

## Studies of Tungsten-183 Magnetic Shielding by Heteronuclear Magnetic Double and Triple Resonance

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$^1\text{H}$ - $\{^{183}\text{W}\}$ ,  $^1\text{H}$ - $\{^{31}\text{P}\}$ , and  $^1\text{H}$ - $\{^{183}\text{W}, ^{31}\text{P}\}$  nuclear magnetic double- and triple-resonance experiments have been used to determine tungsten-183 chemical shifts and other parameters in 35 tungsten(0) complexes with tertiary phosphine,  $\eta$ -cyclopentadienyl, and other ligands. The observed chemical shifts are several thousand p.p.m. to high field of those for derivatives of  $\text{WF}_6$ , and this is attributed to the occupancy of the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  valence orbitals in addition to the  $d_{x^2-y^2}$  and  $d_{z^2}$ , which reduces the  $d$ -electron imbalance and gives a smaller paramagnetic term.  $\pi$ -Back bonding with ligands produces a high-field shift and the marked sensitivity of the shielding to temperature and isotopic substitution is attributed to changes in electronic excitation energies.

ALTHOUGH several of the transition metals have naturally occurring isotopes with a nuclear spin quantum number  $I$  of  $\frac{1}{2}$  and are therefore specially suitable for study by high-resolution n.m.r. spectroscopy, surprisingly little work has been done in this area. Indeed, only  $^{195}\text{Pt}$  (abundance 34%) and  $^{59}\text{Co}$  (abundance 100%, but unfortunately  $I = \frac{7}{2}$ ) have been studied systematically,<sup>1-7</sup> and the neglect of the others may be attributed to a combination of low natural abundance (e.g.  $^{57}\text{Fe}$ , 2.1%;  $^{187}\text{Os}$ , 1.6%), low inherent sensitivity to n.m.r. detection (e.g.  $^{103}\text{Rh}$ ,  $3.1 \times 10^{-5}$  times that of  $^1\text{H}$ ), or an inconvenient resonant frequency at commonly available magnetic field strengths.

Most of these difficulties have been alleviated by the introduction of multinuclear pulsed Fourier-transform spectrometers, but for nuclei of very low sensitivity to n.m.r. detection such as  $^{183}\text{W}$ , the only naturally occurring isotope of tungsten with  $I = \frac{1}{2}$  (natural abundance 14.3%, sensitivity  $7.0 \times 10^{-5}$  times that of  $^1\text{H}$ ), there are considerable advantages in using  $^1\text{H}$ - $\{\text{X}\}$  or  $^{19}\text{F}$ - $\{\text{X}\}$  double-resonance experiments<sup>8</sup> to obtain the n.m.r. parameters of X whilst benefiting from the relatively high sensitivity to detection of  $^1\text{H}$  or  $^{19}\text{F}$ . For such experiments to succeed there must be detectable coupling between  $^1\text{H}$  (or  $^{19}\text{F}$ ) and X, and with nuclei of low magnetogyric ratio this is not always so. This problem is exacerbated if X is of low natural abundance, for the satellites due to  $^1\text{H}$ -X or  $^{19}\text{F}$ -X coupling may then appear only as shoulders of the main peak in the  $^1\text{H}$  or  $^{19}\text{F}$  spectrum, or may not be detectable at all. In a series of derivatives of  $\text{WF}_6$  this problem was not significant [ $J(^{183}\text{W}-^{19}\text{F}) \simeq 40 \text{ Hz}$ ] and tungsten chemical shifts were obtained easily by double resonance;<sup>9</sup> however, in many complexes and cyclopentadienyl derivatives of tungsten(0) the coupling  $^nJ(^{183}\text{W} \cdots \text{H})$  is very small indeed. This problem was circumvented<sup>10</sup> in two phosphine complexes by using  $^{31}\text{P}$ - $\{^{183}\text{W}\}$  experiments which were made feasible by values of  $^1J(^{183}\text{W}-^{31}\text{P})$  of

several hundred hertz. In the present work we have established that provided that  $^nJ(^{183}\text{W} - \text{H}) \geq 1 \text{ Hz}$  successful double-resonance experiments can be performed, and this condition is generally fulfilled by the protons of  $\eta$ -cyclopentadienyl groups bound to tungsten.

In a number of other complexes, particularly of trimethyl phosphite,  $J(^{183}\text{W} \cdots \text{H})$  is effectively zero, and double-resonance experiments do not succeed. However, in these complexes both  $^1J(^{183}\text{W}-^{31}\text{P})$  and  $^3J(^{31}\text{P} \cdots \text{H})$  have substantial values, and it is therefore possible to use  $^1\text{H}$ - $\{^{183}\text{W}, ^{31}\text{P}\}$  triple-resonance experiments, similar to the  $^1\text{H}$ - $\{^{77}\text{Se}, ^{31}\text{P}\}$  ones described previously,<sup>11</sup> to determine the tungsten resonance frequencies in such complexes. In the present paper we include results obtained by these triple-resonance experiments, for which in several cases the interpretation is more complicated, either because the condition  $\gamma(^{31}\text{P})B_2/2\pi \ll J(^{183}\text{W}-^{31}\text{P})$  was not always fulfilled,\* or because when the molecule contains more than one phosphorus atom the spectra are not strictly first order.

This study was undertaken with a view to establishing the factors which determine tungsten magnetic shielding: such information should be important both from a theoretical standpoint and for diagnostic purposes. In the early work on cobalt<sup>6,7</sup> it appeared that transition-metal shielding was dominated by changes in electronic excitation energies which contribute to the paramagnetic term in Ramsay's expression.<sup>12</sup> However, work on platinum has suggested that, although this factor is significant, changes in the bulk and polarizability of the ligands and in the covalency of the bonds are in many cases more important.<sup>1-5</sup> Studies of oxo-derivatives of tungsten hexafluoride tended to confirm the earlier view, but in this work the immediate neighbours of the tungsten atom were always either oxygen or fluorine which may have reduced the amount of variation of these other parameters.<sup>9</sup>

\*  $B_2$  is the amplitude of the r.f. field  $\nu_2$ .

