

^{183}W NMR Spectroscopy of W(VI) Imidoaryl and Imidoalkyl Complexes Using Inverse Detection Based on Non-Specific Long-Range Interactions

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^{183}W NMR spectra for a series of octahedral W(VI) imidophenyl, 'W \equiv NPh' and W(VI) imidoethyl, 'W \equiv NEt,' complexes were obtained using inverse detection based on non-specific long-range interactions. The metal couples to both the *ortho* and *para* protons of the NPh moiety (four and six bonds, respectively). The ^{183}W shift is shown to be sensitive to the nature of the ligand and the coordination number. The effect of geometric isomerism on $\delta^{183}\text{W}$ is shown to be several hundred ppm. Some $\delta^{14}\text{N}$ and $\delta^{15}\text{N}$ and $^1J(^{183}\text{W}, ^{15}\text{N})$ data are reported. A number of new geometric isomers, involving the position of the NR ligand with respect to the remaining ligands, have been identified.

KEY WORDS ^{183}W NMR Inverse detection W(VI) imidophenyl compounds $^{14,15}\text{N}$ NMR

INTRODUCTION

Tungsten complexes in higher oxidation states have been shown to be interesting precursors in metathesis chemistry.¹ The tungsten co-catalyst can be a simple tungsten-halogen complex² or contain alkoxide and/or carbene ligands.³ Given this interest, we considered it useful to investigate the ^{183}W ($I = 1/2$, natural abundance = 14.3%) NMR characteristics of a series of W(VI) compounds with chloride and alkoxide ligands. We focus in this work on complexes containing the 'W \equiv NR' fragment, as these have received some special attention in connection with metathesis catalysis.⁴ The ^{183}W NMR literature is still relatively sparse,⁵ partially owing to the lack of knowledge concerned with long-range spin-spin interactions involving tungsten and protons, thereby inhibiting the use of inverse detection methods for this nucleus.^{6–9} We show here that the imido, NR ligand shows interesting and unexpected long-range coupling constants to tungsten and that these spin-spin interactions can be used in the detection of the metal resonance.

RESULTS AND DISCUSSION

Table 1 gives the NMR parameters for complexes 1–15 studied.

Figure 1 shows the proton-tungsten correlation for the W(VI) \equiv NPh complex 10, from which it can be seen

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that the ^{183}W spin-spin couples not only through four bonds to the *ortho* but also through six bonds to the *para* protons of the phenyl group. This is the first report of such long-range proton-tungsten interactions (and the first ^{183}W chemical shifts for this class of complex). The coupling constants to the *ortho* protons of the phenyl group are less than 1 Hz (0.7 and 0.4 Hz in 1 and 3, respectively) and even smaller for the *para* protons (*ca.* 0.5 and 0.3 Hz in 1 and 3, respectively). As shown in Fig. 2, there are a number of other interesting metal-proton coupling constants, e.g. a selective $^3J(\text{W}, \text{H})$ to one of the NCH₂ protons of 5 (presumably the result of a dihedral angle dependence) and $^3J(\text{W}, \text{H})$ to the *ortho* aromatic proton of the cyclometallated ligand, and these can also be used to detect the metal. There is also a *ca.* 11 Hz $^3J(\text{W}, \text{H})$ interaction to the imido-ethyl group in 13–15 (see Fig. 3); however, the long-range proton-tungsten interactions from ^{183}W to the NPh ligand are general for this class of compounds and have been used to detect the ^{183}W resonances in complexes 1–12.

The ability to obtain tungsten-183 spectra on complexes such as 1 opens the way to the study of other related complexes containing ligands which need not have conveniently placed protons spins. Although we obtain good quality spectra using spin-spin interactions of the order of 1 Hz or less, there are instrumental (and instrument environmental) restrictions which suggest that we are approaching the current limit with conventional equipment. A further step might require gradient-assisted spectroscopy to reduce T_1 noise. We normally obtain spectra on 10–20 mg of sample in less than 30 min.

