2826 *Inorg. Chem.* **1987**, *26*, 2826–2829

Contribution from the Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr, West Germany,
and Fachbereich Chemie der Universität Marburg, D-3550 Marburg, West Germany

Rapid Access to ^{183}W NMR Parameters of Tungsten Complexes via Reverse 2D ^{1}H,^{183}W and ^{31}P,^{183}W NMR Spectroscopy

Reinhard Benn,*[1a] Herbert Brenneke,[1a] Jürgen Heck,[1b] and Anna Rufińska[1a]

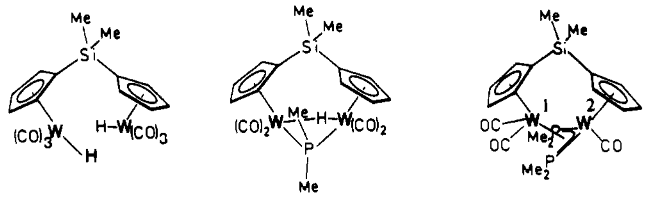
Received February 2, 1987

The indirect two-dimensional ^{31}P,^{183}W and ^{1}H,^{183}W shift correlation spectroscopy is presented for the most efficient access to ^{183}W NMR parameters of tungsten complexes that exhibit a *J*(W,P) or *J*(W,H) coupling. For the Cp-bridged binuclear tungsten complex with terminal hydrido groups $[W(CO)_3H]_2[\mu\text{-}[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2]]$ (**1**) as well as the complexes $[W(CO)_2]_2(\mu\text{-}H)(\mu\text{-}PMe_2)\text{-}[\mu\text{-}[(\eta^5\text{-}C_5H_4)_2SiMe_2]]$ (**2**) and $[W_2(CO)_3](\mu\text{-}PMe_2)_2[\mu\text{-}[(\eta^5\text{-}C_5H_4)_2SiMe_2]]$ (**3**), it is shown that the indirect observation scheme is at least by a factor of 100 more sensitive than the one-dimensional polarization transfer (INEPT) technique. Moreover, the ^{1}H- and ^{31}P-detected multiple-quantum NMR spectroscopy is much more insensitive to misset of the tungsten carrier frequency, and therefore larger ^{183}W shift ranges can be covered within one reverse two-dimensional experiment. In addition $\delta(^{183}W)$ and the magnitude and relative signs of *J*(W,H), *J*(W,P), and *J*(P,H) can be easily extracted from such experiments.

Introduction

Complexes of tungsten are of considerable interest in preparative, mechanistic inorganic[2] and organometallic[3] chemistry as well as in many industrial processes.[4] Characterization of dissolved tungsten complexes via ^{183}W NMR spectroscopy can be extremely informative, because the spectral range is large and the line widths of the signals of this magnetically active spin-$^1/_2$ nucleus are narrow.[5] Unfortunately the NMR receptivity of the ^{183}W isotope is rather low.[6] Until now methods for sensitivity improvement were based on one-dimensional double-resonance experiments,[7] special pulse excitation techniques,[8] use of large sample volumes and relaxation reagents,[9] and polarization transfer techniques like INEPT.[10] Recently, the reverse two-dimensional NMR technique was introduced[11–15] by which NMR shifts of insensitive low-γ nuclei such as ^{15}N,[12,13,16] ^{103}Rh,[17] ^{183}W,[18] ^{57}Fe,[19] and ^{187}Os[20] were obtained via observation of the protons coupled to these nuclei. However many tungsten complexes only have very small or even no scalar couplings to protons.[5] On the other hand, phosphorous compounds are frequently used as ligands in tungsten chemistry and *J*(W,P) couplings are rather large.[5] We have therefore modified a standard multinuclear NMR spectrometer for reverse two-dimensional detection of low-γ nuclei via the ^{31}P nucleus. In this paper the sensitivity and versality of this approach is investigated on a semiquantitative level by using the Cp-bridged binuclear tungsten complexes **1**–**3**[21,22] with terminal hydrido groups as well as hydrido and/or phosphido bridges (cf. Chart I). Furthermore, it will be demonstrated how easily the tungsten NMR parameters $\delta(^{183}W)$, *J*(W,P), and *J*(W,H) as well as the relative signs of these couplings in **2** can be extracted from reverse two-dimensional ^{1}H,^{183}W and ^{31}P,^{183}W experiments, giving further evidence that this technique is superior to any other reported so far for recording the NMR spectra of low-γ nuclei that exhibit a scalar coupling to a more sensitive nucleus.

