_{ipso}, $^1J_{WC}$ = 103 Hz); 150 (C_{ipso} NPh); 148–125 (Ar C); 69 (*C*H(Me)N); 47, 45 (NMe_2); 10 (CH(*Me*)N).

$W(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}6)Cl_3({=}NPh)$ (3c). $Zn(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}6)_2$ (4.97 g, 13.7 mmol) in Et_2O (15 mL) was added dropwise to a solution of $WCl_4({=}NPh)(OEt_2)$ (13.57 g, 27.6 mmol) in Et_2O (50 mL) at −78 °C. After addition of the zinc compound the reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, leaving a red

Table VII. Crystal Data and Details of the Structure Determination of Complexes 1b and 5

	Crystal Data	
formula	$WC_{10}H_{14}Cl_3NO$ (**1b**)	$WC_{19}H_{26}Cl_2N_2O$ (**5**)
mol wt	454.44	553.18
cryst syst	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
a, *b*, *c* (Å)	8.182(1), 12.100(1), 13.885(1)	9.0035(5), 25.182(1), 9.3131(5)
β (deg)	90.04(1)	97.621(4)
V (Å^3)	1374.6(2)	2092.9(2)
Z	4	4
D_{calc} (g cm^{-3})	2.196	1.755
$F(000)$	856	1080
μ (cm^{-1})	91.5	59.0
cryst size (mm)	0.13 × 0.28 × 0.50	0.15 × 0.15 × 0.20
	Data Collection	
temp (K)	295	298
θ_{min}, θ_{max} (deg)	1.5, 27.5	1.0, 27.5
radiation	Mo Kα (Zr filtered), 0.710 73 Å	Mo Kα (Zr filtered), 0.710 73 Å
$\Delta\omega$ (deg)	$0.60 + 0.35 \tan\theta$	$1.19 + 0.35 \tan\theta$
horiz and vert aperture (mm)	3.00, 4.00	3.00, 4.00
X-ray exposure time (h)	139.4	91.2
linear decay (%)	6	7
ref rflns	0,2,–1, 2,0,–2, 310	–2,2,3, 1,2,–4, –1,6,2
data set	0–10; –13 to +15; –18 to +18	–11 to +11; –32 to 0; –12 to +12
total no. of data, no. of unique data, R_{int}	9280, 5145, 0.025	6084, 4784, 0.039
no. of obsd data ($I > 2.5\sigma(I)$)	4563	2786
Abs cor range (DIFABS)	0.77, 1.12	0.88, 1.21
	Refinement	
no. of refined params	308	228
no. of rflcns	4561	2785
weighting scheme	$1/[\sigma^2(F) + 0.00028F^2]$	$1/[\sigma^2(F) + 0.00068F^2]$
final R, R_w, S	0.033, 0.041, 1.54	0.047, 0.040, 3.64
U overall istro H atoms	0.090(11), 0.097(10)	0.050(8), 0.20(3)
$(\Delta/\sigma)_{av}$ in final cycle	0.027	0.042
min, max resd dens (e/Å^3)	–1.39, 1.78	–1.65, 1.39 (near C17)

solid, which was extracted with 50 mL of CH_2Cl_2. The CH_2Cl_2 solution was concentrated *in vacuo*. The resulting solid was washed with 20 mL of cold pentane, yielding a purple solid (13.3 g, 91%). ^1H NMR (δ): 7.30–6.80 (m, 7, Ar H); 6.45 (t, 1, *p*-H NPh); 4.00 (s, 2, CH_2N); 2.85 (s, 6, NMe_2); 2.83 (s, 3, Me-6). ^{13}C NMR (δ): 217 (C_{ipso}, $^1J_{WC}$ = 103 Hz); 151 (C_{ipso} NPh); 148–122 (Ar C); 72 (CH_2N); 52 (NMe_2); 29 (Me-6).

$W(C_6H_4CH_2OMe\text{-}2)Cl_3({=}NPh)$ (4). This product was prepared from $WCl_4({=}NPh)(OEt_2)$ (2.12 g, 4.32 mmol) and $Zn(C_6H_4CH_2OMe\text{-}2)_2$ (0.66 g, 2.14 mmol) by a procedure similar to that described for **3a**. Yield: 1.76 g (72%). ^1H NMR (δ): 8.65 (d, 1, *o*-H); 7.30–6.70 (m, 7, Ar H); 6.50 (t, 1, *p*-H NPh); 4.65 (s, 2, CH_2O); 3.95 (s, 3, OMe). ^{13}C NMR (δ): 212 (C_{ipso}, $^1J_{WC}$ = 104 Hz); 150 (C_{ipso} NPh); 141–121 (Ar C); 84 (CH_2O); 64 (OMe).