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## EXPERIMENTAL

The phosphine complexes derived from  $[\text{W}(\text{CO})_6]$  were prepared using essentially standard procedures. Analytical data and physical properties of new complexes are shown in Table 1. The indirect u.v.-irradiation method<sup>13</sup> was found to be most convenient; a 75-W medium-pressure mercury lamp inside a water-cooled quartz jacket was used as the u.v. source in a concentric reaction vessel. Complexes (1), (3), (6),<sup>14</sup> (8),<sup>14</sup> (9),<sup>14,15</sup> (11), (12), and (14)<sup>16</sup> were prepared by this method as follows. A stirred solution of tungsten hexacarbonyl in tetrahydrofuran (distilled from calcium hydride) was irradiated for 2–3 h until carbon monoxide evolution ceased (an inverted burette filled with liquid paraffin being used to monitor the carbon monoxide evolution and to make the pressure inside the reaction vessel slightly less than atmospheric).<sup>17</sup> A stoichiometric amount of ligand was added to the resulting orange-yellow solution, which was then stirred for *ca.* 1 h. The tetrahydrofuran was pumped off, and the product was purified by distillation and/or recrystallization. For complex (5), dimethyl phosphite was added to the irradiated solution: no colour change was apparent after 1 h; triethylamine was then added, the solution was left overnight, and then

before and the first ligand,  $\text{P}(\text{OMe})_3$  in the cases of (16)–(19), was added and the solution stirred for *ca.* 1 h until the solution was almost colourless. The solution was re-irradiated for 2–3 h until carbon monoxide evolution ceased, and then the second ligand was added. The n.m.r. spectra of the crude product after removal of solvent showed that it contained 20–25% of the monosubstituted product (4), identified from its values of  $^1J(^{31}\text{P}-^{183}\text{W})$ ,  $\delta(^{31}\text{P})$ , and  $\delta(^{183}\text{W})$ . Complexes (17)–(19) were isolated by crystallization and purified by recrystallization, but (16) did not crystallize readily and was not purified. Complex (22)<sup>19</sup> was also prepared by the double, indirect, irradiation method. Complexes of the type  $[\text{W}(\text{CO})_4(\text{L})\text{L}']$  have been prepared previously<sup>20</sup> by direct u.v. irradiation of tetrahydrofuran (thf) solutions of  $[\text{W}(\text{CO})_5\text{L}]$  and  $\text{L}'$ , but the indirect method described in the present work has not been reported before. Complexes (2), (4),<sup>13,21</sup> (7),<sup>14,22</sup> (10), (15),<sup>18</sup> and (20)<sup>21</sup> were prepared by thermal-substitution reactions in diglyme (distilled from sodium–benzophenone), following literature methods.<sup>15,23</sup> Complex (2), isolated by distillation (b.p. 160–180 °C, 0.1 mmHg), contained *ca.* 10% of a complex which the n.m.r. spectrum suggested was *cis*- $[\text{W}(\text{CO})_4\{\text{P}(\text{OMe})(\text{OPh})_2\}_2]$  but which was not analyzed.

TABLE 1  
Physical properties and analytical data for new complexes

Complex	Colour	M.p. (°C)	Recrystallization solvent	Analysis (%)							
				Found				Calc.			
				C	H	P	N	C	H	P	N
$[\text{W}(\text{CO})_5\{\text{P}(\text{OMe})[(\text{OCH}_2)_2\text{CMe}_2]\}]$ (3)	White	97–99	$\text{OEt}_2$	27.15	2.65	6.15		27.1	2.7	6.35	
$[\text{NEt}_3\text{H}][\text{W}(\text{CO})_5\{\text{PO}(\text{OMe})_2\}]$ (5)	White	54–55	$\text{OEt}_2$ - $\text{C}_6\text{H}_{14}$	29.2	4.25	5.75	2.5	29.2	4.15	5.8	2.6
$[\text{W}(\text{CO})_5(\text{PMe}_2\text{Ph})]$ (10)	White	35–37	(sublimed)	33.7	2.3	6.7		33.8	2.4	6.7	
$[\text{W}(\text{CO})_5(\text{PH}_2\text{Ph})]$ (11)	White	46–48	$\text{C}_6\text{H}_{14}$	30.5	1.6	7.2		30.4	1.65	7.15	
$[\text{W}(\text{CO})_5(\text{PPh}_2(\text{SnMe}_3))]$ (12)	Pale yellow	decomp. 115	$\text{C}_6\text{H}_6$ - $\text{C}_6\text{H}_{14}$	35.5	2.9	<i>a</i>		35.7	2.85		
$[\text{W}(\text{CO})_4(\text{NCPh})\{\text{P}(\text{OMe})_3\}]$ (17)	Rust-brown	63–65	$\text{OEt}_2$ - $\text{C}_6\text{H}_{14}$	32.15	2.8	5.8	2.6	32.15	2.7	5.9	2.7
$[\text{W}(\text{CO})_4(\text{NC}_5\text{H}_4\text{Me-4})\{\text{P}(\text{OMe})_3\}]$ (18)	Yellow	75–77	$\text{OEt}_2$ - $\text{C}_6\text{H}_{14}$	30.45	3.15	6.0	2.7	30.4	3.15	6.05	2.75
$[\text{W}(\text{CO})_4\{\text{P}(\text{OMe})_3\}\{\text{S}(\text{SnMe}_3)_2\}]$ (19)	Yellow	50–52	$\text{C}_6\text{H}_{14}$	19.9	3.4	<i>a</i>	4.1 <sup>b</sup>	20.0	3.5		4.1 <sup>b</sup>

<sup>a</sup> There was interference in the phosphorus determination. <sup>b</sup> Percentage of sulphur.

worked up as before. Complex (13)<sup>18</sup> was prepared by the direct-irradiation method, the ligand being present during the irradiation; the disadvantage of this method was that it was difficult to know exactly when to stop the irradiation as carbon monoxide evolution did not cease after monosubstitution. Complex (1), a pale yellow-green liquid (b.p. 62 °C, 0.1 mmHg) which solidified on standing,\* was extremely hygroscopic and was not analyzed. Disubstituted complexes (16)–(19) were prepared by a double, indirect, irradiation method. One molecule of carbon monoxide was removed from  $[\text{W}(\text{CO})_6]$  by irradiation as

Complexes (15) and (20) were obtained by distillation as a 1 : 1 mixture and were examined as such. Complex (24)<sup>19</sup> was prepared from the tetrahydroborate-catalyzed substitution reaction.<sup>24</sup> Complex (25) was kindly loaned by Professor M. F. Lappert. Complex (26) was made from  $\text{K}(\text{C}_5\text{H}_5)$  and  $[\text{W}(\text{CO})_6]$  in dimethoxyethane,<sup>25</sup> and (27)–(36) were prepared from (26) by published procedures.<sup>26–28</sup> Complex (37) was prepared from  $\text{WCl}_6$ ,  $\text{Na}[\text{BH}_4]$ , and  $\text{Na}(\text{C}_5\text{H}_5)$  in thf.<sup>29</sup> Complexes (16)–(19) were identified as *cis* isomers from their i.r. spectra in the carbonyl-stretching region and from their values of  $^1J(^{183}\text{W}-^{31}\text{P})$ . Assignments

\* 1 mmHg  $\approx 13.6 \times 9.8$  Pa.