Chart I



1 **2** **3**

Experimental Section

Materials. The synthesis and structure of complexes **1**–**3** were reported recently.[21,22] The NMR measurements were carried out on solutions of **1** and **2** in the THF-d_8 and of **3** in toluene-d_8 in sealed 5-mm sample tubes. The concentration of **2** was less than 1 mg and that of **1** and **3** about 10 mg in 0.5 mL.

NMR Spectra. All NMR spectra of **1**–**3** were recorded under temperature control (*T* = 308 K) on a multinuclear Bruker WH 400 spectrometer equiped with an ASPECT 2000 and a fast-pulse programmer. A special 5-mm probe head was used. It is supplied with a deuterium lock channel, a doubly tuned inner coil (for ^{1}H and ^{31}P), and an outer coil for X nuclei in the frequency range between 10 and 20 MHz. Pulsing and 90° phase cycling of the ^{1}H and ^{31}P frequencies is achieved via the standard homo- and heteronuclear facilities of the spectrometer. The X-frequency (e.g. ^{183}W = 16.61 MHz) and its 90° phase cycling are generated via a PTS 160 synthesizer. Pulsing of this frequency is achieved with a BSV 3 unit. Thereby arbitrary pulsing of two heteronuclei like ^{31}P and ^{183}W can be performed under computer control. Additionally, the ^{1}H decoupler (BB or CW) can be used in a computer-controlled multiple power level decoupling mode. The 90° ^{1}H pulse via the normal ^{1}H transmitter is 8 μs as against 16 μs via the ^{1}H decoupler. The 90° ^{31}P pulse is 24 μs, and the 90° pulse for the X nucleus

---

[1] (a) Max-Planck-Institut für Kohlenforschung. (b) Universität Marburg.

[2] Cotton, F. A.; Wilkinson, G. *Anorganische Chemie*; Verlag Chemie: Weinheim, FRG, 1982; pp 861 ff.

[3] Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, pp 1321 ff.

[4] (a) Weissermel, K.; Arpe, H. J. *Industrielle Organische Chemie*; Verlag Chemie: Weinheim, FRG, 1978. (b) Dragutan, V.; Balaban, A. T.; Dimonic, M. *Olefin Metathesis and Ring-Opening Polymerization* of *Cyclo-Olefins*, 2nd ed.; Wiley: New York, 1985.

[5] Minelli, M.; Enmark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

[6] (a) Harris, R. K., Mann, B. E., Eds. *NMR and the Periodic Table*; Academic: London 1978. (b) Benn, R.; Rufińska, A. *Angew. Chem.* **1986**, *98*, 851; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.

[7] McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

[8] Schwenk, A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1985**, *17*, 69.

[9] Keiter, R. L.; Vander Velde, D. G. *J. Organomet. Chem.* **1983**, *258*, C34.

[10] Brevard, C.; Schimpf, R. *J. Magn. Reson.* **1982**, *47*, 528.

[11] Maudsley, A. A.; Müller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.

[12] Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185.

[13] (a) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301. (b) Bax, A.; Griffey, R. G.; Hawkins, B. L. *J. Am. Chem. Soc.* **1983**, *105*, 7188. (c) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.

[14] Bendall, M. R.; Pegg, D. T.; Doddrell, D. M. *J. Magn. Reson.* **1983**, *52*, 81.