$W(C_6H_4CH_2NMe\text{-}2)Cl_2({=}NPh)(OCMe_3)$ (5). $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$ (1.68 g, 5.04 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a cooled solution (0 °C) of $[WCl_4({=}NPh)(OCMe_3)][Et_4N]$ (6.25 g, 10.08 mmol) in CH_2Cl_2 (50 mL). After it was warmed to room temperature, the reaction mixture was stirred overnight. The reaction mixture was centrifugated after the volume had been reduced to 35 mL *in vacuo*, and 50 mL of pentane was added. The solvent was removed *in vacuo*, leaving the crude product as a microcrystalline solid. After it was washed with cold hexane (2 × 15 mL), the pure product was obtained as a light brown solid (4.20 g, 75%). Orange crystals, suitable for an X-ray diffraction study, were obtained by cooling a hexane solution to –30 °C. ^1H NMR (δ): 8.36 (d, 1, *o*-H); 7.48–7.04 (m, 7, Ar H); 6.67 (t, 1, *p*-H NPh); 4.19 (d, 1, CH_AH_BN, $^2J_{H_AH_B}$ = 13.9 Hz); 3.53 (d, 1, CH_AH_BN, $^2J_{H_BH_A}$ = 13.9 Hz); 2.93, 2.53 (2 s, 6, NMe_2); 1.16 (s, 9, $OCMe_3$). ^{13}C NMR (δ): 192.5 (C_{ipso}, $^1J_{WC}$ = 120.4 Hz); 151.9 (C_{ipso} NPh); 144.7, 140.8, 129.2–125.0 (Ar C); 90.4 ($OCMe_3$); 71.7 (CH_2N); 51.3, 51.2 (2 NMe); 30.0 ($OCMe_3$). Anal. Calcd for $C_{19}H_{26}Cl_2N_2OW$: C, 41.25; H, 4.74; N, 5.06. Found: C, 41.52; H, 4.88; N, 5.11.

$W(C_6H_4CH_2NMe\text{-}2)Cl({=}NPh)(OCMe_3)_2$ (6a). This product was prepared from $[WCl_3({=}NPh)(OCMe_3)_2][Et_4N]$ (3.66 g, 5.56 mmol) and $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$ (0.93 g, 2.78 mmol) by a procedure similar to that described for **5**. Recrystallization of the crude product from the minimum amount of pentane by cooling to –30 °C gave 2.05 g (61%) of light brown crystals. ^1H NMR (δ): 8.43 (d, 1, *o*-H); 7.38–7.08 (m, 7, Ar H); 6.68 (t, 1, *p*-H NPh); 3.72 (s, 2, CH_2N); 2.62 (s, 6, NMe_2); 1.29 (s, 18, $OCMe_3$). ^{13}C NMR (δ): 184.7 (C_{ipso}, $^1J_{WC}$ = 140.6 Hz); 153.9 (C_{ipso} NPh); 145.2, 141.7, 128.6–125.1 (Ar C), 85.1 ($OCMe_3$); 71.0 (CH_2N), 50.3 (NMe_2); 31.4 ($OCMe_3$). Anal. Calcd for $C_{23}H_{35}ClN_2O_2W$: C, 46.76; H, 5.97; N, 4.74. Found: C, 46.37; H, 5.94; N, 4.75.

$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]Cl({=}NPh)(OCMe_3)_2$ (6b). This enantiomerically pure product was prepared from $[WCl_3({=}NPh)(OCMe_3)_2][Et_4N]$ (4.41 g, 6.70 mmol) and $Zn[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]_2$ (1.21 g, 3.34 mmol) by a procedure similar to that described for **5**. Recrystallization of the crude product from hexane by cooling to –30 °C gave 3.16 g (78%) of bright yellow crystals (mp 138 °C). ^1H NMR (δ): 8.47 (d, 1, *o*-H); 7.37–7.11 (m, 7, Ar H); 6.69 (t, 1, *p*-H NPh); 4.48 (q, 1, *CH*(Me)N); 3.03, 2.19 (2 s, 6, NMe_2); 1.34, 1.27 (2 s, 18, $OCMe_3$); 1.12 (d, 3, CH(*Me*)N). ^{13}C NMR (δ): 185.9 (C_{ipso}, $^1J_{WC}$ = 139.5 Hz); 153.8 (C_{ipso} NPh); 149.3, 141.8, 128.4–125.0 (Ar C); 85.6, 84.7 ($OCMe_3$); 67.2 (*C*H(Me)N); 46.9, 42.0 (NMe_2); 31.8, 31.2 ($OCMe_3$); 9.7 (CH(*Me*)N). Anal. Calcd for $C_{24}H_{37}ClN_2O_2W$: C, 47.66; H, 6.17; N, 4.63. Found: C, 47.72; H, 6.25; N, 4.69.

