Synthesis and ^{1}H-, ^{15}N-, ^{31}P-, ^{183}W-Multinuclear Magnetic Resonance Study of the Cyclotriphosphazenes $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2]$ and $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4]$ and Their $W(CO)_5$ Complexes (dobp = 2,2′-dioxybiphenyl)

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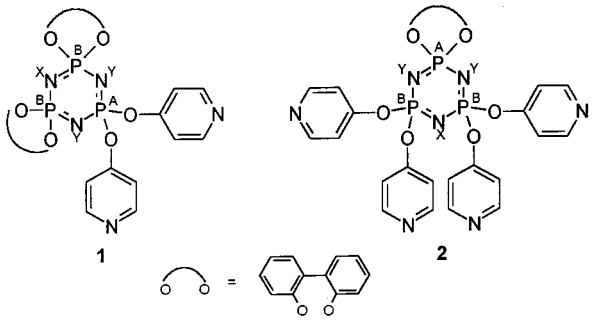
The reactions of $[N_3P_3(dobp)_2Cl_2]$ and $[N_3P_3(dobp)Cl_4]$ with a mixture of HOC_5H_4N-4 and K_2CO_3 in acetone give the cyclotriphosphazenes $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2]$ and $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4]$, respectively. These compounds react with $[W(MeOH)(CO)_5]$ in methanol to give mixtures of the polymetallic complexes $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2\{W(CO)_5\}_x]$ (x = 1, 2) and $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4\{W(CO)_5\}_x]$ (x = 1–4), which are unstable in solution, slowly undergoing loss of the pentacarbonyl moiety. A complete characterization by multinuclear ^{1}H, ^{15}N, ^{31}P, ^{183}W magnetic resonance has revealed that the complexation of the N atom of one 4-oxypyridine ligand by the $W(CO)_5$ fragment has a measurable effect on other parts of the phosphazene molecule very far away from the coordination site. The changes observed in $\delta^{183}W$ have been used to identify the components in mixtures of compounds incorporating different numbers of tungsten atoms in the molecule. The characterization of less sensitive nuclei has been accomplished by means of indirect detection methods.

Introduction

Polyphosphazenes bearing aryloxy side groups are materials with interesting properties. For example, they exhibit fire-retardant properties,[1] have high refractive indices,[2] and might find application in non-linear optics,[3] as ferroelectric materials,[4] as liquid crystals,[5] or as photoactive materials.[6] In all applications, their properties depend on the substituents linked to the aryloxy rings. One way of modifying the phenoxy moiety would be the introduction of a nitrogen atom into the ring. The resulting polymers would then contain pyridine side groups with N-donor sites available for metal complexation,[7] opening new possibilities for modifying their properties. The key aspect of this chemistry can be envisaged as being the incorporation of transition metals into the structure of the polymer.

At a macromolecular level, the evaluation of structural effects induced by the side groups bonded to phosphorus is difficult. However, a reasonable starting point would be to focus on small model compounds suitable for NMR-spectroscopic characterization. This strategy is well documented with cyclotriphosphazenes as model molecules,[8] although the number of cyclotriphosphazenes complexed to transition metals through the side groups remains relatively few.[9][10] Recently, we reported the synthesis of several carbonylmanganese complexes of cyclic phosphazenes bearing either nitrile or pyridine ligands.[11] In principle, the incorporated transition metal atom might have constituted a probe for assessing structural and bonding effects of the coordination, in view of the high sensitivity of such nuclei to subtle electronic and steric effects in the molecule.[12] However, ^{55}Mn is a quadrupolar nucleus (I = 5/2) with a medium-sized quadrupole moment ($Q = 0.55 \times 10^{-28}$ m^2). Consequently, very broad signals can be expected,[13] which would be useless for the measurement of small changes in the nuclear shielding. On the contrary, ^{183}W would give the characteristic sharp signals of a spin 1/2 nucleus, albeit with the difficulty presented by its low sensitivity. Fortunately, this drawback can easily be overcome through the use of indirect detection methods.[14] In fact, ^{183}W is one of the most extensively studied transition metal nuclei.[12a,15]

In this article, we describe the multinuclear magnetic resonance characterization of the cyclotriphosphazenes **1** and **2** (Scheme 1), as well as that of their pentacarbonyltungsten complexes **3**–**11**, formed by adding variable amounts of the labile complex $[W(MeOH)(CO)_5]$ in methanolic solution. The study extends to the nuclei ^{1}H, ^{15}N, ^{31}P, and ^{183}W.