[15] Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

[16] Sarkar, S. K.; Glickson, J. D.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 6814.

[17] Benn, R.; Brenneke, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *320*, 115.

[18] Benn, R.; Brevard, C.; Rufińska, A.; Schroth, G. *Organometallics* **1987**, *6*, 938.

[19] Benn, R.; Brevard, C. *J. Am. Chem. Soc.* **1986**, *108*, 5622.

[20] Cabeza, J. A.; Mann, B. E.; Brevard, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1985**, 65.

[21] Abriel, W.; Heck, J. *J. Organomet. Chem.* **1986**, *302*, 363.

[22] Heck, J. *J. Organomet. Chem.* **1986**, *311*, C5.

0020-1669/87/1326-2826$01.50/0

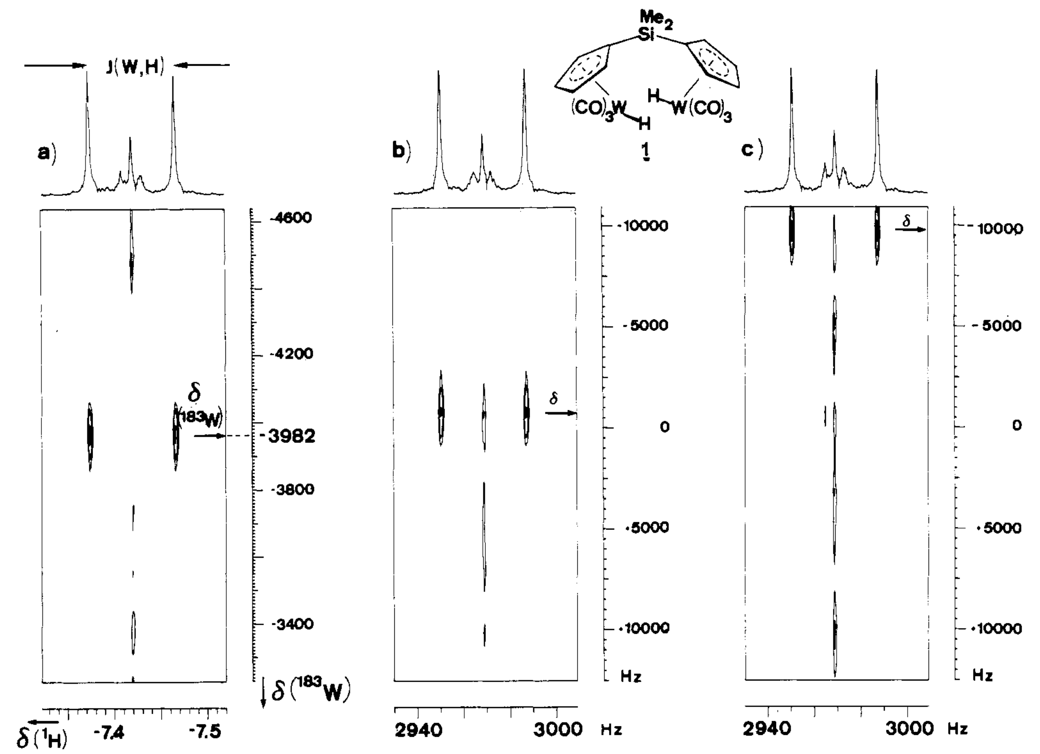
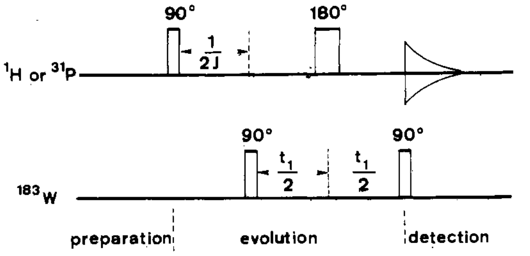


