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PAPER

Imidotungsten(VI) complexes with chelating amino and imino phenolates†

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The reaction of $WOCl_4$ with 2,4-di-*tert*-butyl-6-((isopropylamino)methyl)phenol followed by the reaction with phenyl isocyanate leads to the formation of imidotungsten(VI) complex [W(NPh)Cl_3(OC_6H_3(CH_2NH-*i*-Pr)-2-*t*-Bu_2-4,6)] **4** with a chelating aminophenolate ligand. When the same procedure was applied using aminophenols with bulkier substituents in the amino group, the final product was an unexpected Schiff-base complex [W(NPh)Cl_3(OC_6H_3(CH═NPh)-2-*t*-Bu_2-4,6)] **5**, where the ligand is derived from 2,4-di-*tert*-butyl-6-((phenylimino)methyl)phenol. Complex **5** is also formed in the thermal degradation of **4**. On the whole, **5** appears to be formed by a disproportionation of intermediate compounds, which are analogous to complex **4**. The solid-state structures of **4** and **5** have been determined by X-ray crystallography whereas the solution structures were studied by ^{1}H and ^{13}C NMR.

Introduction

Aryloxide derivatives of tungsten(VI) are traditional catalyst precursors for the metathesis of alkenes when activated by main-group organometallic co-catalysts.[1] Well-known examples of these precursors include chloride derivatives such as $WOCl_{4-x}(OAr)_x$ and $WCl_{6-x}(OAr)_x$. Although the metathesis reactions can be catalysed by well-known and commercially available Mo or Ru based catalysts, there is still use for some simple two-component catalyst systems.[2] Especially, the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene and other norbornene derivatives is catalysed by simple tungsten-based catalyst systems to produce elastomers and other valuable materials.[3] As typical for high-valent metal chlorides, these catalysts are rather sensitive towards water and other nucleophiles. Especially, if the coordination number of the metal centre is low, these compounds must be handled under an inert atmosphere using rather tedious practices. The stability of high-valent tungsten complexes can be improved by coordinative protection, *i.e.* by using chelating ligands, which carry a potentially coordinating neutral group within the molecule (Fig. 1).[4,5] For example, the phenylimido tungsten(VI) aryloxides [W(NPh)Cl_3(OC_6H_2(CH_2NMe_2)$_2$-2,6-Me-4)] (**1**)[4a] and [W(NPh)Cl_3(OC_6H_3(CH_2NMe_2)-2-*t*-Bu_2-4,6)] (**2**)[5] (Scheme 1) are stable under ambient atmosphere and can be melted in air without decomposition. We may assume that the stability of the tungsten imido complexes with the *O*,*N*-bidentate amino phenolate ligand depends on the strength of the coordinative W–N bond.

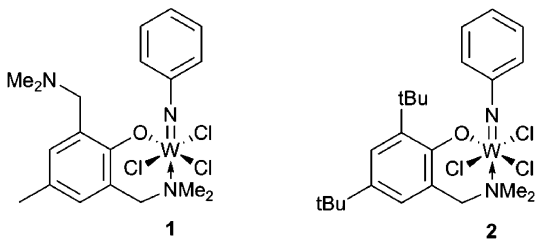

Fig. 1 Stable aminophenol complexes.

Scheme 1 Preparation of aminophenols.

Previously, we prepared compound **2** and its molybdenum analogue and used them as catalyst precursors for ROMP of norbornene derivatives.[5] It was found that the use of aluminium co-catalyst Et_2AlCl was necessary to obtain any activity. Although these catalysts showed good activity for ROMP of norbornene, the activity for the reactions of other monomers was poor. Thus, it seems that the rather strong coordinative M–N bond deteriorates the catalytic activity of activated complexes, as a high activity requires a low coordination number of the reacting metal centre. To weaken the M–N bond and thus improve

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the catalytic performance, we decided to prepare a series of corresponding tungsten compounds with varying substituents in the amino group. Particularly, we assumed that the elongated W–N bond may transform the coordination mode of the ligand into monodentate in solution, consequently erasing the stability of the complex derived from the chelate effect and inducing the 5-coordination favourable for the catalytic application. To keep the synthetic procedure as simple as possible, a straightforward two-step reaction was chosen for the preparation of a family of these new complexes. However, this procedure ended up with some unexpected results, as it was found that the reaction outcome depends strongly on the substituents in the amino group of the phenolate ligand. Depending on these substituents, the final product may carry either amino or imino nitrogen as the neutral donor atom.

Results and discussion

Computational studies on the iminotungsten(VI) complexes with aminophenolates

In our earlier studies, we have experienced some difficulties isolating the aminophenolate complexes of W(VI) ion, hence we studied the stability of the complexes computationally in addition to experimental studies. The coordinative bond between tungsten(VI) ion and the amine nitrogen is most likely the weakest bond in these compounds thus defining the stability of the complex. Generally, the factors contributing to the strength of the above mentioned bond are the sterical hindrance induced by alkyl substituents, inductive effect and resonance effect. To study the influence of the preceding effects on the W–N bond, we performed the geometry optimizations (at the DFT BP86/def2-TZVP level) and partial atomic charge calculations to the group of the simplified model complexes of iminotungsten(VI) chloride with different aminophenolate ligands (Fig. 2).

