

Phenylimido Complexes of Tungsten(VI). The Effects of Ancillary Ligand Changes on Phenyl Ring ^{13}C NMR Resonance Positions

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Abstract

Phenyl ring ^{13}C NMR data for a series of tungsten(VI) phenylimido complexes, $\text{L}_5\text{W}\equiv\text{NPh}$ ($\text{L} = \text{Cl}$ and OR) show that the position of the *ipso* carbon resonances varies with changes in the ancillary ligands L . X-ray crystal structure data for $[\text{W}(\text{NPh})(\text{OCMe}_3)_3\text{Cl}(\text{NH}_2\text{CMe}_3)]$ and $[\text{W}(\text{NPh})(\text{OEt}_2)(\mu\text{-OEt})\text{Cl}]_2$, which have significantly different *ipso* carbon shifts, indicate that $\text{W}-\text{N}$ π -bonding is weaker in the latter, as the complex relies less on π -electron density from the imido ligand to satisfy overall π -bonding requirements in attaining an 18-electron configuration. Changes in the shielding observed at the *ipso* carbon for the other complexes can also be related to $\text{W}-\text{N}$ π -bonding variations. The *para* carbon shifts appear sensitive to inductive effects arising in the ancillary ligands of the $\text{L}_5\text{W}\equiv\text{N}-$ substituent, becoming more shielded as the number of alkoxide groups increases over chloro ligands (decreasing $-I$ effect) and as the number of methyl groups attached to the alkoxide α -carbon increases (increasing $+I$ effect). The *ortho* carbons are generally shielded or deshielded as found for the *para* carbons but to a lesser extent. Assessment of the data suggests π and σ components in the substituent may act independently to produce the variations in the chemical shifts observed.

Introduction

^{13}C NMR spectral studies of monosubstituted benzenes have shown that the chemical shift of the ring carbons depends on the nature of the substituent [1–3]. Metal complexes form a unique system in which the electronic structure can be dramatically affected by changes in the ligands making up the coordination sphere. Where the complexes contain ligands with aromatic rings attached, changes in electron distributions might be expected to show up in the chemical shift of the aromatic ring carbons.

We have been interested in the study of complexes containing the multiple-bonded organoimido function, ($\text{M}\equiv\text{NR}$) [4], in which there is a π -bonding compo-

nent involving donation of the nitrogen lone pair to the metal. In particular, changes in the π -bonding system are of interest as an increase in electron density on nitrogen is expected to enhance the reactivity of the imido function [5–8]. Organoimido complexes are relatively unreactive [4] and have not shown the diversity of reactions exhibited by the related alkylidene and alkylidyne complexes ($\text{M}\equiv\text{CHR}$ and $\text{M}\equiv\text{CR}$) [9]. ^{13}C NMR studies of *t*-butylimido complexes of a variety of metals indicate that the position of the α -carbon resonance is sensitive to the extent of lone pair donation to the metal [10] while similar studies of a series of tungsten(VI) isopropylimido complexes in combination with structural studies, have shown that overall π -bonding requirements of the complexes are important [11].

A variety of phenylimido complexes of tungsten(VI) has recently been prepared in our laboratories [12–14] for which phenyl ring ^{13}C NMR data have been obtained. It was thus of interest to establish in qualitative terms if the aromatic ring resonances of these complexes were sensitive to bonding changes occurring in the imido function and also to structural changes in the ancillary ligands.

Results and Discussion

Theoretical treatment has shown the total shielding constant, σ , for a particular nucleus is affected mainly by paramagnetic contributions involving charge polarization, variation in bond order, and average excitation energy [3, 15, 16]. Where these do not vary much for related compounds, a relationship between chemical shift and local electron density on carbon may be apparent [17]. For phenylimido complexes, ($\text{L}_5\text{W}\equiv\text{NPh}$), the $\text{L}_5\text{W}\equiv\text{N}-$ group may be regarded as a 'substituent' on the aromatic ring and, as such, changes in the ancillary ligands L , or changes in the electron density making up the $\text{W}-\text{N}$ multiple bond, represent changes that might be expected to show up as a small substituent effect.