Scheme 1. Starting cyclotriphosphazenes

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Results

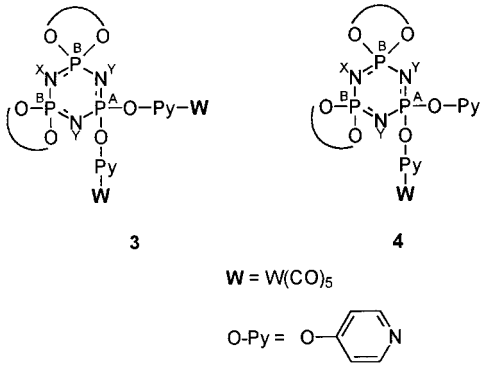
The phosphazenes bearing oxypyridine groups $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2]$ (**1**) and $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4]$ (**2**) were prepared from the corresponding chlorophosphazenes and HOC_5H_4N-4 with K_2CO_3 in acetone, following the general method published previously.[16]

The NMR spectra of **1** and **2** are relatively simple and the relevant ^1H, ^{31}P, and ^{15}N data are collected in Table 1. For the discussion below we will focus on the protons *ortho* to the nitrogen atom of the pyridine ring (hereafter denoted H^o), since these are subject to the largest shielding modifications upon coordination of tungsten. Their signals appear at $\delta = 8.65$ and $\delta = 8.55$ in compounds **1** and **2**, respectively {cf. $\delta H^o = 7.68$ in 4-hydroxypyridine and $\delta H^o = 8.5$ in $[N_3P_3(OC_5H_4N\text{-}4)_6]$[11]}.

The ^{15}N chemical shifts of **1** and **2** lie within the expected range for nitrogen atoms incorporated into cyclotriphosphazene[17][18] or pyridine rings.[19] The nitrogen atoms of the phosphazene could be straightforwardly identified through their correlations in the 2D $^{31}P,^{15}N\{^1H\}$-HMQC spectra. The phosphorus nucleus labelled A shows a cross-peak with only one nitrogen atom, while that labelled B correlates with the two heterotopic nitrogen nuclei of the ring. The $^1J(^{31}P,^{15}N)$ coupling constants were measured from the ^{15}N satellites in the ^{31}P-NMR spectra obtained by performing the $^{31}P,^{15}N\{^1H\}$-HMQC pulse sequence in the 1D mode.

Addition of phosphazene **1** to a solution of two equivalents of $[W(MeOH)(CO)_5]$ in methanol resulted in a mixture of the bi- and monometallic complexes $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2\{W(CO)_5\}_x]$, $x = 2$ (**3**), $x = 1$ (**4**) (Scheme 2), containing a slightly variable amount of unreacted **1**, depending on the isolation procedure used. Increasing the amount of the pentacarbonyltungsten reagent gave mixtures richer in **3**, but a very large excess had to be used in order to generate exclusively this bimetallic complex. Moreover, the ^1H- and ^{31}P-NMR spectra showed that the latter, as well as the mixtures, continuously lose $W(CO)_5$ in solution (ca. 8% per month), a process which is much slower in the solid state as monitored by NMR measurements on freshly prepared samples from different stocks of tungsten complexes. By monitoring the relative intensities of the signals of the *ortho* protons of the three species, it could be concluded that the step from **3** to **4** is slightly faster than that from **4** to **1**. The assignment of the signals to the complexes **4** and **3** was based on the variation of their intensities with the $W(CO)_5$ content in the mixtures.