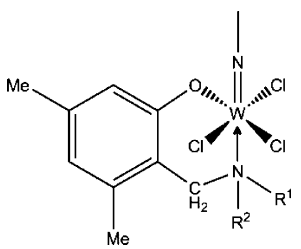


Fig. 2 Schematic presentation of simplified model complexes.

The amine ligands in the model complexes can be divided into primary (entry 1 in Table 1), secondary (entries 2–4) and tertiary amines (entries 5–7). Furthermore, the geometries of two related Schiff base complexes (entries 8–9) were optimized although the bonding mode is different compared with the aminophenolate complexes. In these models, the C=N double bond may provide some π-contribution to the W–N bond thus shortening the bonding distance and increasing the stability of the Schiff base complexes.

The effect of the alkyl group on the W–N bond can be clearly seen from the calculated data, *i.e.* the bond length increases upon the size of the substituents. The most significant result from the theoretical study is the notable shortening of the W–N bond in the complexes with secondary amines compared to the more common tertiary amine complexes. In general, the calculated W–N bond lengths for secondary amine complexes are from 0.2 to 0.6 Å shorter than with corresponding tertiary amines. The calculated bond lengths are in good agreement with the experimental data where available. The small differences between the theoretical and experimental results (approximately 0.1 Å) in W–N bond distances are most likely due to the relativistic and solid-state packing effects which are not counted in calculations.

Table 1 Calculated W–N bond lengths, MPA and NPA charges for the N donors and ϕ angles of model complexes

Entry	R_1	R_2	r(W–N)Å	Q (MPA)	Q (NPA)	ϕ/°
1	H	H	2.38	–0.800	–0.459	38.9
2	H	Me	2.44	–0.601	–0.335	38.2
3	H	Et	2.46	–0.609	–0.306	39.1
4	H	^{i}Pr	2.47	–0.619	–0.317	37.9
5	Me	Me	2.60	–0.407	–0.232	37.2
6	Et	Et	2.68	–0.411	–0.205	35.8
7	^{i}Pr	^{i}Pr	3.06	–0.416	–0.184	34.7
8	Me	—	2.38	–0.424	–0.155	—
9	Ph	—	2.41	–0.442	–0.210	—

In order to explain this trend we calculated the atomic charges of the complexes. Although the partial atomic charges are rather arbitrary models they provide some useful and chemically interpretable information on the properties of the molecules. Hence, we performed Mulliken Population Analysis (MPA) and Natural Population Analysis (NPA) for the preceding model compounds (see Table 1). According to the extensive study by Hadad *et al.* on the competence of different atomic charge schemes, NPA gives truthful charges on the nitrogen atoms in substituted anilines.[6] Consequently, we assume that the NPA analyses could provide reasonable results on the partial atomic charges in amine complexes as well.

The electron releasing ability (inductive effect) of alkyl substituents follows the order H > CMe_3 > $CHMe_2$ > CH_2Me > CH_3. Accordingly, the calculated MPA and NPA charges for the nitrogen donors in the primary and secondary amines are more negative than in the tertiary amines. This trend is in line with the W–N bond lengths as the bond length decreases when the negative partial charge of nitrogen increases. Since the partial atomic charge of tungsten remains in practice at the same level through whole series the charge difference between tungsten and nitrogen atoms (see Table 1 and ESI†) increases thus adding to the attractive ionic contribution of the bond.

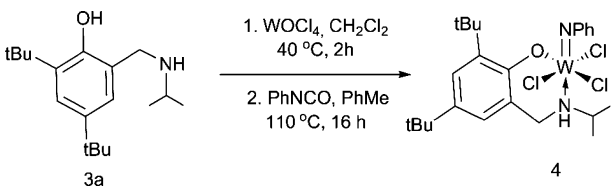
In addition to the partial charge of the nitrogen donor, there exists a correlation of the calculated W–N bond lengths with the pyramidality (dihedral angle CH_2–R^1–R^2–N, ϕ) of the nitrogen atom. The pyramidality of a nitrogen atom indicates the steric hindrance of the donor group. Hence, the more pyramidalized (*i.e.* larger ϕ angle) the nitrogen atom the better donor it can be. Keeping these results in mind, we decided to prepare a series of imidotungsten(VI) complexes with substituted aminophenols.

Synthesis and structural characterization of imidotungsten(VI) aminophenolate 4

The aminophenols **3a–3e** (Scheme 1) were prepared applying a simple solvent-free Mannich reaction starting from

2,4-di-*tert*-butylphenol, primary or secondary amine and paraformaldehyde.[7] All new aminophenols are colourless, crystalline solids at room temperature and can be isolated in 50–80% yields.