^{13}C NMR data for the aromatic ring carbons of the phenylimido complexes of tungsten(VI) are con-

TABLE I. Phenyl Ring ^{13}C NMR Shifts for Phenylimido Complexes of Tungsten(VI)^a

Complex ^b	MEC ^c	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i> ^e
1 [W(NPh)(OCMe ₃) ₄]	14	+25.4	-1.5	-0.8	-3.3(2)
2 [W(NPh)(OCMe ₃) ₃ Cl(NH ₂ CMe ₃)] ^d	16	+25.1	-2.8	-1.1	-2.8(3)
3 [W(NPh)(OCHMe ₂) ₄ (NH ₂ CMe ₃)]	16	+24.4	-1.8	-0.91	-3.8(1)
4 [W(NPh)(OCH ₂ CMe ₃) ₄ (NH ₂ CMe ₃)]	16	+24.0	-2.0	-2.0	-2.0(5)
5 [W(NPh)((OEt) ₃ (μ-OEt)) ₂]	16	+23.8	-1.1	-0.6	-2.7(4)
6 [W(NPh)(OMe) ₃ (μ-OMe)] ₂	16	+22.9	-0.7	-0.7	-1.8(6)
7 [W(NPh)(OEt) ₂ (μ-OEt)Cl] ₂ ^d	16	+22.6	-0.5	-0.7	-0.1(7)
8 [W(NPh)(OEt)(μ-OEt)Cl] ₂	16	+21.9	+0.6	-0.8	+2.8(9)
9 [W(NPh)(μ-OEt)Cl] ₃	16	+21.2	+1.3	-0.7	+3.2(12)
10 [W(NPh)Cl ₄ (OEt)] [CPh ₃]	16	+20.9	+1.0	-0.9	+2.8(10)
11 [W(NPh)Cl ₄ (NCEt)]	16	+20.5	+3.2	+3.1	+6.0(13)
12 [W(NPh)(OEt)Cl ₃ (NH ₂ CMe ₃)]	16	+20.2	+1.7	-0.9	+2.9(11)
13 [W(NPh)(OEt)Cl ₄][NEt ₄]	16	+20.0	+1.5	-0.9	+2.0(8)

^aPositive values indicate ring carbon is deshielded with respect to benzene (128.5 ppm); negative values indicate shielding.

^bComplexes in decreasing order of *ipso* carbon magnitude. ^cMaximum electron count based on W = 6, NPh = 4, Cl = 1, OR = 1, bridging and neutral ligands = 2. ^dSingle crystal X-ray structure data in Table III. ^eFigure in parenthesis indicates order of increasing +ve *para* carbon chemical shift.

tained in Table I. Using the method for comparing substituent effects in monosubstituted benzenes [1, 2] the resonances are compared with benzene for which the aromatic ring carbons appear as a single resonance at 128.5 ppm in CDCl₃. The values appearing in the Table are then either positive or negative in relation to benzene indicating that the ring carbons are either deshielded or shielded.

The Table shows the complexes arranged in decreasing order of *ipso* carbon deshielding, the values ranging from +25.4 for [W(NPh)(OCMe₃)₄] (1) to +20.0 for [W(NPh)(OEt)Cl₄][NEt₄] (13). Arranged in this order the *ortho* and *para* carbons of the phenyl rings at the top of the Table are shielded with respect to benzene and those at the bottom are deshielded, the *para* carbon showing the largest effect. In accordance with data obtained for a variety of monosubstituted benzenes [2], the *meta* carbons typically show the smallest change from the value for benzene. For comparison, data for a series of monosubstituted benzenes are contained in Table II.

*Ips*o Carbons

Studies of isopropylimido complexes of tungsten(VI) [11] have shown that the position of the α -carbon to the imido nitrogen is sensitive to the degree of π -bonding in the W-N multiple bond and this in turn depends on how the complexes are able to attain an 18-electron count.

Assuming the imido ligand of the phenylimido complexes represents a true 4-electron donor, the alkoxide and chloro ligands act formally as one electron donors and neutral or bridging ligands coordinating via lone pairs act as 2-electron donors, then the complexes all have electron counts of less than 18.