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TABLE 2

N.m.r. parameters of derivatives of tungsten(0)

Complex <sup>a</sup>	<sup>1</sup> J( <sup>31</sup> P- <sup>183</sup> W) <sup>b</sup>	$\delta(^{183}\text{W})$ <sup>c</sup>	$\Xi(^{183}\text{W})$ <sup>d</sup>	$\delta(^{31}\text{P})$ <sup>e</sup>	$\Xi(^{31}\text{P})$ <sup>d</sup>	$\delta(^1\text{H})$ (Me) <sup>f</sup>	<sup>2</sup> J( <sup>31</sup> P... <sup>1</sup> H) (Me) <sup>g</sup>
	Hz	p.p.m.	Hz	p.p.m.	Hz	p.p.m.	$\pm 0.2$ Hz
(1) [W(CO) <sub>5</sub> {PCl <sub>2</sub> (OMe)}] <sup>g</sup>	429.5 $\pm$ 1.0	-2 029.3 $\pm 0.4$	4 153 335 $\pm 2$	123.45 $\pm 0.02$	40 485 787.4 $\pm 0.8$	3.37	16.4
(2) [W(CO) <sub>5</sub> {P(OMe)(OPh) <sub>2</sub> }] <sup>h</sup>	407 $\pm$ 1	-2 323.4 $\pm 2.0$	4 152 110 $\pm 8$	132.66 $\pm 0.01$	40 486 160.3 $\pm 0.04$	3.78	11.6
(3) [W(CO) <sub>5</sub> {P(OMe)[(OCH <sub>2</sub> ) <sub>2</sub> CMe <sub>2</sub> ]}]	400 $\pm$ 8	-2 352.3 $\pm 2.0$	4 151 990 $\pm 8$	129.8 $\pm 0.1$	40 486 045 $\pm 4$	3.61 <sup>j</sup>	12.5
(4) [W(CO) <sub>5</sub> {P(OMe) <sub>3</sub> }] <sup>k</sup>	+386.4 $\pm$ 0.4	-2 365.5 $\pm 2.0$	4 151 935 $\pm 8$	137.99 $\pm 0.01$	40 486 376.1 $\pm 0.4$	3.64	+11.8
(5) [NEt <sub>3</sub> H][W(CO) <sub>5</sub> {PO(OMe) <sub>2</sub> }] <sup>g</sup>	354.5 $\pm$ 0.5	-2 327.3 $\pm 1.0$	4 152 094 $\pm 4$	107.12 $\pm 0.01$	40 485 126.4 $\pm 0.4$	3.36 <sup>j</sup>	11.4
(6) [W(CO) <sub>5</sub> {PPh(OMe) <sub>2</sub> }] <sup>g</sup>	330 $\pm$ 4	-2 282.3 $\pm 2.0$	4 152 282 $\pm 8$	153.05 $\pm 0.04$	40 486 985 $\pm 2$	3.19	12.2
(7) [W(CO) <sub>5</sub> {P(NMe <sub>2</sub> ) <sub>3</sub> }] <sup>i</sup>	310 $\pm$ 5	-2 281.4 $\pm 2.0$	4 152 285 $\pm 8$	125.9 $\pm 0.1$	40 485 888 $\pm 5$	2.66	10.6
(8) [W(CO) <sub>5</sub> {PPh <sub>2</sub> (OMe)}] <sup>i</sup>	280 $\pm$ 2	-2 236.3 $\pm 2.0$	4 152 473 $\pm 8$	123.16 $\pm 0.1$	40 485 776 $\pm 2$	3.36	13.2
(9) [W(CO) <sub>5</sub> (PMePh <sub>2</sub> )] <sup>i,l</sup>	+237 $\pm$ 2	-2 203.6 $\pm 0.4$	4 152 609 $\pm 2$	-5.33 $\pm 0.04$	40 480 574 $\pm 2$	2.21	-6.9 <sup>m</sup>
(10) [W(CO) <sub>5</sub> (PMe <sub>2</sub> Ph)] <sup>i,n</sup>	+230 $\pm$ 3	-2 216.2 $\pm 0.6$	4 152 557 $\pm 3$	-25.2 $\pm 0.2$	40 479 759 $\pm 8$	1.91	-7.6 <sup>m</sup>
(11) [W(CO) <sub>5</sub> (PPhH <sub>2</sub> )] <sup>g</sup>	+220 $\pm$ 4	-2 310.3 $\pm 0.8$	4 152 165 $\pm 3$	-90.2 $\pm 0.1$	40 477 138 $\pm 3$	5.06 <sup>o</sup>	+343.5 <sup>p</sup>
(12) [W(CO) <sub>5</sub> {PPh <sub>2</sub> (SnMe <sub>3</sub> )}] <sup>g,q</sup>	200 $\pm$ 5	-2 171.2 $\pm 2.0$	4 152 744 $\pm 8$	-52.6 $\pm 0.1$	40 478 663 $\pm 4$	0.21	+3.6
(13) [W(CO) <sub>5</sub> {PPh(SnMe <sub>3</sub> ) <sub>2</sub> }] <sup>g,q</sup>	173 $\pm$ 10 <sup>r</sup>	-2 178.2 $\pm 2.0$	4 152 715 $\pm 8$	-172.6 $\pm 0.1$	40 473 802 $\pm 2$	0.305	+3.5
(14) [W(CO) <sub>5</sub> {P(SnMe <sub>3</sub> ) <sub>3</sub> }] <sup>g,q</sup>	143 $\pm$ 3	-2 191.0 $\pm 1.0$	4 152 661 $\pm 4$	-346.6 $\pm 0.1$	40 466 758 $\pm 2$	0.295	+3.4
(15) <i>trans</i> -[W(CO) <sub>4</sub> {P(OMe) <sub>3</sub> } <sub>2</sub> ] <sup>i</sup>	420 $\pm$ 10	-2 323.4 $\pm 2.0$	4 152 110 $\pm 8$	147.05 $\pm 0.2$	40 486 743 $\pm 8$	3.59	11.8 <sup>s</sup>
(16) <i>cis</i> -[W(CO) <sub>4</sub> (NC <sub>5</sub> H <sub>5</sub> ){P(OMe) <sub>3</sub> }] <sup>g</sup>	390 $\pm$ 10	-1 537.3 $\pm 2.0$	4 155 382 $\pm 8$	145.8 $\pm 0.2$	40 486 691 $\pm 8$	3.37	11.0
(17) <i>cis</i> -[W(CO) <sub>4</sub> (NCPH){P(OMe) <sub>3</sub> }] <sup>g</sup>	388 $\pm$ 2	-1 858.7 $\pm 1.0$	4 154 045 $\pm 4$	143.97 $\pm 0.01$	40 486 618.1 $\pm 0.4$	3.59	11.5
(18) <i>cis</i> -[W(CO) <sub>4</sub> (NC <sub>5</sub> H <sub>4</sub> Me-4){P(OMe) <sub>3</sub> }] <sup>g</sup>	387 $\pm$ 2	-1 550.4 $\pm 2.0$	4 155 328 $\pm 8$	146.17 $\pm 0.02$	40 486 706.9 $\pm 0.8$	3.38 <sup>j</sup>	11.3
(19) <i>cis</i> -[W(CO) <sub>4</sub> {P(OMe) <sub>3</sub> }{S(SnMe <sub>3</sub> ) <sub>2</sub> }] <sup>g,t</sup>	377.5 $\pm$ 1.0	-1 813.7 $\pm 2.0$	4 154 232 $\pm 8$	141.49 $\pm 0.01$	40 486 517.7 $\pm 0.1$	3.46 <sup>j</sup>	11.1
(20) <i>cis</i> -[W(CO) <sub>4</sub> {P(OMe) <sub>3</sub> } <sub>2</sub> ] <sup>i</sup>	375 $\pm$ 10	-2 297.4 $\pm 2.0$	4 152 219 $\pm 8$	141.7 $\pm 0.2$	40 486 526 $\pm 8$	3.58	11.4 <sup>s</sup>
(21) <i>trans</i> -[W(CO) <sub>4</sub> (PBu <sup>n</sup> ) <sub>2</sub> ] <sup>u</sup>	270 $\pm$ 1	-2 021 $\pm 1$		-2.6			
(22) <i>cis</i> -[W(CO) <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ] <sup>i,v</sup>	225 $\pm$ 2.5	-2 007.1 $\pm 1.0$	4 153 427 $\pm 4$	-25.8 $\pm 0.1$	40 479 744.5 $\pm 0.4$	1.62	-6.7 <sup>w</sup>
(23) <i>cis</i> -[W(CO) <sub>4</sub> (PBu <sup>n</sup> ) <sub>2</sub> ] <sup>i,u</sup>	224 $\pm$ 1	-1 965 $\pm 1$		-10.4			
(24) <i>fac</i> -[W(CO) <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>i,x</sup>	+218 $\pm$ 3	-1 708.3 $\pm 2.0$	4 154 671 $\pm 8$	-25.8 $\pm 0.2$	40 479 746 $\pm 8$	1.52	-5.7 <sup>y</sup>
(25) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> (SnMe <sub>3</sub> )] <sup>g,z</sup>		-2 933.9 $\pm 0.2$	4 149 570 $\pm 1$				
(26) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> H] <sup>g</sup>		-2 909.0 $\pm 0.2$	4 149 680 $\pm 1$			4.83 *	1.5 $\dagger$
(27) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> D] <sup>g</sup>		-2 919.0 $\pm 0.2$	4 149 633 $\pm 1$			4.83 *	1.5 $\dagger$
(28) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ] <sub>2</sub> <sup>g</sup>		-2 930 $\pm 0.5$	4 149 584 $\pm 2$			4.79 *	1.5 $\dagger$
(29) [WMe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ] <sup>g</sup>		-2 439 $\pm 1$	4 151 630 $\pm 3$			4.60 *	1.4 $\dagger$
(30) [WEt( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ] <sup>g</sup>		-2 358 $\pm 1$	4 151 968 $\pm 3$			4.71 *	1.35 $\dagger$
(31) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> Cl] <sup>g</sup>		-1 296 $\pm 0.5$	4 156 387 $\pm 3$			4.83 *	1.5 $\dagger$
(32) [WBr( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ] <sup>g</sup>		-1 474 $\pm 0.5$	4 155 645 $\pm 2$			4.71 *	1.5 $\dagger$
(33) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> I] <sup>g</sup>		-1 886 $\pm 2$	4 153 930 $\pm 8$			4.64 *	1.5 $\dagger$
(34) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> H{P(OMe) <sub>3</sub> }] <sup>g</sup>	444 $\pm$ 4	-2 784 $\pm 2$	4 150 196 $\pm 6$	161.2 $\pm 0.1$	40 487 314 $\pm 4$	3.40	12.3
(35) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> H(PMe <sub>2</sub> Ph)] <sup>g</sup>	285 $\pm$ 4	-2 570 $\pm 5$	4 151 086 $\pm 20$	-4.3 $\pm 0.2$	40 480 615 $\pm 7$	1.77	9.4 <sup>m</sup>
(36) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> H(PMePh <sub>2</sub> )] <sup>g</sup>	274 $\pm$ 10	-2 571 $\pm 7$	4 151 081 $\pm 25$	+18.3 $\pm 0.2$	40 481 530 $\pm 7$	2.14	8.6 <sup>m</sup>
(37) [W( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> H <sub>2</sub> ] <sup>g</sup>		-3 562 $\pm 1$	4 146 961 $\pm 3$				