Table 1. ^{183}W and ^{14}N NMR data^a

Compound	$\delta^{183}\text{W}$ (ppm)	$\delta^{14}\text{N}$ (ppm)	^{14}N linewidth (Hz)
W(NPh)Cl ₄ (OEt ₂) (1)	2382	59.1	113
W(NPh)Cl ₃ (OEt ₂)(O-2,6Me ₂ Ph) (2)	1598	39.4	195
W(¹⁵ NPh)Cl(CH ₂ SiMe ₃) ₃ (3) ^b	4001	-45.3	
W(NPh)Cl ₃ (C ₆ H ₄ CH ₂ NMe ₂ -2) (4)	2638	31.8	101
W(NPh)Cl ₂ (C ₆ H ₄ CH ₂ NMe ₂ -2)(OCMe ₃) (5)	1593	6.7	135
W(NPh)Cl(C ₆ H ₄ CH ₂ NMe ₂ -2)(OCMe ₃) ₂ (6)	960	-9.1	265
W(NPh)(C ₆ H ₄ CH(Me)NMe ₂ -2)(OCMe ₃) ₂ (CH ₂ SiMe ₃) (7)	2774	-15.4	239
W(NPh)(C ₆ H ₄ CH ₂ NMe ₂ -2)(OCMe ₃)(CH ₂ SiMe ₂) ₂ (8) ^c	A 2069 B 2520 C 1675	-43.6 ^d	15
W(NPh)(C ₆ H ₄ CH ₂ NMe ₂ -2)(O-C ₆ H ₃ Me ₂ -3,5-)(CH ₂ SiMe ₃) ₂ (9) ^e	2547	-25.0	19
W(NPh)Cl ₃ (OC ₆ H ₄ CH ₂ NMe ₂ -2) (10)	1782	37.9	148
W(NPh)Cl ₃ (O-C ₆ H ₂ CH ₂ NMe ₂ -2,Me-4,CH ₂ NMe ₂ -6) (11)	1760	36.2	189
W(NPh)(C ₆ H ₃ NCH ₂ NMe ₂ -2)(=CHSiMe ₃)(CH ₂ SiMe ₃) (12)	2552	-6.8	670
W(NEt)Cl ₄ (13)	2051	95.0	161
W(NEt)Cl ₄ (OEt ₂) (14)	2016	78.6	178
	1464	86.4	120
W(NEt)Cl ₄ (OCH ₂ CH ₂ CH ₂ CH ₂) (15)	2070	79.7	111
	1566	72.8	227

^a C₆D₆ unless specified.

^b The nitrogen-15 shift is given; $^1J(^{183}\text{W},^{15}\text{N}) = 102$ Hz. The value of $^1J(^{183}\text{W},^{15}\text{N})$ for **1** is 109 Hz.

^c $^1J(^{183}\text{W},^{14}\text{N}) = 77$ Hz.

^d There are two shifts, -14.1 and -19.1 for B and C, but these are not assigned.

^e $^1J(^{183}\text{W},^{14}\text{N}) = 80$ Hz.

^{183}W chemical shifts

The total range of ^{183}W chemical shifts for the complexes studied is 3041 ppm (960–4001 ppm, relative to WF₆). These values lie within the known window for this nucleus in the VI oxidation state.¹⁰ One can debate whether these complexes are indeed in the VI oxidation state and whether the 'NR' is formally 2- or neutral (as implied by writing a triple bond); however, we consider this partially a question of semantics since strong σ -donors, e.g. alkoxides and NR²⁻, will certainly also be π -donors to some extent. The ^{183}W chemical shift for WCl₆ is 3298, so that by comparison with

W(NR)(OEt₂)Cl₄ complexes, R = Ph or Et, $\delta = 2382$ and 2016 ppm, respectively, there is a marked low frequency shift on introduction of the imido ligand.

