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^{183}W NMR Data ($\delta(^{183}W)$, $^nJ(W,H)$, and $^1J(W,F)$) for tungsten(II) metallacycles via two-dimensional indirect (^1H, ^{183}W) NMR spectroscopy

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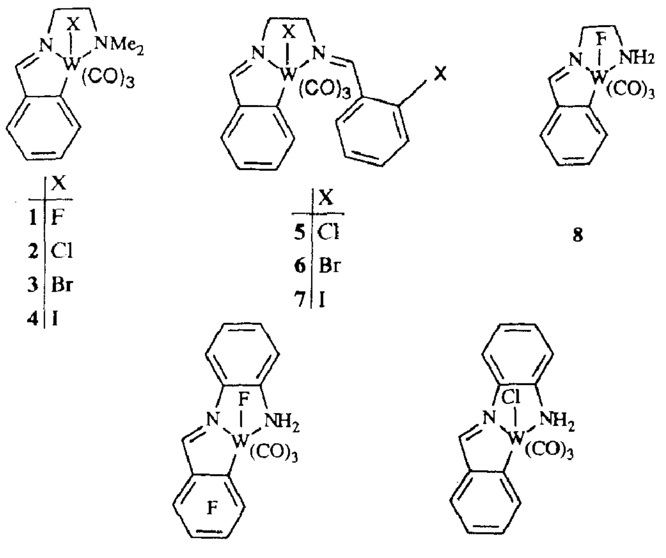
Abstract

The ^{183}W data for the tungsten(II) metallacycles $(Me)_2N(CH_2)_2N(CHC_6H_4)W(CO)_3X$ (**1**: X = F; **2**: X = Cl; **3**: X = Br; **4**: X = I), $(C_6H_4XCH)N(CH_2)_2N(CHC_6H_4)W(CO)_3X$ (**5**: X = Cl; **6**: X = Br; **7**: X = I), $H_2N(CH_2)_2N(CHC_6H_4)W(CO)_3F$ (**8**), $H_2N(C_6H_4)N(CHC_6F_4)W(CO)_3F$ (**9**), and $H_2N(C_6H_4)N(CHC_6H_4)W(CO)_3Cl$ (**10**) have been obtained by using $^nJ(W,H)$ ($n \geq 3$) couplings and the indirect two-dimensional (^1H,^{183}W) detection scheme. The chemical shifts $\delta(^{183}W)$, $^3J(H,W)$, together with its dihedral angle dependence, and the values $^1J(F,W)$ for these complexes are discussed.

Introduction

Recently it was shown that facile chelate-assisted oxidative addition of an aromatic carbon halogen bond takes place at tungsten(0) under mild conditions to afford the stable tungsten(II) metallacycles **1**–**10** (cf. Scheme 1), involving the halogen atom bound to the metal center [1,2]. The structure of the complexes **1**–**10** was established from IR, ^{19}F, ^{1}H NMR spectroscopic data and confirmed by a single crystal X-ray diffraction study of **6**, **9**, and **10** [1,2]. In the proton spectra of individual complexes, the imine signals showed tungsten satellites with coupling constants of several Hz. Although one bond scalar spin–spin couplings between tungsten and hydrides have been known for some time (they range between 20 and 80 Hz except for a few particular cases), knowledge of these $^nJ(W,H)$ coupling is relatively scarce [3]. Among the few cases for which they are known are tris(η^4-butadiene)tungsten complexes, in which $^2J(H,W)$ couplings of a few Hz were reported [4]. Information about such couplings is extremely useful for structure



Scheme 1

characterization of organotungsten compounds by modern NMR pulse techniques [5], since many of these techniques rely on the existence of spin–spin coupling between the insensitive tungsten and the sensitive proton nuclei. The indirect NMR observation scheme resting on double quantum coherences [6,7] is highly sensitive for detection of even small scalar spin–spin couplings, since with this technique the satellites are filtered out with high selectivity and the parent signals stemming from isotopomers with magnetically inactive tungsten nuclei are suppressed. We thus employed the indirect two-dimensional detection scheme [8*] for NMR investigations of the complexes **1–10** in order to gain more information about these $^{n}J(\mathrm{W,H})$ couplings, as well as of the $J(\mathrm{W,F})$, and the $^{183}\mathrm{W}$ shifts for these tungsten(II) metallacycles.