of (20) as a *cis* and (15) as a *trans* isomer are based on comparison with literature values for  $\delta(^{31}\text{P})$ ; <sup>21</sup> assignments of (22) as a *cis* and (24) as a *fac* isomer are based on the similarity of the values of  $^1J(^{183}\text{W}-^{31}\text{P})$  to that in (10).

Hydrogen-1 n.m.r. spectra were recorded on a JEOL C-60-H spectrometer for which the probe had been modified by addition of a coil system double-tuned to accept frequencies of 24.28 ( $^{31}\text{P}$ ) and 2.49 MHz ( $^{183}\text{W}$ ). Phosphorus-31 and  $^{183}\text{W}$  chemical shifts were determined from standard  $^1\text{H}$ - $^{31}\text{P}$  and  $^1\text{H}$ - $^{183}\text{W}$  double-resonance experiments,<sup>8</sup> except for the  $^{183}\text{W}$  shifts in complexes (1)–(8) and (12)–(20), where there is no  $^1\text{H}$ - $^{183}\text{W}$  spin-spin coupling and  $^1\text{H}$ - $^{31}\text{P}$ ,  $^{183}\text{W}$  triple-resonance experiments were necessary. The instrumental set-up and the experimental technique for the triple-resonance experiments has been described previously.<sup>11</sup> An alternative arrangement for obtaining a variable frequency from the home-built crystal oscillator was found to be useful. A variable capacitor inserted between the crystal and ground was used to pull the crystal frequency with no significant loss of frequency stability; when the capacitor was controlled through a reduction drive it was easy to adjust the frequency to the nearest hertz. The advantage of this system over the earlier one<sup>11</sup> involving audio modulation was that the whole, instead of half, of the power output of the oscillator was available for use; a possible disadvantage if a radiofrequency counter is not always available is that the output frequency needs monitoring every time the variable capacitor is adjusted.