For WCl₄(NEt)(THF) (**15**) in C₆D₆, we observed two ^{183}W resonances at 2070 and 1566 ppm, two sets of NEt proton signals but broad THF proton lines. A measurement in toluene-*d*₈ at 253 K afforded two sets of sharp lines for the THF and two for the NEt ligand, with the two compounds in a ratio of ca. 2.6:1. A two-dimensional (2D) ¹H-exchange spectrum shows that these two complexes are in slow exchange. Addition of excess THF has no effect on the proton lines of the complexes. As the ^{183}W shifts at 253 K are very similar

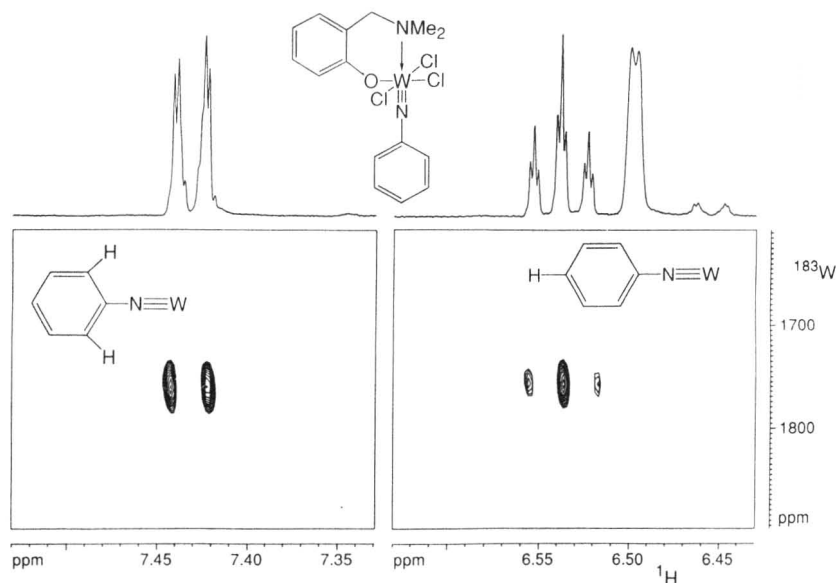


Figure 1. Sections of the 11.7 T ^{183}W -H inverse shift correlation for **10**. Note that there are cross peaks for both the *ortho* and *para* protons of the imidophenyl group (C₆D₆).

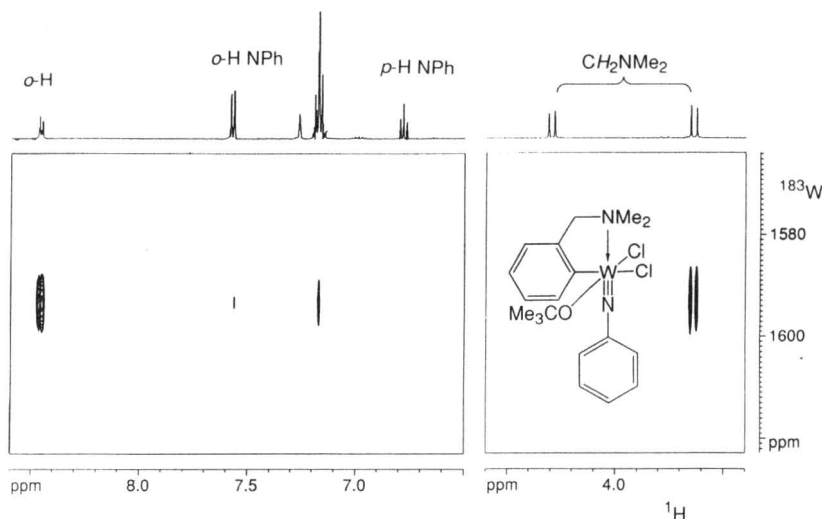


Figure 2. Sections of the 11.7 T ^{183}W -H inverse shift correlation for **5**. The lowest field proton resonance stems from the *ortho* proton of the cyclometallated ring. The high-field half of the NCH_2 ABX spin system shows a relatively strong coupling to ^{183}W (C_6D_6).

to those at room temperature, we conclude that we are dealing with *cis* and *trans* geometric isomers and consequently that we have an estimate of this geometric effect on $\delta^{183}\text{W}$. For **14** we also observe two isomers but for $\text{WCl}_4(\text{NPh})(\text{OEt}_2)$ (**1**) we find only one isomer.