Figure 1. Reverse two-dimensional ^{1}H,^{183}W spectra of **1** in dependence on the tungsten pulse frequency: (a) on-resonance ^{183}W pulse; (b) 1000 Hz off-resonance ^{183}W pulse; (c) 10 000-Hz off-resonance ^{183}W pulse (^{1}H at 400.13 MHz; recording time for each experiment 13 min). In the upper traces the corresponding F_2 projections are shown. Note that the incomplete suppression of the parent signals results from the small number of scans (8) per t_1 increment (cf. also Figure 3 where the parent ^{1}H and ^{31}P signals are completely suppressed).

is approximately 25 μs in the frequency range 10–20 MHz. For ^{183}W the 90° pulse was 22 μs.[23]

The ^{1}H and ^{31}P chemical shifts are presented as δ values relative to external Me$_4$Si and 85% H$_3$PO$_4$, respectively. The ^{183}W chemical shifts were calculated via their absolute frequencies using a conversion factor: 16.613142 MHz corresponds to δ(^{183}W(CO)$_6$) = −3484 relative to Na$_2$WO$_4$.[18]

Recording of the one-dimensional unrefocused ^{1}H→^{183}W and ^{31}P-{^{1}H}→^{183}W INEPT spectra was performed with the standard sequence and a 16-step phase cycling. Two-dimensional reverse spectra were recorded by using sequence 1. This sequence yields δ(^{183}W) in the F_1 dimension and ^{1}H or ^{31}P NMR parameters in the F_2 dimension. Typically both the preparation and detection time were chosen around 1 s. The number of transitions for each t_1 increment varied between 16 (for **1**) and 1600 scans (in the ^{31}P-detected and ^{1}H-CW-decoupled spectra of **2**, cf. Figure 3). Between 16 and 96 data points were chosen for generation of the F_1 dimension, and a spectral width up to 50 000 Hz was covered within one experiment.



(1)

The two-dimensional spectra were subjected to sine bell and shifted sine bell apodization functions in the F_1 and F_2 dimensions before Fourier transformation and are presented in magnitude mode.

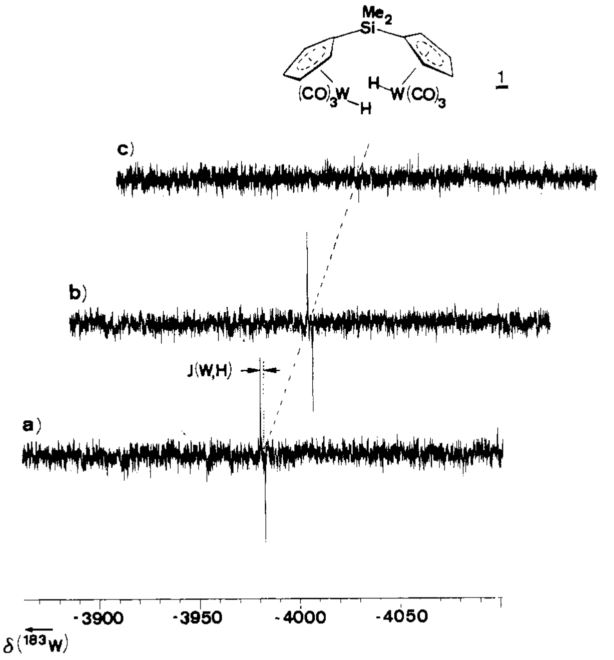


Figure 2. ^{1}H→^{183}W INEPT spectra of **1** in dependence on the tungsten pulse frequency in stacked presentation: (a) on-resonance ^{183}W pulse; (b) 1000-Hz off-resonance and (c) 10 000 Hz off-resonance ^{183}W pulse (^{183}W at 16.61 MHz; recording time for each experiment 6 h).