TABLE II. ^{13}C Substituent Effects of Monosubstituted Benzenes^a

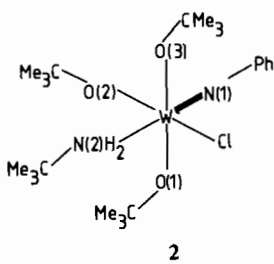
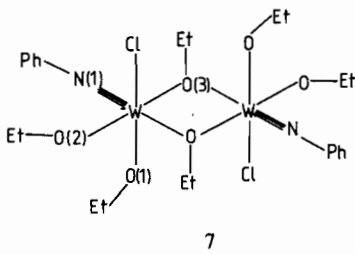
Substituent	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
CH ₃	+8.9	+0.7	-0.1	-2.9
Cl	+6.2	+0.4	+1.3	-1.9
NH ₂	+18.0	-13.3	+0.9	-9.8
SCH ₃	+10.2	-1.8	+0.4	-3.6
OAc	+23.0	-6.4	+1.3	-2.3
NMe ₂	+22.6	-15.6	+1.0	-11.5
NO ₂	+20.0	-4.8	+0.9	+5.8
CO ₂ Me	+1.3	-0.5	-0.5	+3.5
CHO	+9.0	+1.2	+1.2	+6.0
COCH ₃	+9.1	+0.1	0.0	+4.2

^aValues taken from refs. 1 and 2.

Table I shows that the majority are 16-electron species while the monomeric complex [W(NPh)(OCMe₃)₄] (1) has a 14-electron count. To obtain an 18-electron configuration, π -bonding is necessary from the ancillary ligands and this information is available for two of the complexes from structural data. We have previously carried out single crystal X-ray structure determinations of [W(NPh)(OCMe₃)₃Cl(NH₂CMe₃)] (2) [12], and [W(NPh)(OEt)₂(μ-OEt)Cl]₂ (7) [13], which show *ipso* carbon resonances at +25.1 and +22.6, respectively, the difference of 2.5 ppm representing approximately 50% of the total range of values observed in the Table for these carbons. Structural information for the two complexes is contained in Table III.

Alkoxide and chloro ligands are both capable of donating lone pair electron density to a metal and thus can act essentially as 3-electron donors [5].

TABLE III. Single Crystal X-ray Structure Data for $[\text{W}(\text{NPh})(\text{OCMe}_3)_3\text{Cl}(\text{NH}_2\text{CMe}_3)]$ (2)^a and $[\text{W}(\text{NPh})(\text{OEt})_2(\mu\text{-OEt})\text{Cl}]_2$ (7)^b

Bond lengths (Å)											
	<table border="0"> <tr><td>W–N(1)</td><td>1.71(2)</td></tr> <tr><td>W–O(1)</td><td>1.86(1)</td></tr> <tr><td>W–O(2)</td><td>1.85(1)</td></tr> <tr><td>W–O(3)</td><td>1.91(2)</td></tr> <tr><td>W–Cl</td><td>2.50(2)</td></tr> </table>	W–N(1)	1.71(2)	W–O(1)	1.86(1)	W–O(2)	1.85(1)	W–O(3)	1.91(2)	W–Cl	2.50(2)
W–N(1)	1.71(2)										
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W–Cl	2.50(2)										
	<table border="0"> <tr><td>W–N(1)</td><td>1.759(9)</td></tr> <tr><td>W–O(1)</td><td>1.865(7)</td></tr> <tr><td>W–O(2)</td><td>1.835(9)</td></tr> <tr><td>W–O(3)</td><td>2.003(8)</td></tr> <tr><td>W–Cl</td><td>2.454(3)</td></tr> </table>	W–N(1)	1.759(9)	W–O(1)	1.865(7)	W–O(2)	1.835(9)	W–O(3)	2.003(8)	W–Cl	2.454(3)
W–N(1)	1.759(9)										
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W–O(3)	2.003(8)										
W–Cl	2.454(3)										

^aData taken from ref. 12.^bData taken from ref. 13.