In some of the more complicated compounds the structure of the geometric isomer is well defined based on proton NMR studies, e.g. **6**; however, in many cases we can only be sure of the composition, and presume that the isomer shown is correct. However, for **8**, in which we find three ^{183}W resonances (complexes A-C in the ratio 1:1.4:0.7), we have measured a 2D ^1H NOESY spectrum. These data suggest we have the three isomers shown; isomer B is novel in that it has the NR ligand *trans* to a carbon ligand and its postulation

is based on NOE between the *ortho* protons of the NPh and the NMe groups.

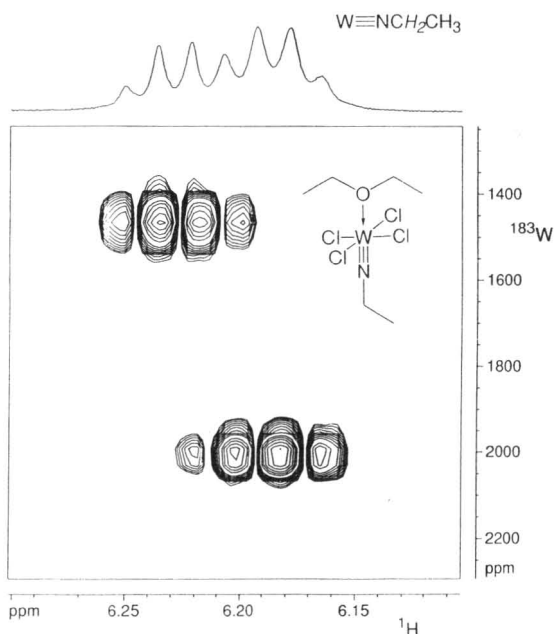
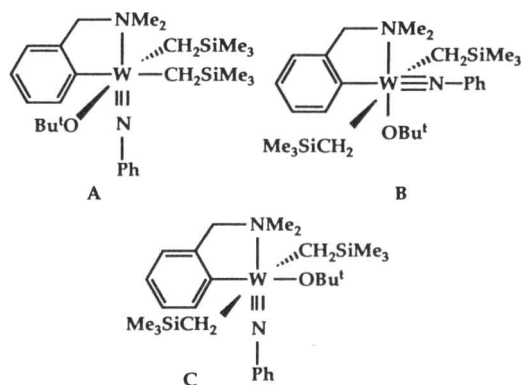
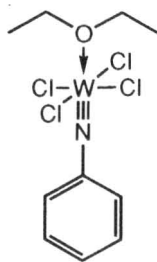


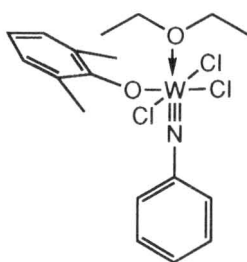
Figure 3. Section of the 11.7 T ^{183}W -H inverse shift correlation for **14** demonstrating the existence of two species in solution with a 552 ppm difference in metal chemical shift (C_6D_6).

The clearest trend involving change in metal chemical shift as a function of ligand arises from a consideration of the effect on $\delta^{183}\text{W}$ when a Cl^- is replaced by an alkoxide and amounts to a low frequency of the order of 600–800 ppm (see **1–3** and **4–6**). Going from **8** to **9**, in which a *tert*-butoxide is exchanged for the 3,5-dimethylphenoxide ligand, points out the known¹¹ substituent effect on $\delta^{183}\text{W}$ when going from OBu^t to a sterically smaller alkoxide. The observed high frequency shift of 478 ppm is consistent with that found in the complexes $\text{W}(\text{O})(\text{OR})_4$, e.g. for $\text{W}(\text{O})(\text{OBu}^t)_4$ and $\text{W}(\text{O})(\text{OMe})_4$ the difference is 324 ppm,¹¹ with the Bu^t complex again at lower frequency. Replacement of an alkoxide with a CH_2SiMe_3 group, e.g. **7** to **8**, affords a *ca.* 700 ppm low frequency shift whereas changing the imide nitrogen substituent from Ph to Et, **1** to **14**, results in a 366 ppm low frequency shift. A comparison of chemical shifts for **14** and **15** (Et_2O vs. THF as coordinated solvent) reveals only modest changes.