To synthesize a new series of imidotungsten(VI) complexes with the above mentioned aminophenolato ligands, we decided to use a simple two-step one-pot reaction. The first step comprises a standard procedure to prepare tungsten(VI) aryloxides, namely a simple reaction of oxotungsten(VI) tetrachloride with a stoichiometric amount of phenolic ligand precursor in an appropriate solvent.[8] The second step involves the reaction of a tungsten oxo compound with phenyl isocyanate in toluene, a reaction which is known to produce corresponding metal imido complexes.[9] As expected, the stoichiometric reaction of a phenolic ligand precursor **3a** with $WOCl_4$ in CH_2Cl_2 led rapidly to the formation of a dark red solution. When all the ligand had reacted (by TLC analyses), the solvent and HCl co-product were evaporated to afford the stable intermediate. This dark red compound reacted further with phenyl isocyanate in PhMe at reflux temperature to yield a purple imido complex **4** (see Scheme 2). Alternatively, **4** can be prepared starting with the known reaction[10] of $WOCl_4$ and phenyl isocyanate in heptane, followed by the phenolysis reaction with **3a** in CH_2Cl_2. However, the latter method is not very convenient, as it involves a slow reaction of poorly soluble $WOCl_4$. Compound **4** is soluble in common organic solvents and it can be easily isolated and purified by column chromatography as a deep red solid material. As a solid, **4** is stable under ambient conditions, although it decomposes slowly in solution. The compound was observed to undergo a slow hydrolysis in $CDCl_3$ due to the ambient water vapor absorbed by the solvent, whereupon traces of the free phenolic ligand appeared in the ^{1}H spectrum after *ca.* 1 day from dissolution and within a week were about 6% of the intensity of the signals of the tungsten complex **4**. This hydrolysis product (*i.e.* aminophenol **3a**) had equivalent chemical shifts for its two methylene protons, as well as for two methyl groups in its isopropyl moiety, since the amine side arm can rotate freely and its amino nitrogen can undergo the usual umbrella inversion.



Scheme 2 Formation of aminophenolate complex **4**.

Compound **4** was crystallized from a toluene–hexane mixture as a toluene hemi solvate **4**·0.5PhMe. The molecular structure consists of neutral mononuclear units, in which the central W(VI) ion is surrounded by one terminal phenyl imido group, one bidentate aminophenolate and three chlorides (Fig. 3). As expected due to the strong structural *trans*-effect of the imido nitrogen,[11] the neutral donor atom of an aminophenolate is situated *trans* to the imido group. The coordination geometry and bonding parameters (see Table 2) around the metal ion are comparable to those found earlier for corresponding aminophenolate compounds.[4a,5] However, as expected by theoretical calculations, the coordinative W–N bond length in **4** is rather short, 2.339 Å. Related bond lengths are 2.451 and 2.452 Å in **1** and **2**, respectively.

Table 2 Selected bond lengths (Å) and angles (°) for **4** and **5**

	4	**5**
W1–N1	1.723(7)	1.712(7)
W1–N8	2.339(8)	2.329(8)
W1–O1	1.870(6)	1.868(6)
W1–Cl1	2.347(3)	2.359(2)
W1–Cl2	2.371(2)	2.3232(9)
W1–Cl3	2.370(3)	2.3630(10)
N1–W1–N8	171.9(4)	173.8(4)
W1–O1–C1	145.22(19)	143.1(5)
N1–W1–O1	98.6(3)	96.4(3)

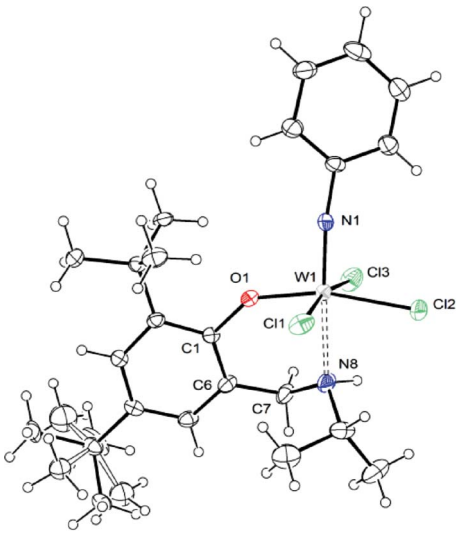


Fig. 3 The molecular structure of **4** with 30% probability.

As the solid-state structure of **4** suffers some conformational disorder, the molecular structure was verified by careful NMR measurements. The ^{1}H and ^{13}C NMR spectra of **4** in $CDCl_3$ solution were consistent with the expected constitution and atom–atom connectivity of the compound, and the NMR signals could be straightforwardly assigned with the help of standard 2D NMR experiments (COSY, HSQC, HMBC), excluding stereochemistry. The NMR data are given in the Experimental section and Table 3 (*cf.* Fig. 4 for the atom numbering). The ^{1}H chemical shifts of the two methylene protons at C7, and also the ^{1}H and ^{13}C chemicals shifts of the two methyl groups at C9, were seen to be non-equivalent indicating that each pair is diastereotopic. Below, the diastereotopic groups will be distinguished by labels *x* and *y*, label *x* referring to the atom or group with a larger ^{1}H chemical shift.