Taking compound **1** as a reference, coordination at one of the pyridine rings in compound **4** leads to a deshielding of 0.16 ppm of the protons *ortho* to the nitrogen atom. This shift increases to 0.20 ppm in **3**, where both pyridine rings are coordinated to tungsten (Table 1). The signal due to the *ortho* protons of the uncoordinated pyridine of **4** is practically unaffected. A similar trend is observed in the ^{31}P-NMR signals: P_A is deshielded by 0.06 ppm in **4** and by 0.09 ppm in **3**. Interestingly, P_B seems to be more sensitive to the coordination to $W(CO)_5$ than P_A and is shifted to lower δ values rather than being deshielded: $\Delta\delta(P_B) = -0.55$ and -1.01 ppm for **4** and **3**, respectively. Substituent effects in excess of 1 ppm on phosphorus shielding transmitted through phenoxy groups have previously been observed for aryl phosphates.[20]



Scheme 2. Tungsten complexes of cyclotriphosphazene **1**

The successive coordination of pyridine substituents to tungsten also has a measurable effect on the nitrogen atom of the phosphazene ring: N_Y is deshielded by 0.6 ppm in **4** and by 1.5 ppm in **3**. Unfortunately, the intensity of the N_X signal is too low to allow its discernment above the noise. Obviously, the largest $\delta^{15}N$ variation is observed for the pyridine nitrogen atom, which is shielded by about 75 ppm upon coordination to the tungsten atom. The 5.5 ppm shielding shown by the ^{15}N of the free pyridine in **4** is, however, also noteworthy. Similar substituent effects have previously been reported for fluorinated monophosphazenes.[21]

Considering the high sensitivity of transition metal nuclei to very small electronic modifications in their environment, the shielding effect in the present case should also be detectable on the tungsten atom. Indeed, in the $^1H,^{183}W$-HMQC correlation spectrum, the chemical shift of **3** is deshielded by 4 ppm compared to that of **4**, which represents a relatively large shift for an interaction between two apparently distant groups (Table 1).

The spectra of the mixtures of **3** and **4** obtained in various independent experiments showed the presence of small amounts (not reproducible, but never exceeding 5 mol-%) of another species **5** with $\delta^{183}W = -2728$. However, all attempts to characterize this contaminant were unsuccessful.

Like **1**, the phosphazene **2** reacted with $[W(MeOH)(CO)_5]$ in methanol to give mixtures of the polymetallic complexes $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4\{W(CO)_5\}_x]$, $x = 4$ (**6**), $x = 3$ (**7**), $x = 2$ (**8**, **9**, **10**), $x = 1$ (**11**) (Scheme 3). Thus, upon addition of 4.4 equivalents of the pentacarbonyltungsten reagent to **2**, two major products **6** and **7** (> 97%) were formed in a relative ratio of 85:15, as measured from the integrals of H_{meta} in the ^1H-NMR spectrum. For the mixture, the spectral region corresponding to the H^o protons ($\delta = 8.5-9.0$, Figure 1) features only one intense multiplet at $\delta = 8.85$ attributable to **6**, while at least three signals at $\delta = 8.65$, 8.76 and 8.82 of equal relative intensity

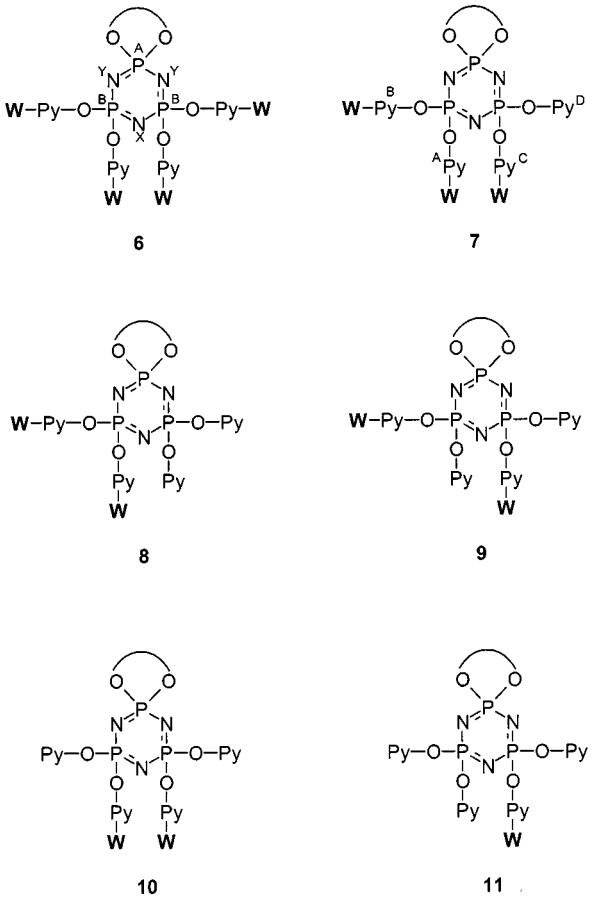
Table 1. NMR data for compounds **1**−**11** (δ in ppm, *J* in Hz)