Experimental

The synthesis and structural characterization of the complexes **1–10** was recently reported [1,2]. All the NMR measurements were carried out with a modified Bruker WH 400 spectrometer. Standard procedures were applied for recording and assignment of the $^{1}\mathrm{H}$ NMR spectra. The hard and software configuration for the indirect two-dimensional ($^{1}\mathrm{H},^{183}\mathrm{W}$) experiments has been described in detail previously [9]. The experiments on **1–10** were performed by the original Bax pulse sequence employing double quantum coherences [7]:

$$90(^{1}\mathrm{H})\text{–}1/2 \cdot J(^{183}\mathrm{W},^{1}\mathrm{H})\text{–}90(^{183}\mathrm{W})\text{–}t_1/2\text{–}180(^{1}\mathrm{H})\text{–}t_1/2\text{–}90(^{183}\mathrm{W})\text{–}\mathrm{FID}(^{1}\mathrm{H},t_2) \qquad (1)$$

The delay between the first 90^{0} proton and 90^{0} tungsten pulse was varied between

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* Reference number with asterisk indicates a note in the list of references.

0.0625 and 0.1 s, which yields optimum magnetization transfer from protons to tungsten when J(W,H) is 8 and 5 Hz, respectively. In view of the ^3J(W,H^{13}) and ^3J(W,H^{14}) the latter choice is a compromise, but with this value correlations resulting from signals with small and unknown J(W,H) can be detected (cf. Fig. 1d)). Typically a repetition time of 1–2 s was employed, and for each of the 128 t_1-time increments 64 scans were added, yielding an acquisition time of around 3 h per spectrum. For each sample (5 mm tube, ca. 5–8% concentration) two experiments with a different spectral width in F_1 dimension were carried out in order to confirm that the cross peaks were not folded and to determine $\delta(^{183}W)$ within small limits of error (± 1 ppm). Before Fourier transformation in the absolute value mode sine bell apodization functions were used in F_1 and F_2 dimensions.

Results and discussion

It is straightforward to assign all the resonances in the 400 MHz ^1H NMR spectra of the complexes **1–10**. For example for **6**, dissolved in THF-d_8 all the proton signals were identified by monitoring the scalar couplings either by homonuclear decoupling experiments or a two-dimensional COSY sequence [5]. Even in the one-dimensional spectrum, for the signals from the imine protons H^{13} and H^{14} tungsten satellites can be directly detected. These ^3J(W,H) couplings are 8.0 and 6.0 Hz respectively. They provide the basis on which the two-dimensional indirect (^1H,^{183}W) technique can be used in order to determine the ^{183}W NMR data for complexes **1–10**.

Expansions of the indirect two-dimensional (^1H,^{183}W) correlation spectra of **6** (recorded by applying sequence 1) are illustrated in Fig. 1. In this experiment J(H,H) is conserved in F_1 and F_2 dimensions. Thus within a cross peak the individual components of a multiplet resulting from homonuclear proton couplings are tilted, while the splittings arising from J(W,H) are displayed in the F_2 dimension. From the contour plot (c) the cross peaks of the imine protons H^{13} and H^{14} can be directly identified, thus yielding $\delta(^{183}W)$. Since the cross peaks belonging to H^{13} are on a horizontal line, it is immediately evident that the imine proton H^{13} possesses a ^3J(W,H) coupling much larger than its long range J(H,H) couplings. In addition, the phenyl protons H^1 and H^2 exhibit cross peaks, and therefore must also possess scalar coupling to tungsten. Moreover, this Figure illustrates very nicely that with the two-dimensional detection scheme individual signals which exhibit a J(W,H) coupling such as H^1 and H^2 can be separated from overlapping multiplets arising from neighbors such as H^5 and H^3, respectively, which are not coupled with tungsten. Inspection of the contour plot in the region of the chelating CH_2 groups (contour plot (d)) indicates that only two of the four methylene protons show small (1–2 Hz) scalar couplings to tungsten. The metal and the two nitrogen atoms and methylene carbons form a nearly planar five-membered ring [1]. In this ring two of the methylene protons are in a quasi-axial and the remaining two in a quasi-equatorial position. From the vicinal J(H,H) couplings these protons were unambiguously identified. It is noteworthy that the quasi-axial protons H^9 and H^{12} (dihedral angle with tungsten around 90°) exhibit no scalar coupling to the metal, while the two equatorial protons H^{10} and H^{11} (dihedral angle around 180°) show a 1–2 Hz coupling to tungsten. Although the hybridization of the neighboring carbon atom is also different, for the imine protons H^{13} and H^{14} where the dihedral angle is around