Results and Discussion

Sensitivity Considerations. In Figure 1 several two-dimensional reverse ^{1}H,^{183}W spectra of compound **1** are presented. Identical acquisition parameters were used except for the tungsten carrier frequency. In Figure 1a it was set on resonance and in parts b and c of Figure 1 it was set at 1000 and 10 000 Hz off-resonance, respectively, from the ^{183}W resonance frequency in **1**. The digital resolution in the F_1 dimension was 1560 Hz/point before zero filling. The exact δ(^{183}W) values were obtained from reverse two-dimensional spectra with ±100 Hz spectral width in the F_1 dimension and a digital resolution of less than 5 Hz/point. The ^{1}H carrier frequency was set on the hydride signal δ(^{1}H) = −7.42, which is known from the one-dimensional spectrum of the sensitive nucleus. Each of the spectra (parts a–c of Figure 1) was recorded

---

[23] A comprehensive paper on the reverse two-dimensional ^{31}P,X technique (X = low-γ nucleus) with a detailed description of the experimental set up is in preparation.

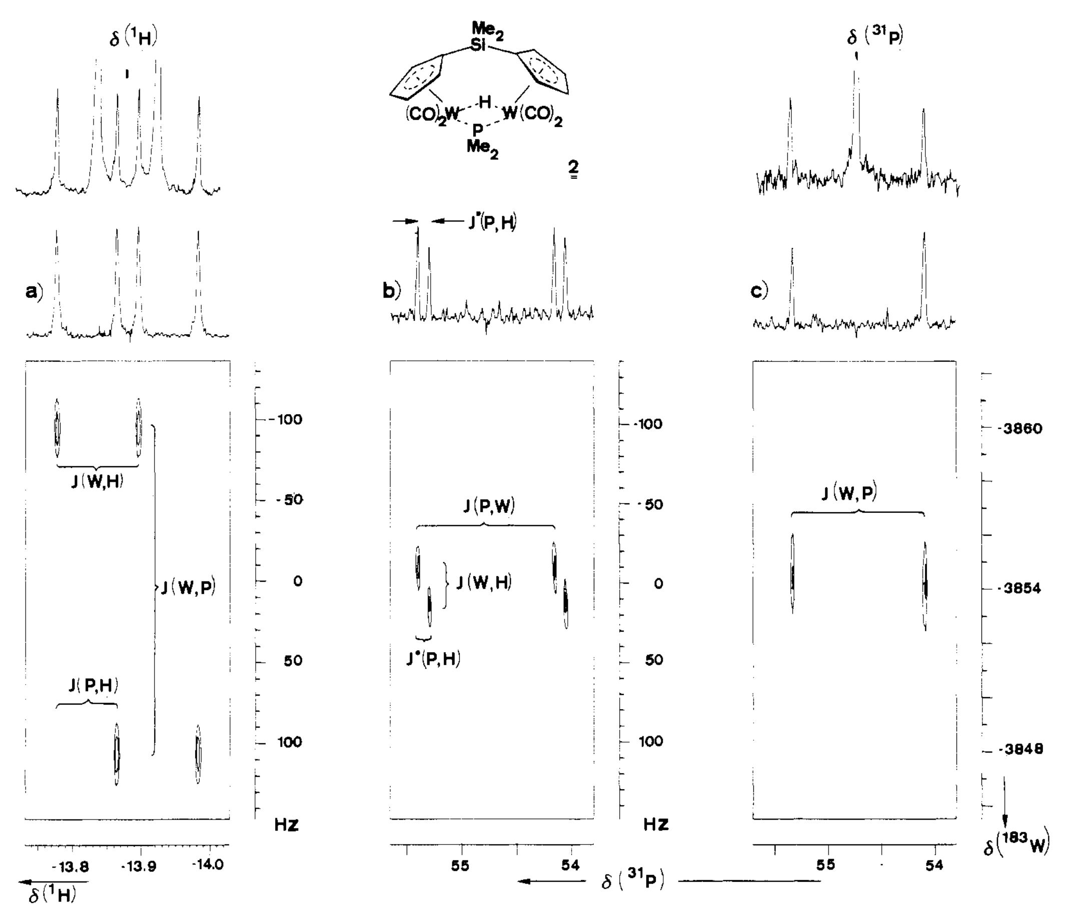


Figure 3. Reverse two-dimensional spectra of **2** at 9.4 T: (a) ^{1}H,^{183}W spectrum (recording time 1 h); (b) ^{31}P,^{183}W spectrum with CW decoupling of the PMe$_2$ protons (recording time 21 h); (c) F_1, F_2 proton-decoupled ^{31}P,^{183}W spectrum (recording time 5 h). J^*(P,H) denotes the scaled J(P,H) coupling resulting from the CW decoupling of the inequivalent methyl protons of the bridging PMe$_2$ group. In the upper traces the corresponding F_2 projections are shown. A total of 2000 transients were collected for the one-dimensional ^{1}H (a) and ^{31}P{^{1}H} (c) spectra, which are shown on top. (This corresponds to a recording time of 1.5 and 1 h, respectively.) Note that the low concentration of **2** makes measurement time for the corresponding one-dimensional polarization transfer spectra prohibitively long.