	δ^1H^o Coord.	δ^1H^o Non-coord.	$\delta^{31}P_A$	$\delta^{31}P_B$	$^2J_{PA,PB}$	$\delta^{15}N$ pyridine Coord.	$\delta^{15}N$ pyridine Non-coord.	δ^{15} Ncycle X	δ^{15} Ncycle Y	$\delta^{183}W$
1		8.65	9.09	25.13	95.7		−76.3	−312.4[a]	−307.9	
2		8.55	23.89	8.19	95.3		−74.5	−306.8[b]	−310.5	
3	8.85		9.18	24.12	96.2	−150.8			−306.4	−2707
4	8.81	8.69	9.15	24.58	95.9	−151.8	−81.8		−307.3	−2711
6	8.85		21.90	7.04	92.9	−147.9				−2696
7	8.85 (A)	8.65 (D)	22.41	7.42	92.9	−149.0				−2699
	8.82 (C)					−149.8				−2701
	8.76 (B)					−148.2				−2699
8	8.78		22.94[c]	7.85	94.5					−2700
9	8.76		22.45	7.52	94.0					−2703
10	8.82		22.45	7.52	94.0					−2703
11	8.75		23.41	8.06	94.5					−2706

[a] $^1J_{PBNX}$ = 11.7; $^1J_{PANY}$ = 7.4; $^1J_{PBNY}$ = 4.7. − [b] $^1J_{PBNX}$ = 5.7; $^1J_{PANY}$ = 11.6; $^1J_{PBNY}$ = 3.5. − [c] Calculated values have been approximated to an AB_2 spin system.

are observed for **7**. The excess of $[W(MeOH)(CO)_5]$ used implies that **6** must be the tetracoordinated $W(CO)_5$ complex of **2**, and consequently **7** must be its tricoordinated tungsten derivative. Furthermore, on the basis of a statistical distribution of tungsten on the pyridine nitrogen atoms of **2**, the two additional multiplets at δ = 8.59 and δ = 8.63 of very low intensity (< 3%) may be assigned to the corresponding bimetallic complexes **8**−**10**. Considering the low intensity of the dicoordinated complexes, the monometallic species **11** would not be detectable. The assignment of the ^{31}P-NMR spectra of compounds **7**−**10** was accomplished through titration experiments using different ratios of **2**/$[W(MeOH)(CO)_5]$ (1:1; 1:2; 1:3; 1:4.4). The spectra are summarized in Table 1. As expected, the increase in the tungsten content has a shielding effect on each of the phosphorus nuclei in the phosphazene ring (cf. **4** and **3**). However, the ^{31}P nucleus bonded to the biphenoxy substituent again shows the greatest upfield shift. Due to the similarity of **9** and **10**, there is some overlapping of their ^{31}P signals. Significantly, the ^{31}P nuclei in compound **8** are seen to be deshielded compared to those in **9** and **10**.

Compound **7** contains four different pyridine rings. However, only three signals with an intensity ratio of 1:1:1 are observed for the H^o protons. The fourth multiplet is overlapped by the signal of the H^o protons of **6**, as revealed by the integrals of the multiplet at δ = 8.85 and of the signal due to the *meta* protons of the pyridine rings. This overlap indicates that both types of protons are found in the same environment. By comparison with the H^o signals of **3** and **4**, the most deshielded protons of **7** can be assigned as H^o(A) (Scheme 3), while the most shielded multiplet of **7** should be attributable to H^o of the pyridine molecule not coordinated to tungsten H^o(D). The assignment of H^o(B) and H^o(C) poses some difficulties because the nuclear shielding of these protons will be determined by a combination of the electronic effects induced by the coordination of the nitrogen atom to $W(CO)_5$ and the diamagnetic anisotropy of the neighbouring rings, the latter depending on the orientation of the interacting groups (cf., for example, the crystal structure of the hexasubstituted phosphazene $[N_3P_3(OC_5H_4N\text{-}4)_6]$, where one of the three 4-oxypyridines



Scheme 3. Tungsten complexes of cyclotriphosphazene **2**

on one side of the N_3P_3 plane is oriented almost perpendicular to the other two).