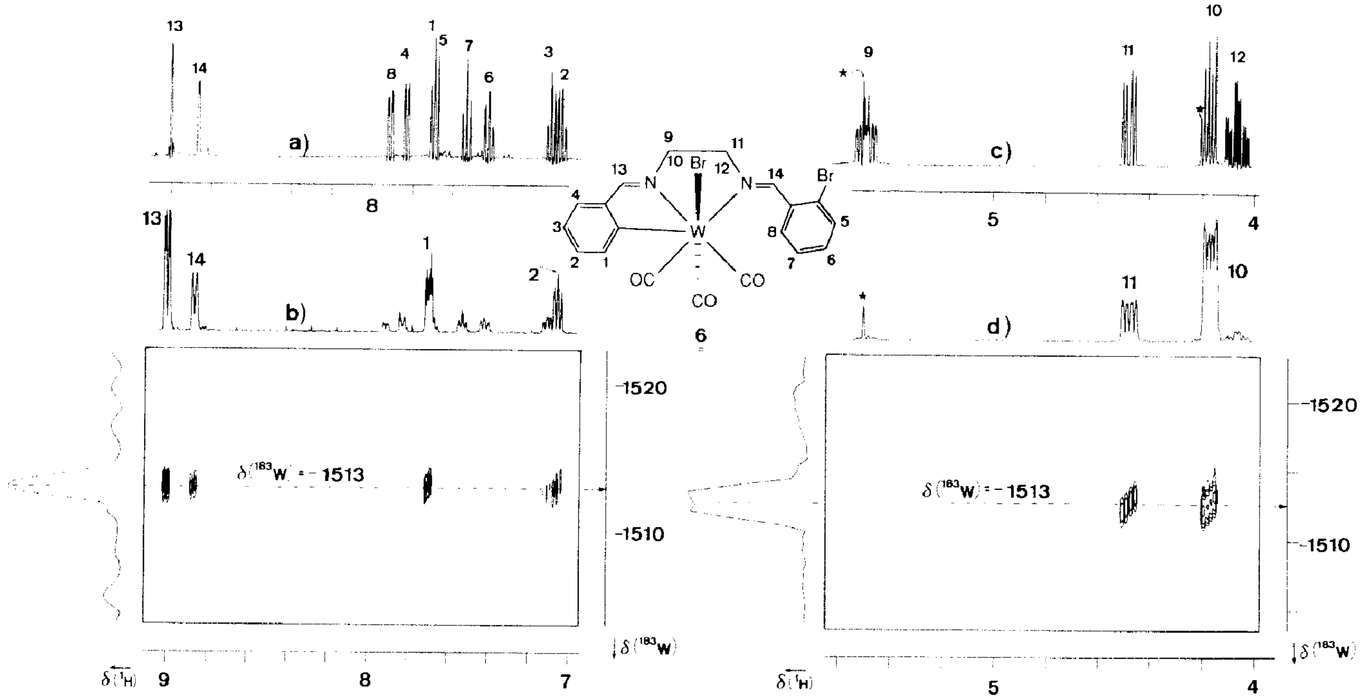


Fig. 1. 400 MHz ^{1}H NMR spectra of **6**. (a) and (c) expansions of the conventional one dimensional proton spectrum; (b) and (d) contour plots and projections in F_1 and F_2 dimension of the indirect (^{1}H, ^{183}W) NMR spectra of **6**. Note that H^{10} and H^{11} are in quasi-equatorial and H^{9} and H^{12} in quasi-axial position. The asterisks denote impurities.

180 °, relatively large vicinal tungsten proton couplings were observed. For all of the complexes **1**–**10** $J(W,H^{13})$ is larger than $J(W,H^{14})$ by 2 Hz. It seems likely that the two-fold coupling pathway may account for the larger value of $J(W,H^{13})$.