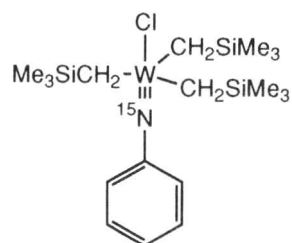
This brings us to the question of coordination number and its effect on the metal resonance frequency. The class of complex $\text{W}(\text{O})(\text{OR})_4$ is thought to exist mostly as dimers,¹¹ e.g. six-coordinate tungsten, whereas for $\text{W}(\text{O})[\text{O}(2,6\text{-Pr}^i\text{C}_6\text{H}_3)]_4$, the metal is five-coordinate¹¹ (presumably due to the large *ortho* Pr^i



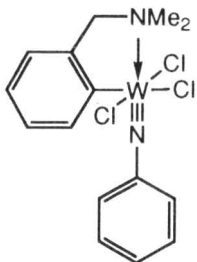
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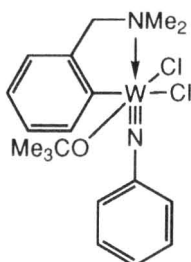
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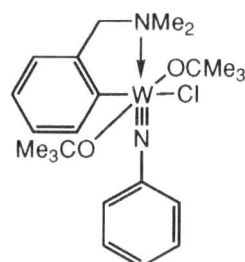
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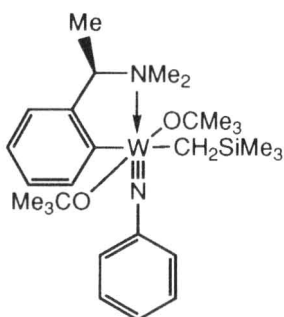
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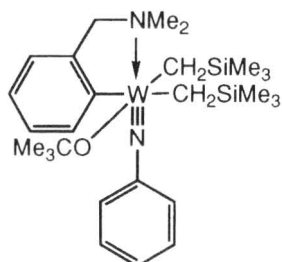
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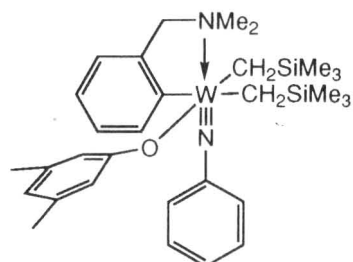
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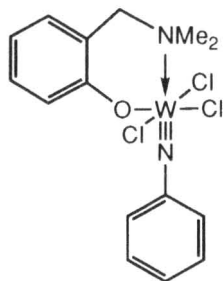
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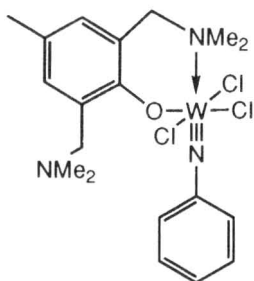
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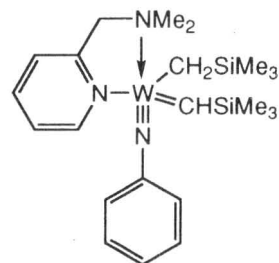
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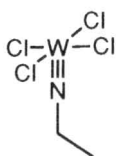
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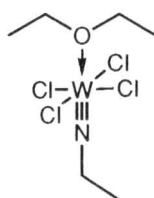
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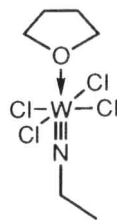
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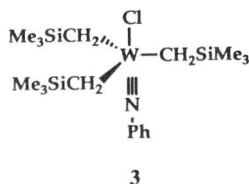