within 13 min. As can be seen from the F_2 projections, in practice there are no significant differences in the intensity of the satellites. Thus we conclude that the reverse 2D technique is very insensitive to misset of the X-nucleus carrier frequency. The opposite is true for the one dimensional ^{1}H→^{183}W INEPT experiment, which is illustrated in Figure 2. Again the ^{1}H carrier frequency was set on resonance while the ^{183}W carrier frequency was varied: in Figure 2a the tungsten pulse was set on resonance, and in Figure 2b it was set at 1000 Hz and in Figure 2c at 10 000 Hz off-resonance from the true ^{183}W frequency. The recording time for each of the spectra (parts a–c of Figure 2) was around 6 h.

A quantitative comparison of the sensitivity of the reverse 2D and the 1D INEPT experiment is difficult, because both types of experiments cannot be optimized by using identical parameters. We therefore compare the sensitivity when the individual experiments are carried out with optimum parameters. The ratio of the sensitivity for these types of experiments is estimated by the expression

$$(\mathrm{time}(1)/\mathrm{time}(2))^{1/2}(S/N(2))/(S/N(1)) \qquad (2)$$

where time and S/N denote the recording time and signal to noise ratio of corresponding 2D reverse or 1D INEPT experiments. (In the two-dimensional spectra the S/N values are taken from the F_2 projections; cf. Figure 1). If the experiments are compared, Figure 1a with Figure 2a and Figure 1b with Figure 2b, the reverse two-dimensional technique is around 300 times more sensitive. (In our case a 1000-Hz misset of the ^{183}W carrier frequency practically causes no loss of the sensitivity of the INEPT experiment.) On the other hand, when the ^{183}W carrier frequency differs by 10 000 Hz or more from the real ^{183}W frequency, we were unable to produce INEPT spectra and the sensitivity gain of reverse two-dimensional experiment is then practically infinity.

Table I. Selected NMR Parameters of **1**–**3**[a]

compd	δ(^{183}W)	δ(^{31}P)	δ(^{1}H) (hydride)	J, Hz
1	-3982		-7.42	J(W,H) = 36.0
2	-3854	+54.8	-13.88	J(W,H) = +39 J(W,P) = +200.6 J(P,H) = -28
3	-3945 (W^1) -3387 (W^2)	+73.1		J(W^1,P) = 95 J(W^2,P) = 389

[a] See Chart I for structures of **1**–**3**.

Moreover, for compound **2** we could not record ^{1}H→^{183}W INEPT spectra within a reasonable time (40 h) although its δ(^{183}W) value was known from the reverse two-dimensional measurement.