These difficulties could be overcome by analysing the ^{183}W-NMR data obtained from the ^{1}H,^{183}W-HMQC correlation spectrum of the mixture of **6** and **7**. This spectrum featurs seven signals, which are labelled **I**−**VII** in Figure 2: $\delta^{183}W$ = −2696 (**I**), −2699 (**II**, **III**), −2700 (**IV**), −2701 (**V**), −2703 (**VI**, **VII**). The ^{183}W chemical shift variations observed between **3** and **4** suggest that $\delta^{183}W$ values are not subject to neighbouring anisotropy effects, but are deter-

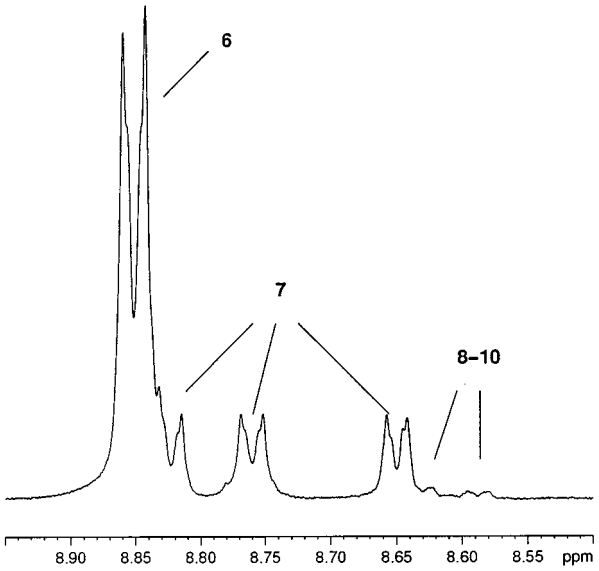


Figure 1. H^o region of the ^{1}H-NMR spectrum of a mixture of **2** with excess [W(MeOH)(CO)$_5$]

mined by the number of W(CO)$_5$ moieties coordinated to the substituents on a given phosphorus atom: the greater the number, the larger the ^{183}W chemical shift. Accordingly, the cross-peak **I** in the ^{1}H,^{183}W-HMQC spectrum of **6** and **7** can be assigned to the tungsten signal of **6**. Following the same reasoning, the two cross-peaks at $\delta^{183}W = -2699$ with the protons at $\delta = 8.85$ and 8.76 (**II**, **III**) can be ascribed to the long-range coupling of H^o(A) and H^o(B) of **7** with W_A and W_B, respectively. Since H^o(A) has been previously assigned to the multiplet at $\delta = 8.85$, it follows that H^o(B) resonates at $\delta = 8.76$. By a process of elimination, H^o(C) must be responsible for the multiplet at $\delta = 8.82$, which correlates with the most shielded ^{183}W of **7** at $\delta = -2701$ (**V**) [i.e. the tungsten bonded to the moiety with the lower W(CO)$_5$ content]. Additionally, the signal at $\delta = 8.65$ can be confirmed as being due to H^o(D), in view of the lack of any correlation with the tungsten atom. The shielding differences between H^o(B) and H^o(C) can be ascribed to differences in the diamagnetic anisotropy effect produced by the adjacent rings on the same side of the phosphazene plane. Upon rotation of the pyridine rings, H^o(B) would temporarily be oriented in a perpendicular arrangement in relation to an unperturbed pyridine and therefore would experience the full shielding effect of the ring current induced by its six π electrons. On the other hand, H^o(C) would, under these circumstances, experience a smaller ring current effect as these protons would be faced by a pyridine coordinated to tungsten, part of the electronic density of which will be involved in bonding to the transition metal.