14



15

groups). Consequently, the 430.7 ppm high frequency change in the ¹⁸³W position on going from W(O)[O(2,6-PrⁱC₆H₃)₂]₄ to W(O)(OMe)₄ does not result from a steric effect on the metal, but rather an electronic effect due to the different coordination numbers. We suggest that W(NEt)Cl₄ (**13**), δ = 2051 ppm, is not five-coordinate, as written, but either a halogen-bridged six-coordinate dimeric complex (for which there is precedence in the solid state¹²) or an aquo complex, W(NEt)Cl₄(H₂O), (which might arise from traces of water) and note the similarity in chemical shift for **13**, δ = 2051 ppm, and **14**, δ = 2016 ppm. In the metal and proton spectra for **13** we find a second component at δ = 1573 ppm and assume that this may arise from either isomerization or hydrolysis, i.e. hydroxide or bridging oxide ligands may be present.¹¹ There are also additional ¹⁸³W low frequency signals in the metal spectra for **14** and **15** (see Table 1). Further, it is possible that we must seek the source of the very high frequency position found in W(NPh)Cl(CH₂SiMe₃)₃ (**16**), δ = 4001 ppm, in terms of coordination number, i.e. five in this complex. As suggested above, the electronic effect of the CH₂SiMe₃ group is to shift the metal resonance to low frequency. Therefore, the observed high frequency shift may arise as a consequence of having three relatively large CH₂SiMe₃ anionic ligands, which induce the metal to accept five-coordination. The high frequency chemical shift for **3** is amongst the lowest recorded. Only dinuclear complexes containing metal-metal bonds appear at higher frequency.^{10,13}



In this work we made no attempt to rationalize the ¹⁸³W chemical shifts using changes in the various contributions to σ_p, the dominant contributor to changes in heavy atom NMR shifts.¹⁴ This is due to the absence of a clear MO picture for complexes with mixed coordination spheres, e.g. in **5–9** five different ligands, a lack of sufficient model complexes and our inability to assess accurately the exact electronic nature of the imido ligand.

Figure 4 shows the proton–tungsten correlation for **3**, prepared using >95 at.-%-enriched ¹⁵N. Apart from its interesting metal chemical shift, obtained via the methylene protons of the Me₃SiCH₂ group, one can measure the one-bond coupling constant ¹J(¹⁸³W, ¹⁵N), 102 Hz, directly from the spectrum. The corresponding value for **1** (also enriched) is 109 Hz, and the values ¹J(¹⁸³W, ¹⁴N) for **8** and **9**, 77 and 80 Hz, respectively, are all not very different (after correction by γ¹⁵N/γ¹⁴N = 1.4), so that it is unlikely that this parameter will be a useful structural tool in these molecules.

¹⁴N chemical shifts

To obtain some feeling for how the nitrogen environment is affected by the changes in the coordination sphere, we have obtained ¹⁴N data for the complexes.

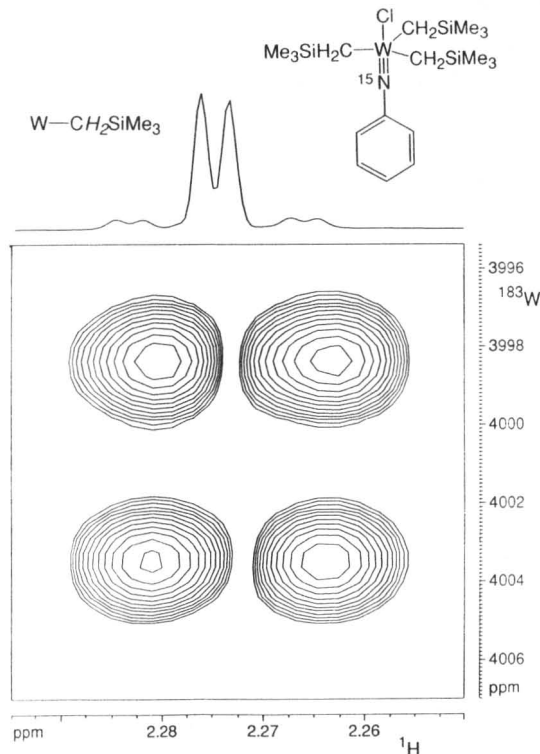
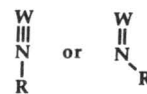


Figure 4. Section of the 11.7 T ¹⁸³W–H inverse shift correlation for **3**. The spacing in the metal direction represents ¹J(¹⁸³W, ¹⁵N). The correlation arises from coupling of the metal to the CH₂ protons (C₆D₆).