Neglecting rf loss factors, the sensitivity gain of the two-dimensional reverse experiment is $(\gamma_H/\gamma_W)^3$ as opposed to γ_H/γ_W when the INEPT technique is employed. Theoretically, therefore, a sensitivity enhancement by a factor of 580 (^{1}H-detected ^{183}W parameters) or 100 (^{31}P-detected ^{183}W parameters) should be expected. The numbers given above indicate that these sensitivity gains can be obtained in practice. (For a comparison between ^{1}H- and ^{31}P-detected ^{183}W NMR parameters cf. also Figure 3). Frequently, however, the sensitivity difference between ^{1}H- and ^{31}P-detected multiple-quantum ^{183}W NMR spectra is less than 5.8:1 because J(^{31}P,^{183}W) is larger than J(^{1}H,^{183}W) and because the ^{31}P signals are not often modulated by homonuclear phosphorous couplings.

^{183}W NMR Parameters of 1–3. The ^{183}W NMR parameters of **1**–**3** are listed in Table I. The δ(^{183}W) values were obtained from the F_1 projections, whereas the relative signs of the spin–spin couplings in **2** can be derived directly from the positions of the cross peaks as shown in Figure 3. All three nuclei, ^{1}H, ^{31}P and

^{183}W, have a positive magnetogyric ratio. Since in Figure 3a the ^{31}P spins are not excited and the ^{183}W high-frequency cross-peak correlates with the low-frequency ^1H peak, it follows that sign $J(W,P) \neq$ sign $J(H,P)$. By the same argumentation Figure 3b yields: sign $J(W,H) \neq$ sign $J(P,H)$. Since $^1J(W,P)$ can be assumed to be positive,[7] the signs of the residual couplings can be fixed.

The $\delta(^{183}W)$ value for the Cp-bridged complex **1** is similar to that observed earlier for $CpW(CO)_3H$.[7] Also the ^{183}W shift of **2** fits well to what has been obtained for $[CpW(CO)_3]_2$.[7] In view of the large ^{183}W scale, in such binuclear tungsten complexes $\delta(^{183}W)$ does not seem to depend significantly upon the type of the substituent (CO, H, PMe_2) that bridges the two tungsten atoms. The ^{183}W parameters of **3** support the assumption that there is a heteroallylic PW^2P moiety.[22] In such a system the phosphorous atoms have partial double bond character that is reflected by (compared to **2**) smaller $J(W^1,P)$ and higher $J(W^2,P)$ values. The relatively unchanged shift for W^1 and the substantial deshielding of W^2 indicate that relevant contributions to the bonding in the heteroallylic system results from interactions of its terminal atoms with W^1.

Conclusion

From our findings we conclude that in practice the sensitivity gain of the reverse two-dimensional NMR technique over the INEPT observation scheme is quite dramatic for low-γ spin-$^1/_2$ nuclei like ^{183}W. In particular since on-resonance conditions for the ^{183}W nucleus to be measured hardly can be met if $\delta(^{183}W)$ is unknown, the advantage of the ^1H- and ^{31}P-detected multiple-quantum ^{183}W spectroscopy becomes evident. Furthermore this technique can also give the relative signs of scalar spin–spin couplings. Even when the scalar coupling of the insensitive low-γ nucleus to a sensitive nucleus like ^1H or ^{31}P is small, we feel that the reverse two-dimensional recording technique is the method of choice.

Registry No. **1**, 106468-74-0; **2**, 109390-34-3; **3**, 109390-35-4.