The coordinative bond between N8 and W1 seems to remain intact in the $CDCl_3$ solution. There is a NOE between *o*-H of the phenylimido ligand and the protons of the 2-*t*Bu group consistent with the assumption of bidentate binding (which prevents rotation of the *t*Bu group away from the phenyl). Also, the proton–proton coupling constants in the amino substituent are not averaged but imply a reasonably fixed torsion angles about the bonds as expected if the N8 is coordinated to tungsten. If the substituent was not bound to W1, and free to rotate about the various bonds, not only would the *J*-coupling constants be averaged but the CH_2 hydrogens and the two 9-methyl groups would be chemically equivalent (assuming fast nitrogen inversion) and display identical chemical shifts, or nearly so, contrary to observation.

Table 3 Selected ^{1}H chemical shifts, $J_{H,H}$ coupling constants and Nuclear Overhauser Effects (NOEs) for compound **4** in $CDCl_3$ at 298 K. The NOE enhancements (in %) were obtained by setting the integral of the inverted ^{1}H signal to −100 (or −300 in case where the methyl signals were selected)

Proton	δ (ppm)	J/Hz (coupl. partner)	NOEs (%)
5	7.11	2.4 (3)	4-*t*Bu(1.5), 7*y*(1.7), 7*x*(0.9)
7*x*	4.79	−14.3 (7*y*), 9.0 (NH)	$CH_{3,y}$(2.2), $CH_{3,x}$(1.0), NH(1.1), 7*y*(13.1), 5(1.3)
7*y*	4.32	−14.3 (7*x*), 2.5 (NH)	$CH_{3,y}$(1.4), $CH_{3,x}$(2.1), NH (2.6), 7*x*(13.8), 5(2.7)
NH	3.24	9.0 (7*x*), 2.5 (7*y*), 1.4 (9)	$CH_{3,y}$(0.4), $CH_{3,x}$(2.3), 7*y*(2.1), 9(2.4), 7*x*(1.0)
9	4.46	6.7 ($CH_{3,y}$), 6.6 ($CH_{3,x}$), 1.4 (NH)	$CH_{3,y}$(1.9), $CH_{3,x}$(2.2), NH(2.2)
$CH_{3,x}$	1.42	6.6 (9)	$CH_{3,y}$(1.4), NH(1.7), 7*y*(1.4), 9(2.0), 7*x*(0.5)
$CH_{3,y}$	1.30	6.7 (9)	$CH_{3,x}$(1.5), 7*y*(1.2), 9(2.4), 7*x*(1.7)

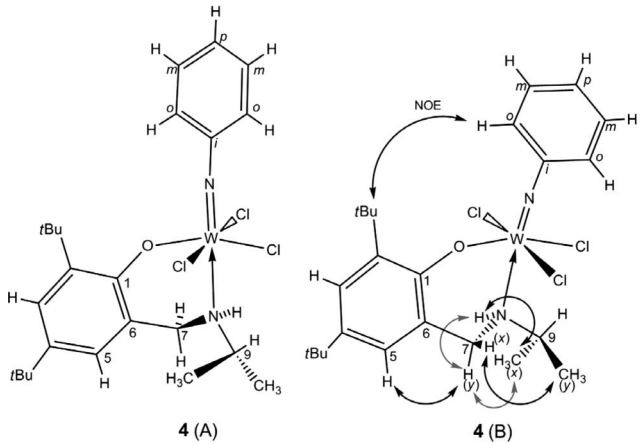


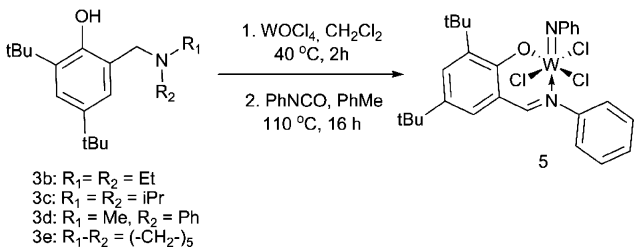
Fig. 4 Conformations A and B of compound **4**. The former corresponds to the X-ray structure of **4** while the latter, obtained by ring-inversion of the C1–C6–C7–N8–W1–O1 ring, represents the preferred conformation in $CDCl_3$ solution as deduced by NMR spectroscopy. Relevant NOE correlations, indicating spatial proximity, are shown as double-headed arrows.

As the first assumption, the structure of **4** in a $CDCl_3$ solution might be expected to resemble the solid-state structure (conformation A in Fig. 4); however, the observed *J*-coupling constants and NOEs involving the diastereotopic protons do not fit well to conformation A regardless of which way the groups *x* and *y* are assigned to the stereopositions. For example, the large observed *J*-coupling constant between the NH and 7*x* protons (9.0 Hz) implies them to be either in *syn*- or antiperiplanar positions with respect to each other (according to the Karplus equation).[12] Of these, only the latter is consistent with the NOEs between NH and the C7 protons (Table 3), but there is no C7-hydrogen antiperiplanar to NH in conformation A. On the other hand, these and the other *J* and NOE parameters of **4** fit well to the conformation B (see Fig. 4 for graphical representation of the NOEs), which is obtained from A by a ring-inversion of the six-membered C1–C6–C7–N8–W1–O1 ring. It is likely that in $CDCl_3$ solution several conformers are populated, including some close to A, but the preferred conformation(s) should resemble the structure B.