For $[\text{W}(\text{NPh})(\text{OEt})_2(\mu\text{-OEt})\text{Cl}]_2$ (7) the W–O(3) bond length of 2.003(8) Å indicates that the bridging ethoxide ligand acts as a 1-electron donor to W(1) [13]. Chloro ligands are poor π -donors in comparison with alkoxides [18] and this is reflected by the W–Cl bond length which at 2.454(3) Å lies towards the upper limit observed for tungsten–chlorine bonds [19]. The two terminal ethoxide W–O bond lengths (1.835(9) Å and 1.865(7) Å) are short, lying within the range found for $\text{W}=\text{OR}$ bonds [18] so that a measure of π -bonding exists in both. Thus the complex is able to attain an 18-electron count using π -electron density from these ligands and this is apparently sufficient to allow the W–N bond length of 1.759(9) Å to become longer than the 1.71 Å predicted for a true 4-electron donor [4].

Structural data for $[\text{W}(\text{NPh})(\text{OCMe}_3)_3\text{Cl}(\text{NH}_2\text{CMe}_3)]$ (2) indicates that the complex attains an 18-electron count using π -electron density from 3 alkoxide ligands. The W–O bond lengths appear marginally longer than in $[\text{W}(\text{NPh})(\text{OEt})_2(\mu\text{-OEt})\text{Cl}]_2$ (7) which suggests less π -electron density is available for bonding. Although the differences are small, the overall π -bonding requirement of the molecule is reflected by shortening of the W–N bond length to 1.71(2) Å which within the standard deviation is close to the value predicted for an imido ligand acting as a 4-electron donor.

Consideration of the shielding experienced at the *ipso* carbon for the two complexes in terms of the W–N bond lengths, indicates that where the W–N bond lengthens, the degree of shielding increases or, shielding increases where π -electron density is released to nitrogen.

Using the π -bonding approach, it is possible to make predictions as to the extent of *ipso* carbon shielding in some of the other complexes. $[\text{W}(\text{NPh})\text{Cl}_4(\text{NCEt})]$ (11) contains 4-terminal chloro ligands which are able to donate electron density equivalent to 2 electrons via π -orbitals, to the metal. Some relaxation of π -bonding in the W–N bond might then be expected in comparison to $[\text{W}(\text{NPh})(\text{OEt})_2(\mu\text{-OEt})\text{Cl}]$ (7) resulting in less deshielding at the *ipso* carbon. Inspection of Table I verifies this prediction.

The monomeric complex $[\text{W}(\text{NPh})(\text{OCMe}_3)_4]$ (1) as a 14-electron species, would require electron density equivalent to two electron pairs from the alkoxide ligands to obtain an 18-electron count while distortion from octahedral geometry is expected for the complex resulting in less efficient orbital overlap. Combination of these factors would point to strong donation of the nitrogen lone pair to tungsten leading to strong deshielding of the *ipso* carbon, and this is found to be the case.

Para Carbons

The carbon *para* to the substituent in mono-substituted benzenes is found to be a special case for which correlation between calculated charge densities and ¹³C chemical shift can be made [3]. Substituents with strong electron-withdrawing properties give rise to deshielded *para* carbons (+ve values) while those that are electron-donating result in shielded *para* carbons (–ve values) [2, 17] (see Table II).

Table I shows that the phenyl ring *para* carbons of the complexes are shielded and deshielded at top and bottom respectively, but magnitude does not follow the order given by the *ipso* carbons.

From the earlier assessment of the *ipso* carbon resonance shifts, small increases in electron density on nitrogen occurring down the list of complexes might be expected to show up as an increase in the electron-donating properties of the $\text{L}_5\text{W}=\text{N}$ -substituent resulting in increased deshielding at the *para* carbon (*i.e.* –ve values). However, Table I shows the reverse is observed. $[\text{W}(\text{NPh})\text{Cl}_4(\text{NCEt})]$ (11) shows a similar value to PhNO_2 (see Table II) where strong electron withdrawal from the ring occurs, while further up the list electron donation is apparent, similar to that found for OAc or SCH_3 substituents in monosubstituted benzenes.