## RESULTS

N.m.r. parameters for complexes (1)–(37) are listed in Table 2. Although coupling constants are given signs only when a sign-determining multiple-resonance experiment was actually made, there can be no reasonable doubt that  $^1J(^{183}\text{W}-^{31}\text{P})$  is positive in all cases. With complexes (9)–(11), (22), and (24) it was possible to detect  $^{183}\text{W}$  satellites of the resonances of protons forming part of the phosphine ligands and thus the various double-resonance experiments and their interpretation were straightforward.<sup>8</sup> With complexes (25)–(33) it was possible to detect  $^{183}\text{W}$  satellites (generally as poorly resolved shoulders) of the  $\eta\text{-C}_5\text{H}_5$  proton resonance and again no problems arose. Additionally with complexes (25), (26), (29), (30), and (34)–(37),  $^{183}\text{W}$  satellites of resonances of other protons in the molecule were visible. The molecules (34)–(36) have square-pyramidal arrangements of the tungsten atom, the two carbonyl, the hydride, and the phosphine ligands.<sup>30</sup> Thus two isomers are possible in each case according to whether the two carbonyl groups are approximately *cis* or *trans*. In benzene solution at ordinary temperatures these

two isomers are interchanging at rates comparable with the proton n.m.r. time scale and the hydride resonance exhibited both sharp and broad bands (with temperature-dependent linewidths) due to the markedly different values of  $^2J(^{31}\text{P}-\text{W}-\text{H})$  in the two isomers. The results of detailed multi-nuclear band-shape studies of these species will be published elsewhere. Presumably the two isomers also have different values of  $\delta(^{183}\text{W})$ ; however, in the present work the poor signal to noise ratio at which it was possible to record the  $^{183}\text{W}$  satellites of the hydride resonance prevented any determination of separate values of  $\nu(^{183}\text{W})$  for the two

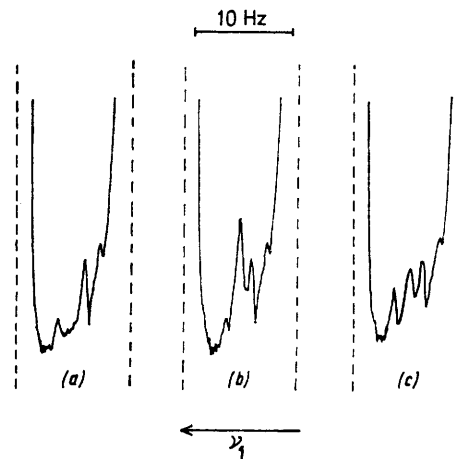


FIGURE 1 Region at the centre of the methoxy-doublet (represented by the vertical broken lines) in the proton spectrum of  $[\text{W}(\text{CO})_5\{\text{P}(\text{OMe})(\text{OPh})_2\}]$  at high spectrometer gain: (a) both  $\nu_2$  and  $\nu_3$  set off-resonance (note the presence of three weak impurity lines which are unaffected in the subsequent experiments); (b) with  $\nu_2$  set to irradiate the high-frequency  $^{183}\text{W}$  satellite in the  $^{31}\text{P}$  spectrum and  $\nu_3$  still off-resonance; (c) with  $\nu_2$  set as in (b) and  $\nu_3$  set to irradiate a  $^{183}\text{W}$  transition

isomers and the results in Table 2 are thus averages. It appeared that the difference in tungsten chemical shift between any pair of isomers was less than 50 p.p.m.

In the species (1)–(8) and (12)–(20) the absence of coupling from  $^{183}\text{W}$  to any protons precluded the use of conventional double-resonance experiments to obtain the tungsten resonance frequencies and the triple-resonance procedure developed for use with  $^{77}\text{Se}$  was therefore used.<sup>11</sup> This is illustrated in Figure 1 for complex (2),  $[\text{W}(\text{CO})_5\{\text{P}(\text{OMe})(\text{OPh})_2\}]$ . Collapse of the proton doublet could be achieved by irradiation at  $\nu(^{31}\text{P})$ , but as  $^1J(^{183}\text{W}-^{31}\text{P})$  is

<sup>30</sup> P. Kalk and R. Poilblanc, *J. Organometallic Chem.*, 1969, **19**, 115.

## Footnotes to Table 2.

<sup>a</sup> All data refer to room temperature (ca. 23 °C). <sup>b</sup> A sign is given only where a relative sign-determining experiment was made. <sup>c</sup> Positive downfield from  $\text{WF}_6$  for which  $\Xi(^{183}\text{W})$  is taken to be 4 161 780 Hz. <sup>d</sup> The  $\Xi$  value is the resonant frequency in a magnetic field where  $\text{SiMe}_4$  resonates at exactly 100 MHz. <sup>e</sup> Positive downfield from 85% aqueous  $\text{H}_3\text{PO}_4$  for which  $\Xi(^{31}\text{P})$  is taken to be 40 480 790 Hz. <sup>f</sup> Positive downfield from  $\text{SiMe}_4$ . <sup>g</sup> Benzene solution. <sup>h</sup> Deuteriochloroform solution. <sup>i</sup> Dichloromethane solution. <sup>j</sup> Refers to the methoxy-group. <sup>k</sup> Neat liquid. <sup>l</sup>  $^3J(^{183}\text{W} \cdots ^1\text{H}) = \pm 2.1 \pm 0.2$  Hz. <sup>m</sup> Refers to  $^2J(^{31}\text{P} \cdots ^1\text{H})$  (Me). <sup>n</sup>  $^3J(^{183}\text{W} \cdots ^1\text{H}) = \pm 2.2 \pm 0.2$  Hz; the  $^{13}\text{C}$  n.m.r. parameters have been published elsewhere (W. McFarlane and D. S. Rycroft, *J.C.S. Chem. Comm.*, 1973, 336). <sup>o</sup> Refers to the protons directly bound to phosphorus. <sup>p</sup> Refers to  $^1J(^{31}\text{P}-^1\text{H})$ . <sup>q</sup> The  $^{119}\text{Sn}$  n.m.r. parameters have been published elsewhere (W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1974, 1977). <sup>r</sup> Calculated from the triple-resonance  $^{183}\text{W}$  spectrum (see text). <sup>s</sup> Refers to  $^3J(^{31}\text{P} \cdots ^1\text{H}) + ^5J(^{31}\text{P} \cdots ^1\text{H})$ . <sup>t</sup>  $\delta(^1\text{H})(\text{SnMe}_3)$  0.51 p.p.m.,  $^2J(^{119}\text{Sn} \cdots ^1\text{H})$  56.1 Hz,  $^3J(^{31}\text{P} \cdots ^{119}\text{Sn})$  26  $\pm$  1 Hz,  $\Xi(^{119}\text{Sn})$  37 295 745  $\pm$  1 Hz. <sup>u</sup> From ref. 10. <sup>v</sup>  $^3J(^{183}\text{W} \cdots ^1\text{H}) + 1.8 \pm 0.2$  Hz. <sup>w</sup> Refers to  $^2J(^{31}\text{P} \cdots ^1\text{H}) + ^4J(^{31}\text{P} \cdots ^1\text{H})$  for the methyl groups. <sup>x</sup>  $^3J(^{183}\text{W} \cdots ^1\text{H})$  could not be obtained because of the broad nature of the spectrum produced by the complexity of the spin system. <sup>y</sup> Refers to  $^2J(^{31}\text{P} \cdots ^1\text{H}) + 2 ^4J(^{31}\text{P} \cdots ^1\text{H})$  for the methyl groups. <sup>z</sup>  $\delta(^1\text{H})(\text{SnMe}_3)$  0.52 p.p.m.,  $^2J(^{119}\text{Sn} \cdots ^1\text{H}) + 48.7$  Hz,  $^1J(^{119}\text{Sn}-^{183}\text{W}) - 150 \pm 5$  Hz,  $^2J(^{183}\text{W} \cdots ^1\text{H})$  1.4 Hz,  $^3J(^{119}\text{Sn} \cdots ^1\text{H})$  0.85 Hz,  $^3J(^{183}\text{W} \cdots ^1\text{H})$  ca. 0.6 Hz,  $\Xi(^{119}\text{Sn})$  37 292 271  $\pm$  8 Hz.