The ^{15}N NMR chemical shifts were obtained indirectly from ^{1}H{^{15}N}-HSQC and -HMBC 2D spectra; the former, being a single-bond correlation experiment, only showed the expected amino-type NH nitrogen at −316.2 ppm whereas in the (long-range) HMBC spectrum also the imino nitrogen at 31.3 ppm was seen. These ^{15}N chemical shifts, relative to nitromethane, are consistent with sp^3 and sp^2 hybridizations, respectively.

Formation and structural characterization of a Schiff-base complex 5

In order to prepare aminophenolate complexes with elongated coordinative W–N bonds, we used selected ligand precursors with bulky substituents in amino groups (Scheme 3).



Scheme 3 Formation of iminophenol complex **5**.

The two-step reaction of $WOCl_4$ with a diethylaminophenol **3b** was carried out by following the same procedure outlined above for the synthesis of **4**. However, these experimental conditions did not produce the expected aminophenol complex, but the reaction led to the formation of a deep purple solution, from which an intense purple compound **5** was obtained as the only isolable product. The solid compound is stable under ambient atmosphere. It is also stable in a $CDCl_3$ solution, but decomposes slowly in coordinating solvents. Compound **5** was characterized by NMR spectroscopy and X-ray diffraction to be an unexpected Schiff-base complex. The ^{1}H NMR spectrum showed resonances for 12 aromatic protons as well as signals for two *tert*-butyl groups in the aliphatic region. A sharp one-proton singlet was found at 8.50 ppm, which is typical for imine N=CH group. Also, the ^{13}C NMR resonance at 167.60 ppm indicates the presence of a sp^2 hybridized imine carbon. X-Ray crystallography verified that compound **5** is a rare example of an imidotungsten(VI) complex with Schiff base imino ligands.[13,14] The structure is made up of mononuclear units, in which the central W(VI) ion is surrounded by one terminal phenyl imido group, one bidentate iminophenolate ligand and three chlorides. In general, complex **5** has a rather similar coordination sphere around the metal centre than the aminophenolate **4** (see Table 2 and Fig. 5). Yet again, the neutral imine nitrogen is bonded *trans* to the phenylimido group, the N–W=N angle being 175.91(9) Å. The NMR data indicate that *the solid state structure* is retained in $CDCl_3$ *solution* as the coordinative bond between N8 and W1 remains intact. As estimated by computational results (entry 9 in Table 1), the coordinative W–N bond length in **5** is relatively long, 2.327(3) Å, whereas related bond lengths are 2.308(11) Å in [W(N^{t}Bu)$_2$L^1]

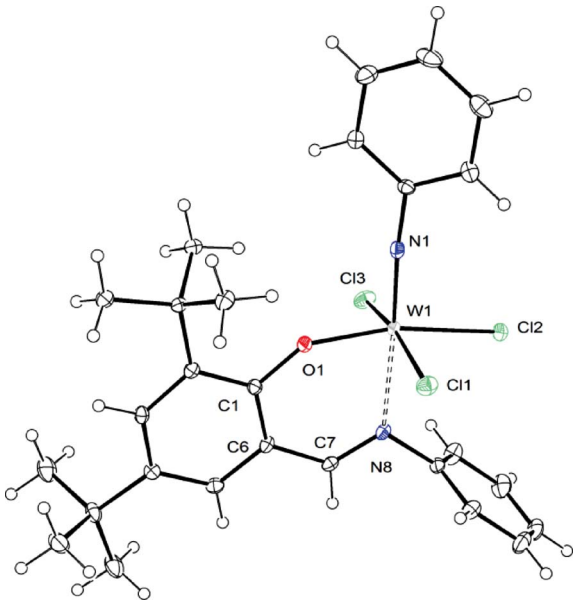


Fig. 5 The molecular structure of **5** with 30% probability.

(L^1 is a dianion of *N*,*N*-bis(3,5-di-*tert*-butylsalicylidene)ethane-1,2-diamine, the neutral imine nitrogen is *trans* to the imido dianion) and 2.234(8) Å in $[WO_2(L^2)(MeOH)]\cdot MeOH$ (L^2 = 2-(salicylideneamino)-5-*t*-butylphenolate dianion, the neutral imine nitrogen is *trans* to the oxo group).[13,15]

When the above mentioned reaction was repeated using aminophenols **3c–3e** as ligand precursors, complex **5** was formed in 30–35% yield (based on tungsten) in all individual experiments.[16] The Schiff-base complex **5** is also formed in the reaction of $W(NPh)Cl_4$ with ligand precursors **3b–3e** in refluxing toluene, which points out that phenyl isocyanate is not required in the formation of the new Schiff-base ligand, but the imino group in this new ligand comes from a W═NPh functionality. The mechanism of this reaction is so far unclear, though formally it appears a disproportionation of an intermediate compound, which is analogous to complex **4**. The weak coordination ability of the amino group in phenols **3b–3e** has obviously some role in this reactivity. To have more evidence on this disproportionation, we investigated a thermal decomposition of well-characterized aminophenolato complexes. Isolated compounds **2** and **4** are stable in toluene under reflux temperature, but if they are heated in 1,2-dichlorobenzene at 150 °C, the above mentioned Schiff-base complex **5** is formed in 35% isolated yield. The higher stability of these complexes is consistent with the observed and calculated coordinative W–N distances.