Cross-peaks **IV**, **VI**, and **VII** in the $^{1\,H,183}$W-HMQC spectrum may be attributed to correlations with the H^o protons in the three possible dicoordinated W(CO)$_5$ complexes **8**–**10**. Applying the same assignment criteria as discussed for **7**, it can be concluded that the most deshielded signal **IV** arises from the two equivalent ^{183}W nuclei of **8**, "pendant" from the same phosphorus atom. The corresponding

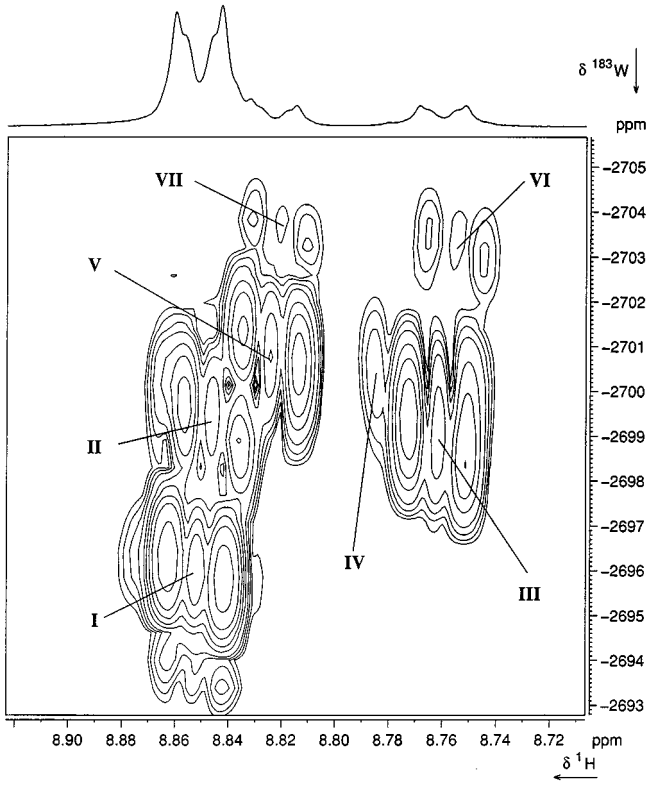


Figure 2. ^{1}H,^{183}W HMQC of a mixture of **2** and [W(MeOH)(CO)$_5$] in a ratio of 1:4.4

H^o protons appear at $\delta = 8.78$ and this signal is partially overlapped by that of H^o(B) of **7**. The two remaining cross-peaks **VI** and **VII** originate from tungsten nuclei bonded to pyridine substituents on different phosphorus atoms. Focusing on the H^o protons of the pyridine ring coordinated to W(CO)$_5$, it can be concluded that the neighbourhood, and therefore the diamagnetic anisotropic effect, of these protons in **9** is very similar to that of H^o(B) in **7**, while the analogous protons in **10** resemble H^o(C) in **7**. On the basis of these observations, the ^{1}H signals at $\delta = 8.76$ and 8.82 can be assigned to **9** and **10**, respectively. Finally, the signals at $\delta = 8.59$ and 8.63 can be assigned to two of the three types of H^o protons of the pyridines not bonded to the metal center. The unobserved third signal is most probably overlapped by the multiplet at $\delta = 8.76$ due to the proton H^o(D) of **7**.

To our surprise, the ^{1}H,^{15}N-HMQC spectrum was much less informative. The signal-to-noise ratio achieved was rather poor and only the H^o protons of the pyridines coordinated to the metal center in **6** and **7** showed correlations with ^{15}N. The data obtained are collected in Table 1. Once the identity of the H^o protons had been established, the assignment of the corresponding ^{15}N signals was trivial. Significantly, the ^{15}N chemical shifts vary in the same way as the δ^{183}W values and by a similar order of magnitude (see Table 1). On the other hand, the solubility of the complexes proved to be too low to allow measurement of ^{15}N data for the nitrogen atoms of the cyclotriphosphazene through phosphorus detection.

The above assignments are supported by the NMR data obtained by performing the reaction in a 1:3 ratio. The ^1H spectrum shows a strong overlap between multiplets in the region corresponding to the H^o protons. The high intensity of the signal at $\delta = 8.75$ indicates that it is attributable to the monometallic species **11**. The ^{31}P spectrum features a large number of lines of different intensity arising from the AB_2-like multiplets produced by the various components of the mixture.