Contribution from the Departments of Chemistry, University of Idaho,
Moscow, Idaho 83843, and Washington State University, Pullman, Washington 99164

Syntheses and Structural Characteristics of New Highly Fluorinated Di-*tert*-butyl-1,3,2,4-diazadiphosphetidines

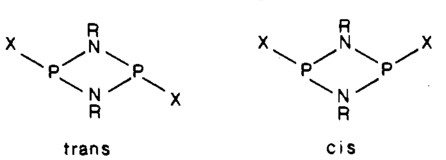
Wan Ahmad Kamil,[1a] Marcus R. Bond,[1b] Roger D. Willett,[1b] and Jean'ne M. Shreeve*[1a]

Received October 24, 1986

A series of lithium salts of polyfluorinated alcohols were reacted with *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine (II) to form the polyfluoroalkoxy derivatives. The acyclic derivatives, i.e., R_fO = CF_3CH_2O, $CF_3CF_2CH_2O$, or $CF_3CF_2CF_2CH_2O$, gave the trans isomer as the major and stable product. The trans isomer also was the sole product with hexamethyldisilazane. However, when R_fO = C_6F_5O or $(CF_3)_2CHO$, the cis isomer was more stable. Silver trifluoroacetate reacted with compound II resulting in the trans isomer as the major product that on standing at 25 °C underwent Arbuzov rearrangement. Reaction with lithiated polyfluorinated diols, $LiOCH_2(CF_2)_{2,3}CH_2OLi$, produced the polyfluorobis(alkoxy-bridged) diazaphosphetidine compounds.

Introduction

Syntheses and structural properties of 1,3,2,4-diazadiphosphetidines, I (R = aryl or alkyl; X = Cl), and their derivatives continue to attract considerable interest among synthetic chemists.[2-6] Although the first such compound, where R = C_6H_5 and X = Cl, was synthesized in 1894,[7] it was not until 1969 that a 1,3,2,4-diazadiphosphetidine (R = t-C_4H_9; X = Cl) was fully characterized.[8] Considerable structural data have been gathered for compound I, especially where R = t-C_4H_9 or C_6H_5 and X = OR or NR′R″ (R = R′ and R″ = alkyl), to learn about the geometry at P(III).[2,9,10] There appears to be a direct correlation between the ^{31}P chemical shift and the geometric isomer present; i.e., the typical chemical shift for the *trans* isomer is on average 80–90 ppm downfield from the cis isomer of I.[2]



I

Advantage has been taken of the labile character of the phosphorus–chlorine bond to introduce alkoxy and dialkylamino substituents by straightforward metathetical reactions with retention of the four-membered heterocyclic ring.[2,9-11] When R = t-C_4H_9 and X = alkoxy or amino, the cis isomers are thermodynamically more stable and the trans isomers that are formed in smaller yield are readily converted to the cis isomers either in solution at 25 °C or upon extended heating. The ^{31}P NMR resonances for the cis isomers are found at higher field. Of particular relevance to our study of 1,3,2,4-diazadiphosphetidines with fluorinated substituents was the report that *only* the cis isomer was obtained when I (R = t-C_4H_9; X = Cl) was reacted with CF_3CH_2OH in the presence of triethylamine to form the first such compound with fluorine-containing substituents at P(III) (I: R = t-C_4H_9; X = CF_3CH_2O).[10,11]

In an attempt to learn more about the effects of introducing nonsterically demanding, as well as bulky, strongly electron-withdrawing, substituents at phosphorus(III) on the formation, stability, and relative amounts of cis and trans isomers, we report the results obtained when metathetical reactions were carried out

---

(1) (a) University of Idaho. (b) Washington State University.
(2) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89.
(3) Chen, H. J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725 and references therein.
(4) Dubois, D. A.; Duesler, E. N.; Paine, R. T. *Organometallics* **1983**, *2*, 1903.
(5) Dubois, D. A.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1985**, *24*, 5.
(6) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D. *J. Chem. Soc., Chem. Commun.* **1979**, 647.
(7) Michaelis, A.; Schroeter, G. *Chem. Ber.* **1894**, *27*, 490.
(8) Scherer, O. J.; Klusmann, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 752.
(9) Bulloch, G.; Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1977**, 99.
(10) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1224.
(11) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* *1980*, 321.

0020-1669/87/1326-2829$01.50/0 © 1987 American Chemical Society