Conclusions

$WOCl_4$ reacts with aminophenol ligand 2,4-di-*tert*-butyl-6-((isopropylamino)methyl)phenol and phenyl isocyanate in a two-step reaction to produce an imidotungsten(VI) complex $[W(NPh)Cl_3(OC_6H_3(CH_2NH\text{-}i\text{-}Pr)\text{-}2\text{-}t\text{-}Bu_2\text{-}4,6)]$ **4**. When the same procedure was applied using tertiary aminophenols with bulkier substituents in the amino group, the final product is a Schiff-base complex $[W(NPh)Cl_3(OC_6H_3(CH{=}NPh)\text{-}2\text{-}t\text{-}Bu_2\text{-}4,6)]$ **5**. Complex **5** is also formed in the thermal degradation of **4**. The 2,4-di-*tert*-butyl-6-((phenylimino)methyl)phenolate ligand found in this complex is formed in the reaction of a coordinated aminophenolate with an imidotungsten group.

Experimental

Materials and methods

$WOCl_4$ and $W(NPh)Cl_4$ were prepared according to known procedures.[17,10] Solvents used in syntheses were freshly distilled over CaH_2 prior to use. Other chemicals were obtained from commercial sources and used without further purification. The NMR spectra were recorded in $CDCl_3$ solutions at 25 °C with a Bruker Avance 400 spectrometer (^{1}H: 399.75 MHz, ^{13}C: 100.52 MHz) (expect for **4**). The NMR spectra of **4** were recorded on a Bruker Avance 500 spectrometer equipped with a broad-band observe probe (BBO-5 mm-Zgrad), with the probe temperature set to 298 K (without calibration). The proton chemical shifts were referenced to internal tetramethylsilane (δ_{TMS} = 0.00 ppm), while the reference frequencies for the ^{13}C and ^{15}N chemical shifts were calculated from the TMS ^{1}H frequency by using Ξ_{13C}(TMS) = 25.145020 and $\Xi_{15N}(CH_3NO_2)$ = 10.136767.[18] The NOE spectra were measured with the 1D DPFGSE-NOE sequence[19] by using a mixing time of 0.3 s. The ^{1}H{^{13}C} HSQC and HMBC experiments were optimized for $^1J_{CH}$ = 145 Hz and J_{CH}(long-range) = 10 Hz, and the corresponding {^{15}N} analogues for 90 Hz and 8 Hz. The ^{1}H chemical shifts and *J*-coupling constants were extracted by simulation and iteration of the proton spectrum with the PERCH NMR software.[20] All samples were kept in vacuum for four hours prior to the NMR analyses.

Preparation of the ligands. The ligand precursors **3a–3e** were prepared applying a simple solvent-free Mannich reaction.[9] The starting materials 2,4-di-*tert*-butylphenol (20 mmol), substituted amine (22 mmol) and paraformaldehyde (22 mmol) were mixed in an open vessel and the reaction mixtures were heated at 120 °C for 16 h, cooled to the room temperature and treated with methanol to obtain white crystalline solids. Secondary amine **3a** was isolated from an etheral solution as a hydrochloride, neutralized by aqueous $NaHCO_3$ solution and re-crystallized from hexane prior to use. All synthesised aminophenols were characterized by NMR.

2,4-Di-*tert*-butyl-6-((isopropylamino)methyl)phenol (3a). 3.0 g (54%). ^{1}H NMR ($CDCl_3$): δ 7.23 (s, 1H, ArH), 6.88 (s, 1H, ArH), 3.95 (s, 2H, $ArCH_2$), 2.92 (septet, *J* = 6.3 Hz, 1H, $CH(CH_3)_2$), 1.44 (s, 9H, 2-*t*Bu), 1.30 (s, 9H, 4-*t*Bu), 1.17 (d, *J* = 6.3 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 154.2 (C1), 140.2 (C4), 137.2 (C2), 123.2 (C5), 122.2 (C3), 121.0 (C6), 50.2 (C9), 46.1 (C7), 34.8 (1C, 2-*t*Bu), 34.7 (1C, 4-*t*Bu), 31.8 (3C, 4-*t*Bu), 30.0 (3C, 2-*t*Bu), 20.7 (2C, 9-CH_3).