On the contrary, the $^1H,^{183}W$-HMQC spectrum of the mixture is much easier to interpret and supports the assignments given above (Figure 3). Now, the signals of W_A in **7** and of the tungsten atom in **8** are slightly shifted to higher field ($\Delta\delta \approx 0.5$ ppm). However, the important point is that a new correlation is observed between a ^1H multiplet at $\delta = 8.75$ and a tungsten signal at $\delta = -2706$, which must correspond to the monometallic complex **11**. This confirms that $\delta^{183}W$ in the series of complexes studied here decreases on decreasing the amount of $W(CO)_5$ in the molecule.

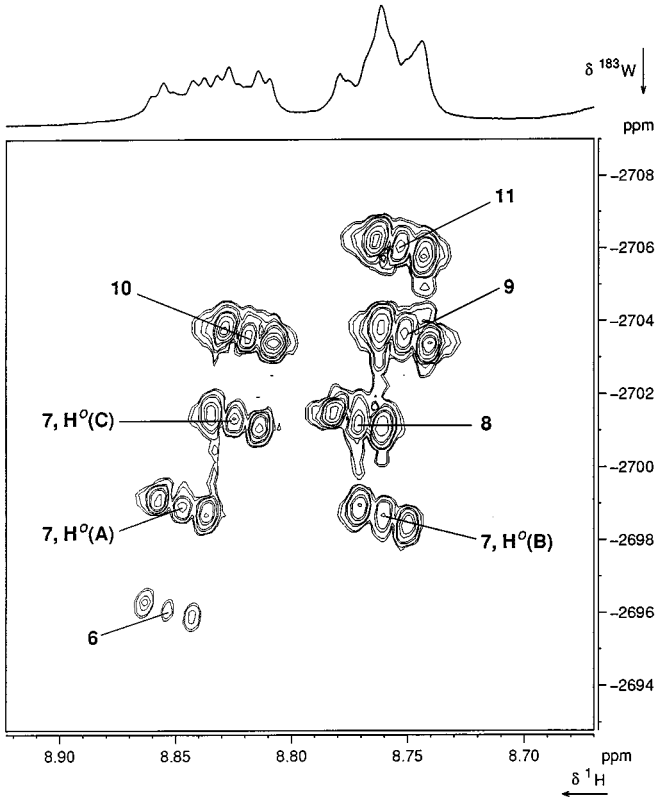


Figure 3. $^1H,^{183}W$ HMQC of a mixture of **2** and $[W(MeOH)(CO)_5]$ in a ratio of 1:3

Conclusions

The multinuclear magnetic resonance study performed on the two model cyclotriphosphazenes and their $W(CO)_5$ complexes has revealed that complexation can be monitored through several nuclei of the molecule. The δ^1H variations can be explained in terms of a mixture of charge polarization and anisotropic effects, which are difficult to predict. Moreover, the ^1H-NMR spectra of the polymetallic complexes show strongly overlapped signals, which render this nucleus of low diagnostic value for identification purposes. However, the high sensitivity of transition metal nuclei to small electronic changes in their coordination spheres has allowed the use of ^{183}W NMR in assigning all the components of the complex mixtures of compounds incorporating different amounts of tungsten, as well as positional isomers, with ^{183}W chemical shift differences in the range of 1−4 ppm. $\delta^{183}W$ values have been found to decrease on increasing the number of tungsten atoms in the molecule, and screening of the ^{15}N nuclei of the pyridine rings bonded to the metal center has revealed the same trend.

Experimental Section

General: All reactions were carried out under dry nitrogen. K_2CO_3 was dried at 140°C prior to use. The acetone used as solvent was predistilled from $KMnO_4$, and distilled twice from anhydrous $CaSO_4$. Methanol was distilled from CaH_2. Petroleum ether refers to the fraction boiling in the range 60−65°C. Hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka) was purified by recrystallization from hot petroleum ether and dried in vacuo. The starting phosphazenes $[N_3P_3(dobp)Cl_4]$ and $[N_3P_3(dobp)_2Cl_2]$ were prepared as described elsewhere.[22] The complex $[W(MeOH)(CO)_5]$ was obtained as described in the literature.[23] − Elemental analyses: Perkin−Elmer 2400. − IR: Perkin−Elmer FT 1720-X, Paragon 1000 (KBr pellets). − NMR: Bruker AMX 400; spectra were referenced to tetramethylsilane for ^1H, neat $MeNO_2$ for ^{15}N, 85% H_3PO_4 for ^{31}P, and Na_2WO_4 for ^{183}W. The spectral parameters for the $^{31}P,^{15}N\{^1H\}$-HMQC[17] and $^1H,^{183}W$-HMQC[24] experiments have been described previously. Linear prediction of the 2D spectra using standard Bruker software was employed. Samples were prepared in $CDCl_3$ and the spectra were measured at 303 K. In view of the very small shifts in δ that we aimed to detect, experiments were performed several times with different samples in order to minimize systematic errors arising from concentration and temperature variations.