Osborn and co-workers³ have already shown that the ¹⁴N chemical shifts in complexes of the type W(NR)(CH₂Bu)₃X fall in the range +106 to –59 ppm (relative to CH₃NO₂) and have linewidths of the order of 7–100 Hz. We found the nitrogen-14 resonances in the same region (see Table 1); however, our linewidths are frequently in excess of 100 Hz. Generally, the ¹⁴N shifts are found at relatively low field when we have the imido together with Cl[–] or OR[–] donors, e.g. **1** and **2** or **13–15**, but shift to higher field when several carbon donors are present, as in **7–9**. Where the complexes are closely related, such as in **4–6** and **7–9**, plots of δ¹⁸³W vs. δ¹⁴N are linear; however, there is no linearity whatsoever if one considers all of the complexes.

Osborn and co-workers³ also considered the possibility that the ¹⁴N line width might be related to whether the imide is linear or bent:



We have nothing new to add on this subject except to note that if in complexes such as **4–9** the imide were bent, one might expect to find geometric isomers, and we have no evidence (from the proton or tungsten spectra) for these. Consequently, we consider these compounds to have a linear W–N–R arrangement, as is known to be the case for **5** [W–N–R angle is 170.4(7)°] based on x-ray diffraction results.¹⁵

Given the potential associated with ¹⁵N (I = 1/2, natural abundance = 0.3%), we have taken the observa-

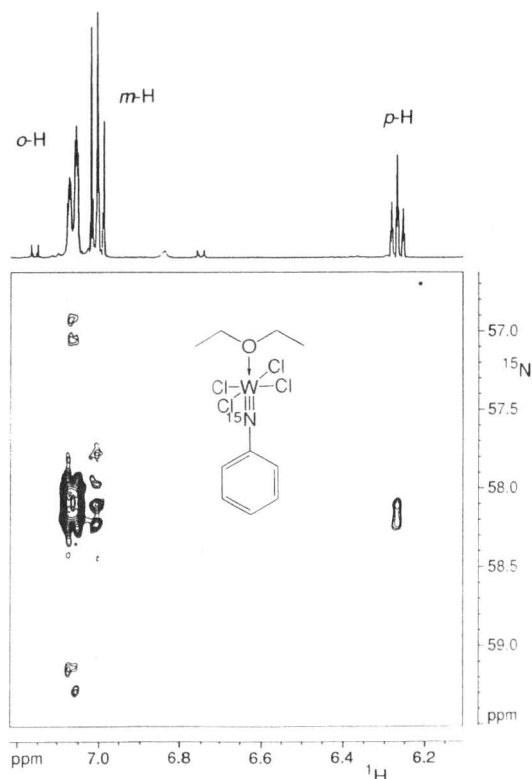


Figure 5. Aromatic region of the ^{15}N -H inverse shift correlation for **14**. Note that all three NPh proton types show cross peaks, with those to the *ortho* protons being the strongest. The splitting in the nitrogen direction arises from proton-proton coupling (C_6D_6).

ble $^3J(^{15}\text{N},^1\text{H})$ value, *ca.* 1.8 Hz, found in the proton spectrum of our >95 at.% ^{15}N -enriched samples, as typical, and attempted an inverse ^{15}N measurement of **1**, as shown in Fig. 5. This spectrum reveals that all of the NPh protons spin-spin couple to the nitrogen, with the ^{183}W tungsten satellites visible in the ^{15}N direction for the *ortho* protons. For **1** $^5J(^{15}\text{N},^1\text{H})$ is *ca.* 0.5 Hz and for **3** $^3J(^{15}\text{N},^1\text{H})$ is *ca.* 1.4 Hz and $^5J(^{15}\text{N},^1\text{H})$ is *ca.* 0.3 Hz. This methodology will be preferable where the ^{14}N line is too broad and/or one has a mixture in which an ^{14}N line is not readily observed. As expected, the ^{15}N shift is identical, within the experimental error, with that found in the ^{14}N spectrum. In any case, the ability to measure both nitrogen isotopes at will should prove valuable.