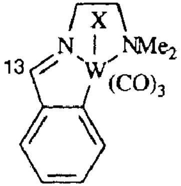
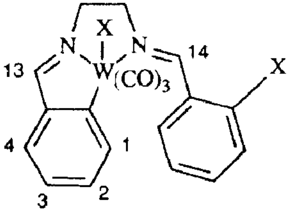
In the two-dimensional detection scheme the couplings of the nuclei displayed in F_1 and F_2 dimension with a third non-excited nucleus are conserved in each of the corresponding domains. In complexes **1**, **8**, and **9** there is a fluorine atom bonded to tungsten, and this should give rise to a $J(W,F)$ coupling. For complexes **8** and **9** this coupling was directly observed in the F_1 dimension of the two-dimensional indirect $(^1H,^{183}W)$ spectra. In each of these compounds this coupling is around 20 Hz and thus lies well within the range (12–84 Hz) reported for $^1J(W,F)$ couplings [3]. The identification of that $J(W,F)$ coupling is definitive evidence for the formation of a tungsten–fluorine bond, and thus also provides confirmation of the oxidative addition of the C–F bond to the metal. It is interesting to note that owing to the half widths of the resonances in the ^{19}F spectra (B_0 9.4 T) this coupling could not be readily observed in the conventional one-dimensional ^{19}F spectra of **1**, **8**, and **9**. Apparently it is easier to detect the $J(W,F)$ coupling in the ^{183}W domain, in which it appears as doublet, rather than in the ^{19}F spectrum where this coupling only produces satellites at the bottom of the parent signal stemming from isotopomers with magnetically inactive tungsten. For complex **1** $J(W,F)$ seems to be around 8 Hz, but it must be added that this coupling could not be determined unambiguously. Since there were no hints of a $J(H,F)$ coupling in **1**, **8** or **9**, the sign of the $J(W,F)$ coupling could not be derived from the arrangement of the cross peaks in the two-dimensional contour diagram.

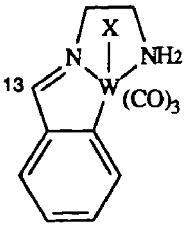
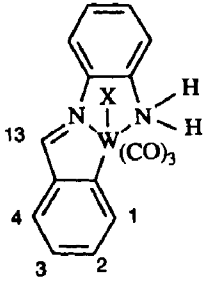
The ^{183}W chemical shifts in **1**–**10** lie between −1300 and −1600 ppm (relative to $\delta([^{183}WO_4]^{2-}) = 0$ and $\delta(^{183}W(CO)_6) = -3468$ as external standard). These values are in the range typical of organotungsten(II) compounds (−4000 to −1000 ppm) [3]. Neglecting the fluorine complexes, within the series **2**–**4**, and **5**–**7** the halogen dependence is normal, and has been observed for the $[(\eta^5\text{-}C_5H_5)(CO)_3]WX$ (X = Cl, Br, I) complexes [3]. In **2**–**4** and **5**–**7** the differences in $\delta(^{183}W)$ between the chlorine and bromine complex are relatively small, while an iodine substituent, as in the above-mentioned cyclopentadienyltungsten complexes, produces a considerably higher shielding of the metal. The fluorine complex **1** has nearly the same $\delta(^{183}W)$ value as the iodine complex **4**. Comparisons of the $\delta(^{183}W)$ values in **1** and **8** indicate that the substitution of the donor amino nitrogen with methyl groups instead of hydrogen atoms leads to a decreased shielding of the neighboring tungsten nucleus. This is in contrast to what one would expect on the basis of electron density effects caused by the altered electronegativity of the substituents. It is noteworthy that in molybdenum(II) isocyanide complexes the opposite shielding is observed; in $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$ the metal is more shielded than in $[Mo(CNCHMe_2)_5(bpy)](PF_6)_2$ [3]. Thus it is suggested that weak intramolecular hydrogen fluoride interactions accounts for these unusual changes for $\delta(^{183}W)$ on going from **1** to **8**. This interpretation is supported by the observation that in complex **9** the fluoride resonance was found to undergo an upfield shift upon addition of D_2O to the sample [2]. Furthermore the $\delta(^{183}W)$ value for **9** is changed by +10 ppm when water was added to the sample. In this context it is also of interest that $^1J(W,F)$ seems to be around 8 Hz for **1**, whereas this coupling was found to be around 20 Hz for in the complexes **8** and **9**.