2,4-Di-*tert*-butyl-6-((diethylamino)methyl)phenol (3b). 3.6 g (62%). ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 1H, ArH), 6.96 (s, 1H, ArH), 3.65 (s, 2H, $ArCH_2$), 2.52 (q, 4H, m, CH_2CH_3), 1.44 (s, 9H, 2-*t*Bu), 1.31 (s, 9H, 4-*t*Bu), 1.02 (t, 6H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 154.7, 141.1, 137.0, 123.5, 122.5, 120.2, 49.0, 45.9, 34.8, 34.2, 34.2, 33.1, 17.3.

2,4-Di-*tert*-butyl-6-((diisopropylamino)methyl)phenol (3c). 4.8 g (75%). ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 1H, ArH), 6.86 (s, 1H, ArH), 3.86 (s, 2H, $ArCH_2$), 3.18 ((septet, *J* = 6.5 Hz, 2H, $CH(CH_3)_2$), 1.43 (s, 9H, 2-*t*Bu), 1.39 (s, 9H, 4-*t*Bu), 1.14

(d, J = 5.4 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): δ 155.1, 140.0, 135.2, 123.2, 122.3, 121.7, 49.3, 47.5, 34.9, 34.1, 31.8, 29.5, 19.8.

2,4-Di-*tert*-butyl-6-((methyl(phenyl)amino)methyl)phenol (3d). 4.5 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.36 (t, J = 7.2 Hz, 2H, ArH), 7.28 (s, 1H, ArH), 7.21 (d, J = 6.4 Hz, 2H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.94 (s, 1H, ArH), 4.35 (s, 2H, ArCH_2), 2.78 (s, 3H, NCH_3) 1.45 (s, 9H, 2-*t*Bu), 1.32 (s, 9H, 4-*t*Bu). ^{13}C NMR ($CDCl_3$): δ 153.9, 151.2, 141.2, 135.9, 129.2, 123.6, 123.2, 122.5, 121.3, 119.2, 60.3, 39.8, 34.9, 34.2, 31.7, 29.7.

2,4-Di-*tert*-butyl-6-(piperidin-1-ylmethyl)phenol (3e). 4.2 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.23 (s, 1H, ArH), 6.84 (s, 1H, ArH), 3.65 (s, 2H, ArCH_2), 2.60 (s, br, 4H, ring-CH_2N), 1.63 (s, br, 4H, ring-CH_2), 1.46 (s, br, 2H, ring-CH_2), 1.43 (s, 9H, 2-*t*Bu), 1.30 (s, 9H, 4-*t*Bu). ^{13}C NMR ($CDCl_3$): δ 154.5, 140.2, 135.4, 123.3, 122.7, 121.1, 62.9, 53.7, 34.9, 34.1, 31.7, 29.6, 25.8, 24.1. Spectra were identical to those reported earlier for **3e**.[21]

Preparation of 4. Method A: $WOCl_4$ (340 mg, 1.0 mmol) was treated with a solution of a ligand precursor **3a** (277 mg, 1.0 mmol) in CH_2Cl_2 (20 ml) under a N_2 atmosphere. The intense red reaction mixture was allowed to reflux while the reaction was monitored by TLC (PhMe as an eluent). After two hours, the TLC analysis showed a single purple spot (R_f 0.9), which discolours in a few minutes in air. The volatiles were then removed in vacuum and remaining dark solid was dissolved in 10 ml of toluene. PhNCO (0.13 ml, 1.2 mmol) was added and the mixture was refluxed for 16 h. Intense red product was isolated by silica column chromatography using PhMe as an eluent and finally crystallized from hot hexane to obtain **4** in a 55% (360 mg) total yield. Method B: 125 mg (0.30 mmol) of W(NPh)Cl_4 and 83 mg (0.30 mmol) of **3a** were mixed with 5 ml of toluene and stirred under reflux for four hours. Product **4** was isolated in a 175 mg (88%) yield, mp 145–147 °C. ^{1}H NMR (500.13 MHz, see Fig. 4 for the numbering scheme): δ 7.61 (m, 2H, *m*-H), 7.42 (d, J = 2.4 Hz, 1H, 3-H), 7.37 (m, 2H, *o*-H), 7.11 (d, J = 2.4 Hz, 1H, 5-H), 7.05 (m, 1H, *p*-H), 4.79 (dd, J = 9.0, 14.3 Hz, 1H, 7-H(x)), 4.46 (septet of doublets, J = 1.4, 6.6(×3), 6.7(×3) Hz, 1H, 9-H), 4.32 (dd, J = 2.5, 14.3 Hz, 1H, 7-H(y)), 3.24 (br d, $J \approx$ 8.5 Hz, 1H, NH), 1.44 (s, 9H, 2-*t*Bu), 1.42 (d, J = 6.6 Hz, 3H, 9-CH_3(x)), 1.33 (s, 9H, 4-*t*Bu), 1.30 (d, J = 6.7 Hz, 3H, 9-CH_3(y)). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 156.1 (C1), 150.9 (*i*-C), 150.6 (C4), 141.6 (C2), 131.6 (*p*-C), 130.1 (2C, *o*-C), 129.4 (C6), 127.6 (2C, *m*-C), 124.2 (C5), 123.7 (C3), 51.0 (C9), 44.0 (C7), 35.4 (1C, 2-*t*Bu), 34.9 (1C, 4-*t*Bu), 31.5 (3C, 4-*t*Bu), 30.6 (3C, 2-*t*Bu), 22.9 (9-CH_3(x)), 18.3 (9-CH_3(y)). ^{15}N NMR (50.70 MHz, $CDCl_3$): −316.2 (N2), 31.3 (W═NPh). Elemental analyses were run for the toluene hemi solvate crystals used in X-ray measurements. Anal. calcd for $C_{27.5}H_{39}Cl_3N_2OW$: C 46.93, H 5.59, N 3.98; found C 47.26, H 5.42, N 4.07.