<sup>†</sup> Refers to  $^2J(^{183}\text{W} \cdots \text{H})(\text{C}_5\text{H}_5)$ . <sup>\*</sup>  $\delta(\text{C}_5\text{H}_5)$ .



large the irradiating power level can be set so that species containing  $^{183}\text{W}$  are essentially unaffected in such an experiment. Conversely, by irradiating at  $\nu(^{31}\text{P}) \pm \frac{1}{2}J(^{183}\text{W}-^{31}\text{P})$  only species containing  $^{183}\text{W}$  will be affected so as to produce a weak singlet at the centre of the proton doublet [Figure 1(b)]; hence  $|J(^{183}\text{W}-^{31}\text{P})|$  may be determined. If, with  $\nu_2$  set at the frequency of one of the tungsten-183 satellites in the phosphorus spectrum, a third radio frequency,  $\nu_3$ , corresponding to a  $^{183}\text{W}$  transition, is now applied to the system the resonance condition associated with  $\nu_2$  will be destroyed and the line at the centre of the proton doublet will split and be reduced in intensity [Figure 1(c)]. Thus positions of transitions in the tungsten spectrum and hence  $\nu(^{183}\text{W})$  may be determined.

In general the field used to irradiate phosphorus was relatively strong [ $\gamma(^{31}\text{P})B_2/2\pi \sim 100$  Hz] so that the  $^{183}\text{W}$  spectrum consisted of four bands arising from splitting first by  $J(^{183}\text{W}-^{31}\text{P})$  and secondly by  $\gamma(^{31}\text{P})B_2/2\pi$ . It was noticed that the splitting corresponding to  $J(^{183}\text{W}-^{31}\text{P})$  in the triple-resonance tungsten spectrum was not quite the same as  $J(^{183}\text{W}-^{31}\text{P})$  determined from the  $^1\text{H}-\{^{31}\text{P}\}$  double-resonance experiments. This arises because the condition  $\gamma(^{31}\text{P})B_2/2\pi \ll J(^{183}\text{W}-^{31}\text{P})$  is not fulfilled. [This complication was not

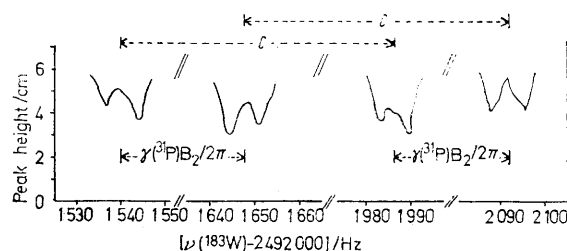


FIGURE 2 Plot of the height of the line appearing at the centre of the methoxy-proton resonance of  $[\text{W}(\text{CO})_6\{\text{PCl}_2(\text{OMe})\}]$  as a function of  $\nu(^{183}\text{W})$  in  $^1\text{H}-\{^{31}\text{P}, ^{183}\text{W}\}$  triple resonance experiments;  $\nu_2$  was adjusted to irradiate a  $^{183}\text{W}$  satellite in the  $^{31}\text{P}$  spectrum with  $\gamma(^{31}\text{P})B_2/2\pi = 107$  Hz, and the splitting  $C$  can be used to calculate  $J(^{31}\text{P}-^{183}\text{W})$  as described in the text. The small repeated splitting of 7 Hz [ $= \frac{1}{2}J(^{31}\text{P} \cdots ^1\text{H})$ ] is due to the transfer of fine structure from the  $^{31}\text{P}$  to the  $^{183}\text{W}$  spectrum by the action of  $\nu_2$ . This is not a conventional INDO spectrum: spectra were recorded for successive 1-Hz increments of  $\nu(^{183}\text{W})$  and the observed peak heights were measured and plotted.

observed in the earlier  $^1\text{H}-\{^{31}\text{P}, ^{77}\text{Se}\}$  experiments because  $J(^{31}\text{P}-^{77}\text{Se})$  is considerably greater than  $J(^{183}\text{W}-^{31}\text{P})$ .] Solution  $^{31}$  of the double-resonance Hamiltonian for an AX system when  $\nu_2 = \nu_X \pm \frac{1}{2}J(\text{AX})$  leads to analytical expressions for the transition frequencies of A which are the same as those for a single-resonance AB system with  $\frac{1}{2}(\nu_A + \nu_B)$  replaced by  $\nu_A$ ,  $(\nu_A - \nu_B)$  replaced by  $J(\text{AX})$ , and  $J(\text{AB})$  replaced by  $\gamma(\text{X})B_2/2\pi$ . Hence  $J(^{183}\text{W}-^{31}\text{P}) = \{C^2 - [\gamma(^{31}\text{P})B_2/2\pi]^2\}^{\frac{1}{2}}$ , where  $C$  is the apparent phosphorus-tungsten splitting. For complex (1) (see Figure 2),  $C = 445$  Hz with  $\gamma(^{31}\text{P})B_2/2\pi = 107$  Hz, giving  $J(^{183}\text{W}-^{31}\text{P})$  431 Hz, which compares very favourably with the double-resonance result of 429 Hz. This method of calculation was necessary for complex (13) where the presence of tin-117 and -119 satellites as well as tungsten-183 satellites in the phosphorus spectrum, and the small difference between the phosphorus- and -tungsten couplings relative to the phosphorus-irradiating field strength necessary, meant that  $^1\text{H}-\{^{31}\text{P}\}$

double-resonance experiments could not be used to measure  $J(^{183}\text{W}-^{31}\text{P})$ .