$W(C_6H_4CH_2NMe_2\text{-}2)(CH_2SiMe_3)({=}NPh)(OCMe_3)_2$ (7a). This compound was prepared *in situ* in an NMR tube by adding 1 equiv of crystalline $LiCH_2SiMe_3$ to a solution of **6a** in benzene-d_6. The NMR tube was centrifugated prior to measurement. ^1H NMR (δ): 8.30 (d, 1, *o*-H), 7.45–7.13 (m, 7, Ar H); 6.72 (t, 1, *p*-H NPh); 3.73 (s, 2, CH_2N); 2.32 (s, 6, NMe_2); 1.12 (s, 1, $OCMe_3$); 0.50 (s, 9, $SiMe_3$); 0.21 (s, 2, CH_2Si, $^2J_{WH}$ = 7.6 Hz). ^{13}C NMR (δ): 185.3 (C_{ipso}, $^1J_{WC}$ = 95.4 Hz); 155.7 (C_{ipso} NPh); 144.6, 141.0, 128.3–124.3 (Ar C); 83.2 ($OCMe_3$); 73.5 (CH_2N); 49.6 (NMe_2); 41.6 (CH_2Si, $^1J_{WC}$ = 71.4 Hz); 31.2 ($OCMe_3$); 4.4 ($SiMe_3$).

$W[(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2](CH_2SiMe_3)({=}NPh)(OCMe_3)_2$ (7b). Crystalline $LiCH_2SiMe_3$ (0.16 g, 1.7 mmol) was added to a solution of **6b** (0.97 g, 1.6 mmol) in benzene (25 mL). After 0.5 h the reaction mixture was centrifugated and the solution was decanted from a white residue (LiCl). The benzene was evaporated *in vacuo*, leaving a yellow solid. The product was recrystallized by cooling a saturated hexane solution, yielding yellow crystals (0.93 g, 89%). ^1H NMR (δ): 8.33 (d, 1, *o*-H), 7.46–7.16 (m, 7, Ar H); 6.73 (t, 1, *p*-H NPh); 4.34 (q, 1, *CH*(Me)N); 2.60, 2.06 (2 s, 6, NMe_2); 1.17 (d, 3, CH(*Me*)N); 1.13, 1.12 (2 s, 18, $OCMe_3$); 0.51 (s, 9, $SiMe_3$); 0.28, 0.25 (sharp AB pattern, 2, CH_2Si, $^2J_{WC}$ = 5 Hz). ^{13}C NMR (δ): 187.2 (C_{ipso}, $^1J_{WC}$ = 94.8 Hz); 155.6 (C_{ipso} NPh); 148.6, 141.1, 128.3–124.7 (Ar C); 83.6, 82.7 ($OCMe_3$); 68.3 (*C*H(Me)N); 46.2, 41.2 (NMe_2); 42.6 (CH_2Si, $^1J_{WC}$ = 72.3 Hz); 31.7, 30.7 ($OCMe_3$); 9.8 (CH(*Me*)N); 4.4 ($SiMe_3$). Anal. Calcd for $C_{28}H_{48}N_2O_2SiW$: C, 51.22; H, 7.37; N, 4.27. Found: C, 51.10; H, 7.48; N, 4.33.

X-ray Structure Determination of Complexes 1b and 5. Crystal data and numerical details of the structure determinations are given in Table VII. A crystal of **1b** suitable for X-ray structure determination was sealed in a Lindemann glass capillary, and a suitable crystal of **5** was mounted on a glass capillary. Both crystals were then transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Lattice parameters were determined by least-squares fitting of the SET4 setting angles of 25 reflections with 9.9° < θ < 13.9° and 10.7° < θ < 14.6° for **1b** and **5**, respectively. The unit-cell parameters were checked for the presence of higher lattice symmetry.[17] Data were collected in the $\omega/2\theta$ scan mode. Data were corrected for Lp and for the observed linear decay of the reference reflections. Absorption correction was applied using the DIFABS procedure.[18] Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (pI)^2$, with $p = 0.01$ and 0.03 for **1b** and **5**, respectively.[19] The structures were solved by automated standard Patterson methods followed by tangent expansion (**1b**) or automated direct methods (**5**) (SHELXS86).[20] Refinement on F was carried out by full-matrix least-squares techniques (SHELX76).[21] The hydrogen atoms were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with two common isotropic thermal parameters: one for hydrogen atoms in the methyl groups and one for the other hydrogen atoms in **1b**; one for the *tert*-butoxy methyl groups and one for the other hydrogen atoms in **5**. Weights were introduced in the final refinement cycles. The low-order reflections (001 and 011) were omitted during the refinement of **1b**; reaction 172 was omitted during the refinement of **5** because of its strongly deviating position. The *tert*-butoxy group of **5** displays some disorder, as is indicated by the high thermal motion and unusually large anisotropy of C(17), C(18), and C(19). This disorder could not be described in a satisfactory way with a disorder model. Atomic scattering factors were taken from Cromer and Mann[22] and anomalous dispersion corrections from Cromer and Liberman.[23] Geometric calculations and illustrations were performed with PLATON[24] on a MicroVAX cluster and a DECstation 5000.

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Supplementary Material Available: Tables of anisotropic thermal parameters, all H atom parameters, bond lengths, and bond angles for both **1b** and **5** (10 pages). Ordering information is given on any current masthead page.

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