Table I indicates the order of increasingly more +ve *para* carbon chemical shift which is not greatly different to the observed *ipso*-carbon order. As a general trend the *para* values become more positive

as the size around the alkoxide α -carbon decreases and also as the number of chloro ligands increases over the alkoxide ligands. This latter trend is especially noticeable in the series $[\text{W}(\text{NPh})(\text{OEt})_n\text{Cl}_x]_2$ (complexes 5, 7, 8 and 9).

In terms of inductive effects, alkoxy groups are less electron withdrawing ($-I$) than chloro groups while larger alkyl groups are more effective electron donors ($+I$). Relating these features to the complexes, it is apparent that as the number of alkoxide groups increases over chloro ligands (decreasing $-I$ effect), and the number of methyl groups attached to the alkoxide α -carbon increases (increasing $+I$ effect) the *para* carbons become more shielded. Thus the *para* carbons appear to be sensitive to the nature of the ancillary ligands coordinated to the metal, and in particular electron density available for bonding if inductive effects are invoked. As the π -bonding situation in the $\text{W}-\text{N}$ bond is not drastically affected by these changes, a sigma inductive effect would appear to be in operation around the metal center, which can compensate for electron withdrawal from the ring at the *para* carbon.

$[\text{W}(\text{NPh})(\text{OEt})\text{Cl}_4][\text{NEt}_4]$ (13) and $[\text{W}(\text{NPh})(\text{OEt})\text{Cl}_4][\text{CPh}_3]$ (10) are clearly anomalous in the list, however both complexes are ionic, being derivatives of $[\text{W}(\text{NPh})(\mu\text{-OEt})\text{Cl}_3]_2$ (9) whereas the remaining examples are neutral so that development of an anion has a significant effect. $[\text{W}(\text{NPh})(\text{OCMe}_3)_4]$ (1) is also anomalous but the expected distortion in the molecule and associated less efficient overlap of bonding orbitals may account for this.

Ortho Carbons

Correlation of *ortho* carbon electron density with chemical shift in monosubstituted benzenes is less successful as the position of the *ortho* resonance can be influenced by a variety of effects [20] and this is similarly expected to be the case for the complexes. It is noted, however, that where the *para* carbons are shielded or deshielded, the *ortho* carbons are affected similarly but to a lesser extent. In the closely related series of complexes $[\text{W}(\text{NPh})(\text{OEt})_n\text{Cl}_x]_2$ the *ortho* resonances become progressively more shielded which may be related to a diminishing $-I$ effect.

Conclusion

The studies indicate that the positions of the *ipso* and *para* carbons are sensitive to changes in electron distributions about the metal center. Complexes which rely more on π -electron density from the imido nitrogen to satisfy overall π -bonding requirements in attaining an 18-electron configuration show an increase in deshielding at the *ipso* carbon.

Shielding is greater at the *para* carbon where the size and number of alkoxide ligands increases over the number of chloro ligands. The *ipso* and *para* carbons appear to be sensitive to separate π - and σ -bonding components arising at the metal center as the data indicate the effects are not mutually reinforcing.

Experimental

The complexes were prepared by reported procedures [12, 14]. ^{13}C NMR spectra were recorded on a Jeol FX60 spectrometer operating at 15.040 MHz. Spectra were obtained as 16 K/4000 Hz spectra giving a digital resolution of 0.49 Hz. Samples were dissolved in dry degassed CDCl_3 , giving solute concentrations of approximately 0.4 per cm^3 . Identification of the *ipso* carbons was made by SFORD spectra and the *para* carbons by relative peak height. *ortho* and *meta* carbon assignments are tentative, based on the *meta* carbon resonance differing by a smaller extent from benzene (128.5 ppm). Spectra run at maximum and minimum concentrations gave a maximum error due to concentration effects and deterioration in solution clarity of ± 0.1 ppm. Data contained in Tables I and II show the resonances in relation to benzene (128.5 ppm). Negative values indicate shielding with respect to benzene and positive values deshielding.

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