We have shown that the indirect $(^1H,^{183}W)$ observation scheme via $^nJ(W,H)$ is

Table 1

^{183}W NMR data of complexes **1–10**. 5–10% in THF-d_8; T 300 K. External Standard $\delta(^{183}W(CO)_6) = -3468$ ppm.

Structure	No	X	$\delta(^{183}W)$ [a]	$\delta(^1H)$		$^3J(W,H)$ (Hz)		Other couplings
				13	**14**	**13**	**14**	
	**1**	F	−1411	8.93	–	8	–	
	2	Cl	−1351	8.93	–	8	–	
	3	Br	−1357	8.92	–	8	–	
	4	I	−1413	8.89	–	8	–	
	**5**	Cl	−1488	9.02	8.99	8	6	
	6	Br	−1513	9.00	8.87	8	6	$^3J(W,H^1)$ 1.5 Hz $^4J(W,H^2)$ 1.5 Hz $^3J(W,H^{10})$ 1.5 Hz [b] $^3J(W,H^{11})$ 1.5 Hz [b]
	7	I	−1598	9.00	8.65	8	6	

	**8**	F	−1576	8.91	–	8	–	${}^{1}J(W,F)$ 20 Hz
	**9**	F	−1466	9.57	–	8	–	${}^{1}J(W,F)$ 20 Hz
	10	Cl	−1529	9.39	–	8	–	${}^{4}J(W,H^{2})$ 1–2 Hz ${}^{3}J(W,H^{1})$ 1–2 Hz

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[a] Error limits for $\delta(^{183}W) \leq \pm 1$ ppm. [b] H^{10} and H^{11} denote the quasi-equatorial methylene protons, cf. also Fig. 1.

very useful for determining ^{183}W NMR data. The ^3J(W,H) couplings depend on the dihedral angle, and for complexes **1**, **8** and **9** the ^1J(W,F) couplings give direct and unambiguous evidence for the oxidative addition of aromatic C–F bonds to tungsten(0) with formation of the tungsten(II) metallacycles.

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References

1 T.G. Richmond, M.A. King, E.P. Kelson, A.M. Arif, Organometallics, 6 (1987) 1995.

2 T.G. Richmond, C.E. Osterberg, A.M. Arif, J. Am. Chem. Soc., 109 (1987) 8091; C.E. Osterberg, A.M. Arif, T.G. Richmond, ibid., 110 (1988) 6093.

3 M. Minelli, J. Enemark, R.T.C. Brownlee, M.J. O'Connor, A.G. Wedd, Coord. Chem. Rev., 68 (1985) 169.

4 R. Benn, C. Brevard, A. Rufińska, G. Schroth, Organometallics, 6 (1987) 938.

5 R.R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987; J.K.M. Sanders, B.K. Hunter, Modern NMR Spectroscopy, Oxford University Press 1987; R. Benn, H. Günther, Angew. Chem., 95 (1983) 381, Angew. Chem. Int. Ed. Engl., 22 (1983) 350.

6 J.S. Cohen, C.W. Chen, A. Bax, J. Magn. Reson., 59 (1984) 181.

7 A. Bax, R.H. Griffey, B.L. Hawkins, J. Magn. Reson., 55 (1983) 301.

8 The most prominent feature of the two dimensional indirect detection scheme is that it gives the most efficient access to insensitive spin-1/2 (metal) nuclei which are scalar coupled to a sensitive nucleus like protons or phosphorus. This and other inherent advantages of this NMR techniques are illustrated in e.g. R. Benn, A. Rufińska, J. Magn. Reson. Chem., 26 (1988) 895.

9 R. Benn, H. Brenneke, A. Rufińska, J. Organomet. Chem., 320 (1987) 115; R. Benn, H. Brenneke, A. Frings, H. Lehmkuhl, G. Mehler, A. Rufińska, T. Wildt, J. Am. Chem. Soc., 110 (1988) 5661.