In conclusion, we can readily measure ^{183}W spectra for this class of complexes using at least four different spin-spin coupling constants to various protons. There are also some unexpected ^{15}N - ^1H interactions and we plan to use these NMR coupling constants to explore further this imido-tungsten chemistry.

EXPERIMENTAL

NMR measurements were performed on C_6D_6 solutions using a Bruker AMX-500 instrument operating in the Fourier transform mode at 500.13, 99.36, 50.67, 36.14 and 20.80 MHz for ^1H , ^{29}Si , ^{15}N , ^{14}N and ^{183}W , respectively. Chemical shifts are given relative to WF_6 for ^{183}W . We take WF_6 as 1117 ppm to high field of

WO_4^{2-} . The nitrogen chemical shifts are referenced to CH_3NO_2 .

^{183}W - ^1H long-range correlations

The heteronuclear shift correlation experiments were performed using the HMQC sequence $^{16}\pi/2(^1\text{H})-\Delta-\pi/2(^{183}\text{W})-t_1/2-\pi(^1\text{H})-t_1/2-\pi/2(^{183}\text{W})$ -acquisition (^1H). The defocusing delay Δ was deliberately set to 100 ms, which, given the natural abundance of 14.4% for ^{183}W , allows detection of $^nJ(^{183}\text{W},^1\text{H})$ interactions in the range 0.5–9.5 Hz with a sensitivity analogous to or better than that for a corresponding ^{13}C - ^1H correlation. Absorption mode data in the tungsten dimension were obtained using the TPPI¹⁷ method. Processing involved zero-filling and apodization with cosine windows in both dimensions prior to double Fourier transformation, phase correction in ω_1 and magnitude calculation¹⁸ in ω_2 . The complexes have all been reported previously.¹⁹

Preparation of ^{15}N compounds

All reactions were carried out in dry oxygen-free dinitrogen using standard Schlenk techniques. Hexane, pentane and diethyl ether were dried and distilled from sodium benzophenone ketyl. CH_2Cl_2 was dried from CaH_2 and octane from Na sand.

^{15}N -labelled PhNCO. Bistrichloromethyl carbonate (2.47 g, 8.43 mmol) was added to a cooled solution (-78°C) solution of [^{15}N]aniline (2.32 g, 24.9 mmol) in 30 ml of ethyl acetate. Warming to room temperature was followed by refluxing until a clear solution was formed. After removal of the solvents under vacuum the product (2.26 g, 76%) was obtained as a colourless oil by vacuum distillation.

$\text{W}(^{15}\text{NPh})\text{Cl}_4(\text{Et}_2\text{O})$. Ph^{15}NCO (2.19 g, 23.5 mmol) was added to a suspension of WOCl_4 (7.5 g, 22 mmol) in 50 ml of octane. The resulting mixture was heated at reflux until the evolution of CO_2 ceased. The resulting suspension contained a green powder, which was filtered and then dissolved in 100 ml of Et_2O . After filtration, the solution was concentrated under vacuum to give the product (9.07 g, 84%) as green crystals.

$\text{W}(^{15}\text{NPh})(\text{CH}_2\text{SiMe}_3)_3\text{Cl}$. $\text{W}(^{15}\text{NPh})\text{Cl}_4(\text{Et}_2\text{O})$ (6.93 g, 14.1 mmol) and Et_4NCl (2.35 g, 14.2 mmol) were dissolved in 50 ml of CH_2Cl_2 . After stirring for 15 min the reaction was cooled to 0°C and then treated in a drop-wise fashion with a solution of $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ (5.08 g, 21.1 mmol) in 10 ml of CH_2Cl_2 . After stirring for 1 h, 20 ml of pentane were added and the reaction mixture was filtered. Zinc salts were extracted with 30 ml of CH_2Cl_2 and the solvent then removed under vacuum. A pure brown crystalline product (6.81 g, 85%) was obtained via recrystallization from hexane.

Acknowledgements

P. S. Pregosin thanks the Swiss National Science Foundation and the ETH Zürich for financial support and Johnson Matthey for the loan of precious metals. P. A. van der Schaaf thanks the Netherlands Foundation for Chemical Research and the Netherlands Organisation for the Advancement of Science.

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