An additional feature of the results of  $^{183}\text{W}$  irradiation was that fine structure could be discerned in the four bands of perturbation caused by the  $^{183}\text{W}$  field. In an  $\text{AXM}_n$  system where  $|J(\text{AX})| \gg |J(\text{MX})|$  and  $J(\text{AM})$  0, irradiation of X at  $\nu_X \pm \frac{1}{2}J(\text{AX})$  with a field such that  $|J(\text{AX})| > \gamma(\text{X})B_2/2\pi > |J(\text{MX})|$  results in the fine structure of the X resonance caused by coupling to M being transferred, with all splittings halved, to the A spectrum. $^{32}$  Hence in the present case irradiation of one tungsten satellite in the phosphorus spectrum produced four bands in the tungsten spectrum, each of which showed the fine structure in the phosphorus spectrum arising from proton coupling. This effect could be observed clearly in experiments with complexes having simple spin systems and is illustrated in Figure 2 for complex (1) which has only one methyl group coupled to phosphorus: a plot of peak height [the peak being produced at the centre of the proton doublet by irradiation at  $\nu(^{31}\text{P}) - \frac{1}{2}J(\text{PW})$ ] against  $\nu(^{183}\text{W})$  showed a doublet splitting of  $7 \pm 1$  Hz, which is half  $J(\text{P} \cdots \text{H})$ ; the doublet is assigned to the central two lines of a 1 : 3 : 3 : 1 quartet with the outer lines being too weak to be observed.

In the case of molecules containing two phosphorus atoms the spin system is a deceptively simple  $\text{A}_n\text{A}'_n\text{XX}'$  one owing to the large value of  $J(^{31}\text{P} \cdots ^{31}\text{P})$ , and the proton spectrum is a sharp doublet [splitting  $J(^{31}\text{P} \cdots \text{H}) + (n+2)J(^{31}\text{P} \cdots \text{H})$ ] together with a broad band containing almost half the total intensity between the components of the doublet. $^{33}$  In fact the *cis* and *trans* isomers (15) and (20) were examined as a *ca.* 1 : 1 mixture and although the two doublets were well resolved the remainder of the two spectra overlapped. Nonetheless it was possible to obtain observable increases in height at the centre of the proton doublet by irradiation at  $\nu(^{31}\text{P}) \pm \frac{1}{2}J(^{183}\text{W}-^{31}\text{P})$  for each isomer and thus perform the  $^1\text{H}-\{^{31}\text{P}, ^{183}\text{W}\}$  triple-resonance experiments needed to obtain  $\nu(^{183}\text{W})$ .

The fine structure detected in the  $^{119}\text{Sn}$  spectrum of (19) during  $^1\text{H}-\{^{119}\text{Sn}\}$  tickling experiments showed that, apart from the splitting due to  $J(^{119}\text{Sn} \cdots ^1\text{H})$ , there was also a coupling of  $26 + nJ(^{119}\text{Sn} \cdots ^1\text{H})$  Hz; the intensity pattern was only consistent with  $n = 0$ , and the 26 Hz splitting is assigned to  $J(^{119}\text{Sn}-\text{S}-\text{W}-^{31}\text{P})$ .

In this work we use  $\text{WF}_6$  as the reference for the tungsten-183 chemical shifts. This is probably not an ideal choice but facilitates comparison with earlier work, $^9$  and the value used for  $\Xi(^{183}\text{W})$  in this compound agrees reasonably with that obtained recently by direct observation of the  $^{183}\text{W}$  resonance. $^{34}$  It should be noted, however, that this reference is subject to significant solvent effects. $^9$  The results in Table 2 were obtained at  $23 \pm 1$  °C, but complexes (34)–(36) were also examined at other temperatures. Shifts to lower applied field of *ca.* 1.5 p.p.m. (°C) $^{-1}$  occurred with increasing temperature.

## DISCUSSION

The complexes discussed in this work all give tungsten-183 chemical shifts very much to high field of the derivatives of  $\text{WF}_6$  studied previously. $^9$  Although colour cannot be used as an exact guide to electronic

$^{32}$  R. Freeman and B. Gestblom, *J. Chem. Phys.*, 1967, **47**, 1472.

$^{33}$  R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

$^{34}$  J. Banck and A. Schwark, *Z. Physik.*, 1975, **B20**, 75.

$^{31}$  R. M. Lynden-Bell and R. K. Harris, 'Nuclear Magnetic Resonance Spectroscopy,' Nelson, London, 1969, p. 146.

excitation energies, it seems likely that the latter are relatively large in the colourless tungsten(vi) complexes, and smaller in the low-valent tungsten derivatives which are often coloured. On this basis the paramagnetic term should be smallest and the shielding greatest in the tungsten(vi) complexes whereas the reverse is observed, and it therefore appears that the differences in chemical shift between the two series cannot be attributed to differences in electronic excitation energies. Of course this reasoning does not preclude the possibility that variations in  $\Delta E$  might be important in determining variations of shielding within a particular series, and indeed it is thought that this was a major factor in the case of the derivatives of  $\text{WF}_6$ .<sup>9</sup>

The most obvious difference between the complexes studied here and the earlier series is the absence of metal  $5d$  electrons in the latter. The availability of these and their use in bonding to ligands might substantially increase the diamagnetic circulation and thus increase the shielding. However, it is generally recognised that the contribution of the outer electrons to the diamagnetic part of the shielding is small, and certainly effects of the order of 1 000 p.p.m. or more are improbable.<sup>35</sup> In both sets of compounds the tungsten hybridization is essentially  $d^2sp^3$ , the tungsten  $5d_x$  and  $5d_{x-y^2}$  orbitals being used in the sigma bonds. According to a treatment by Jameson and Gutowsky<sup>35</sup> the paramagnetic contribution will be largest when the  $p$ - or  $d$ -orbital electron imbalance is a maximum, conditions which appertain when two  $p$  orbitals are filled and one is vacant (or *vice versa*), and when the  $t_{2g}$  set of  $d$  orbitals is filled and the  $e_g$  set is vacant (or *vice versa*). This last situation ( $t_{2g}^6e_g^4$ ) is approached in  $\text{WF}_6$  which consequently has a low-field shift, while in  $[\text{W}(\text{CO})_6]$  (see next paragraph for the probable tungsten chemical shift of this molecule) there is occupancy of the tungsten  $t_{2g}$  orbitals also so that the electronic imbalance in the  $5d$  orbitals is substantially redressed and a high-field shift arises. The argument is more complicated in the cases of the various tungsten(vi) and tungsten(0) derivatives owing to their lower symmetry, but the same basic conclusion emerges: the higher shielding in the latter is due to reduced  $d$ -electron imbalance. Any change in the occupancy of the  $t_{2g}$  set of  $d$  orbitals resulting from  $\pi$  bonding with the ligands will alter the imbalance and hence change the tungsten shielding, but as variations in the amount of  $\pi$  bonding will be accompanied by changes in the  $\sigma$  bonds which will affect the  $e_g$  set of  $d$  orbitals and also the  $p$ -electron imbalance the effect on the  $^{183}\text{W}$  chemical shift may not be simple.