$[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2]$ (1): A mixture of $[N_3P_3(dobp)_2Cl_2]$ (0.304 g, 0.53 mmol), HOC_5H_4N-4 (0.122 g, 1.28 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) in acetone (50 mL) was refluxed for 3 h. The volatiles were then removed in vacuo and the residual solid was washed with water (3 × 80 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated in vacuo. The product was recrystallized from CH_2Cl_2/petroleum ether to give **1** as a very pale yellow crystalline solid. Yield 0.25 g (67%). − $C_{42}H_{24}N_5O_6P_3$ (786.9): calcd. C 59.1, H 3.50, N 10.1; found C 58.4, H 3.60, N 9.82.

$[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4]$ (2): A mixture of $[N_3P_3(dobp)Cl_4]$ (0.461 g, 1 mmol), HOC_5H_4N-4 (0.456 g, 4.8 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) in acetone (50 mL) was refluxed for 6 h. The volatiles were then removed in vacuo and the residual solid was washed with water (3 × 80 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated in vacuo. The product was recrystallized from CH_2Cl_2/petroleum ether to give **2** as a very pale yellow crystalline solid. Yield 0.52 g (75%). − $C_{36}H_{24}N_7O_6P_3$ (742.9): calcd. C 55.3, H 3.48, N 14.1; found C 55.0, H 3.35, N 13.9.

Preparation of the Mixture of Complexes $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2\{W(CO)_5\}_x]$, $x = 1$ (4), $x = 2$ (3): A water-cooled solution of $[W(CO)_6]$ (0.104 g, 0.296 mmol) in methanol (18 mL) was ir-

radiated with UV light until the disappearance of the IR band at 1977 cm^{-1} (ca. 1 h). The resulting orange solution (IR bands at 2075 w, 1932 s, and 1887 m, br. cm^{-1}) was then added to a solution of the phosphazene $[N_3P_3(dobp)_2(OC_5H_4N\text{-}4)_2]$ (**1**) (0.100 g, 0.145 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred at room temperature until the disappearance of the IR band at 1887 cm^{-1} (ca. 4 h). The volatiles were then removed in vacuo and the residue was washed with petroleum ether (2 × 30 mL) to leave a yellow solid. Yield 0.12 g. Variation of the proportions of the carbonyltungsten and the phosphazene resulted in mixtures of different composition. − IR (KBr pellet): $\tilde{\nu}$ = 2072 w cm^{-1}, 1975 w, 1918 s, br. (CO).

Preparation of the Mixture of Complexes $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4\{W(CO)_5\}_x]$, x = 1 (11), x = 2 (8, 9, 10), x = 3 (7), x = 4 (6): A water-cooled solution of $[W(CO)_6]$ (0.208 g, 0.591 mmol) in methanol (24 mL) was irradiated with UV light until the disappearance of the IR band at 1977 cm^{-1} (ca. 1 h). The resulting orange solution (IR bands at 2075 w, 1932 s, and 1887 m, br. cm^{-1}) was then added to a solution of the phosphazene $[N_3P_3(dobp)(OC_5H_4N\text{-}4)_4]$ (**2**) (0.092 g, 0.133 mmol) in CH_2Cl_2 (24 mL) and the mixture was stirred at room temperature until the disappearance of the IR band at 1887 cm^{-1} (ca. 13 h). The volatiles were then removed in vacuo and the residue was washed with petroleum ether (2 × 30 mL) to leave a yellow-brown solid. Yield 0.10 g. Variation of the proportions of the carbonyltungsten and the phosphazene resulted in mixtures of different composition. − IR (KBr pellet): $\tilde{\nu}$ = 2073 w cm^{-1}, 1975 sh, 1910 s, br. (CO).

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