Preparation of 5. The experimental procedures described above for the synthesis and isolation of **4** was repeated using aminophenols **3b–3e** as ligand precursors. Dark purple **5** was isolated in a 30–35% yield in all experiments. Solid compound was crystallized from acetonitrile, mp 195–198 °C. ^{1}H NMR ($CDCl_3$): δ 8.50 (s, 1H, –N═CH–), 7.82 (s, 1H, ArH), 7.63 (t, J = 8.3 Hz, 2H, ArH), 7.47 (s, 1H, ArH), 7.31–7.40 (overlapping signals, 7H, ArH), 1.50 (s, 9H, 2-*t*Bu), 1.38 (s, 9H, 4-*t*Bu). ^{13}C NMR ($CDCl_3$): δ 167.6 (–N═CH–), 154.6, 152.2, 151.1, 150.0, 142.2, 131.6, 131.4, 130.5, 130.0, 128.2, 127.3, 124.1, 123.5, 35.5 (1C, 2-*t*Bu), 34.9 (1C, 4-*t*Bu), 31.4 (3C, 4-*t*Bu), 30.1 (3C, 2-*t*Bu). Anal. calcd for $C_{27}H_{31}Cl_3N_2OW$: C 47.02, H 4.53, N 4.06; found C 46.92, H 4.41, N 4.10.

Degradation of aminophenolate complexes 2 and 4

0.15 mmol (100 mg) samples of **2** and **4** were dissolved in 5 ml of 1,2-dichlorobentsene in thick-walled screw cap vials and heated at 150 °C for 16 h. Reactions produced corresponding Schiff-base complex **5**, which was isolated by column chromatography in *ca.* 35% yields.

Crystal structure determinations†. The single crystals of **4** were grown from a toluene–hexane mixture and the crystals of **5** were grown from acetonitrile. The crystallographic data of both compounds were collected at 123 K on an Enraf Nonius Kappa CCD area-detector diffractometer using graphite monochromatised Mo-Kα radiation (λ = 0.71073 Å). Data collection was performed using φ and ω scans and the data were processed using *DENZO-SMN* v0.97.638.[22] *SADABS* absorption correction was applied to the data of both compounds.[23] The structures were solved by direct methods using the *SHELXS-97* program and full-matrix least-squares refinements on F^2 were performed using the *SHELXL-97* program.[24] Structure figures were drawn using *Ortep-3*.[25]

Crystal data for 4. $C_{27.5}H_{39}Cl_3N_2OW$, M = 703.8, monoclinic, a = 10.15330(40), b = 21.6753(10), c = 13.67660(50) Å, β = 102.8943(25)°, V = 2933.93(21) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 0.423 mm^{-1}, 13 972 reflections measured, 5083 unique (R_{int} = 0.0414), which were used in all calculations. Multi-scan absorption correction made. T_{min} and T_{max} 0.5036 and 0.7457, respectively. Final R_1 = 0.0546, wR_2 = 0.1225, GOF = 1.36. Minimum and maximum residual electron density 2.189 and −1.543 e Å^{-3}.

Crystal data for 5. $C_{27}H_{31}Cl_3N_2OW$, M = 689.74, monoclinic, a = 13.77980(20), b = 14.20330(29), c = 14.75650(20) Å, β = 105.2619(10)°, V = 2786.266(81) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 0.446 mm^{-1}, 18 167 reflections measured, 5464 unique (R_{int} = 0.0310), which were used in all calculations. Multi-scan absorption correction made. T_{min} and T_{max} 0.5346 and 0.7458, respectively. Final R_1 = 0.0228, wR_2 = 0.0507, GOF = 1.067. Minimum and maximum residual electron density 0.568 and −0.594 e Å^{-3}.

Computational details

All calculations were performed with Turbomole 6.1 program package.[26] The geometries of the complexes were optimized at the DFT level of theory using the exchange functional of Becke[27] in conjunction with correlation functional of Perdew[28] (BP86). The def2-TZVP basis set[29] was used in all calculations. The nature of the located stationary points on the potential-energy surface was confirmed by calculation of the two lowest eigenvalues of hessian matrix. Partial atomic charges were calculated using MPA[30] and NPA[31] analyses as implemented in Turbomole 6.1 program package.

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