Extrapolation of the data for the series (10), (22), and (24) in which carbonyl groups are successively replaced by  $\text{PMe}_2\text{Ph}$  suggests that in tungsten carbonyl itself  $\delta(^{183}\text{W}) = -2\,400 \pm 40$  p.p.m., a value which is supported by the trend in the chemical shifts of (4), (15), and (20). In general then, our results show that replacement of carbonyl groups by phosphorus-donor ligands

reduces the tungsten shielding. For many heavier nuclei plots<sup>36</sup> of the shielding of X against  $n$  in series of the type  $\text{XR}_n\text{L}_{m-n}$  (R, L = different ligands or substituents,  $n = 0, 1 \dots m$ ) have a characteristic U shape with maximum deshielding near  $n = m/2$  which is about where the  $p$ -electron imbalance should be greatest.<sup>35</sup> Unfortunately we were unable to obtain  $^{183}\text{W}$  chemical shifts for species containing more than three phosphorus atoms owing to the complexity of the spin systems involved, but it can be remarked that our data are not inconsistent with this type of behaviour by tungsten.

From the values of  $^1J(^{183}\text{W}-^{31}\text{P})$  and on general chemical grounds it is reasonable to assume that the effective electronegativities of the phosphine ligands increase in the order  $\text{P}(\text{SnMe}_3)_3 < \text{PMe}_2\text{Ph} < \text{P}(\text{OMe})_3$ , and the tungsten shielding might therefore be expected to decrease in the order (14) > (10) > (4). In fact the opposite was observed, although within the series of tin derivatives (12)–(14) the shielding does increase as  $^1J(^{183}\text{W}-^{31}\text{P})$  decreases, *i.e.* as the effective electronegativity of the ligand decreases. It is tempting to attribute these anomalies to the effects of  $\pi$  bonding between tungsten and phosphorus. This should be greatest in the phosphite derivatives and its occurrence may permit increased electronic circulation about the tungsten atom and hence increase the shielding. In complexes (16) and (18), in which one of the ligands has a markedly reduced ability to participate in back bonding from tungsten, there is a definite shift to lower field, presumably owing to the electronic imbalance introduced by the electronegative nitrogen ligands. In complex (17) more back bonding is possible and the shift to low field is smaller. It is striking that in these complexes differences in tungsten shielding between pairs of *cis* and *trans* isomers are small. In contrast, for many platinum complexes the  $^{195}\text{Pt}$  is very sensitive to whether phosphine ligands are *cis* or *trans*,<sup>1-5</sup> but it should be noted that this seems to occur mainly when the other ligands are of poor  $\pi$ -bonding ability, which is not the case with carbonyl groups. In connection with relatively small differences in shielding between different compounds, it is important to remember that changes in conformation of the ligands may be expected to have significant effects.<sup>37</sup>

The trends in tungsten shielding displayed by the  $\eta$ -cyclopentadienyl derivatives are largely as expected. Thus a hydride group produces a substantial high-field shift while for complexes (31)–(33) the shielding increases in the order  $\text{Cl} < \text{Br} < \text{I}$ . This can be seen partly as a result of changes in electronegativity affecting the covalency of the bonds, and is also in conformity with the observation that heavy atoms with electron lone pairs produce shifts to higher field even though they may be fairly electronegative.<sup>5,36</sup> This factor is probably also responsible for the high-field shift of the super

<sup>35</sup> C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

<sup>36</sup> J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin, and Lead Compounds*, 1974, **1**, 235; P. R. Wells, *Det. Org. Structures Phys. Methods*, 1971, **4**, 233.

<sup>37</sup> W. McFarlane, *Chem. Comm.*, 1969, 700.

sandwich complex (28). Replacement of hydride in complex (26) by deuterium gives an up-field shift of 10 p.p.m. This is in the direction expected if the vibrational amplitude is reduced so that the effective ligand field is greater and  $(\Delta E)^{-1}$  is correspondingly smaller.<sup>38</sup> In cases where hydrogen bonding is unlikely the effects of replacing  $^1\text{H}$  by  $^2\text{H}$  on shielding are normally smaller than this; however, with a transition metal,  $\Delta E$  itself is probably considerably smaller and so changes in it are relatively more important. In  $\text{K}_3[\text{Co}(\text{CN})_6]$  the  $^{59}\text{Co}$  shielding is increased by *ca.* 0.9 p.p.m. when a  $^{13}\text{C}$  nucleus replaces  $^{12}\text{C}$ , a much smaller percentage mass change,<sup>39</sup> and we have observed similar effects on  $^{195}\text{Pt}$  shielding in replacement of  $^1\text{H}$  by  $^2\text{H}$  in platinum hydrides. In this connection the temperature dependence of  $\sigma(^{183}\text{W})$  of *ca.* 1.5 p.p.m.  $(^\circ\text{C})^{-1}$  is noteworthy. This can be attributed to an increased population of higher vibrational states which effectively lowers  $\Delta E$ ; dependences of shielding on temperature of comparable

<sup>38</sup> R. A. Bernheim and H. Batiz-Hernandez, *J. Chem. Phys.*, 1966, **45**, 2261.

<sup>39</sup> P. C. Lauterbur, *J. Chem. Phys.*, 1965, **42**, 799.

magnitude have been reported for  $^{59}\text{Co}$ ,  $^{103}\text{Rh}$ , and  $^{195}\text{Pt}$ , but not for the nuclei of non-transition elements (unless chemical changes occur).<sup>6, 7, 37, 5</sup>

The dependence of  $^1J(^{183}\text{W}-^{31}\text{P})$  on the electronegativity of the phosphorus substituents has been discussed by Fischer *et al.*<sup>40</sup> and it was suggested that there might be a regular periodicity of  $^1J(^{183}\text{W}-^{31}\text{P})$  with the  $\alpha$ -*P* substituent. In this connection it may be noted that  $^1J(^{183}\text{W}-^{31}\text{P})$  for (14) lies on the straight line for all the complexes except those with phosphorus trihalide ligands. There is therefore a single straight-line relation for  $\alpha$ -*P* substituents from groups 4B, 5B, and 6B at least, and it appears that there is an anomaly with the trihalides rather than a periodic dependence.

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<sup>40</sup> E. O. Fischer, L. Knauss, R. L. Keiter, and J. G. Verkade, *J. Organometallic Chem.*, 1972, **37**, C7.