

### Preliminary communication

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## DIRECT OBSERVATION OF $^{183}\text{W}$ NMR OF $\text{W}(\text{CO})_6$ AND PHOSPHINE DERIVATIVES

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### Summary

$^{183}\text{W}$  NMR spectra of  $\text{W}(\text{CO})_6$ ,  $(\text{OC})_5\text{WPPH}_3$ ,  $(\text{OC})_5\text{WPPH}_2\text{CH}=\text{CH}_2$  and  $(\text{OC})_5\text{WPPH}(\text{CH}=\text{CH}_2)_2$  have been obtained directly with the aid of  $\text{Cr}(\text{acac})_3$  as relaxation agent.

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The low receptivity of the  $^{183}\text{W}$  nucleus (0.059 relative to  $^{13}\text{C}$ ) [1] and its slow relaxation have discouraged organometallic chemists from using  $^{183}\text{W}$  NMR as a source of structural information. However, its potential usefulness is considerable, as suggested by extensive  $^{183}\text{W}$  NMR studies of heteropolytungstates [2] (where the information gained is not readily available from more conventional techniques), and the significant attention  $^{95}\text{Mo}$  NMR has begun to receive among organometallic chemists [3]. Direct observation of  $^{95}\text{Mo}$  NMR signals is much more favorable than  $^{183}\text{W}$  because of its much higher receptivity (2.88 relative to  $^{13}\text{C}$ ) and shorter  $T_1$  values as a result of quadrupole relaxation, but the  $^{183}\text{W}$  NMR can be taken if the complex is reasonably soluble ( $> 0.1\text{ M}$ , preferably  $1\text{ M}$ ), available on the gram scale, stable in the presence of a relaxation agent, and appropriate instrumentation is used. In this work we have obtained  $^{183}\text{W}$  NMR spectra of  $\text{W}(\text{CO})_6$ ,  $(\text{OC})_5\text{WPPH}_3$ ,  $(\text{OC})_5\text{WPPH}_2\text{CH}=\text{CH}_2$ , and  $(\text{OC})_5\text{WPPH}(\text{CH}=\text{CH}_2)_2$  [4] using a homebuilt 5.9 T spectrometer with a 20 mm sideways spinning probe [5] (sample volume  $\sim 8\text{ ml}$ ) and a Nicolet Nic-80 data system, operating at 10.4 MHz.

The tungsten chemical shift of tungsten hexacarbonyl has been determined previously by  $^{13}\text{C}\{^{183}\text{W}\}$  experiments which require a sequential search for the signal of interest [6]. A saturated solution in THF of  $\text{W}(\text{CO})_6$  gave  $\equiv(^{183}\text{W}) =$

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4.151878 MHz [7]. For a saturated dichloromethane solution (0.18 M), containing 35 mmol Cr(acac)<sub>3</sub>, we have obtained a value of 4.151866 MHz in good agreement with that previously reported [8]. The spectrum obtained (S/N 18/1) was the sum of 38,000 scans for which ca. 30° pulses and a recycle time of 2.1 s were used. These parameters proved to be conservative, as the flip angle could be doubled and the recycle time halved with no appreciable saturation. Under the latter conditions a clear sharp signal (S/N 4/1 in 1000 scans) could be found in as little as 20 min. In the absence of Cr(acac)<sub>3</sub>, the *T*<sub>1</sub> for W(CO)<sub>6</sub> was too long to allow direct observation even when pulse delays of up to 80 s were used.

The phosphine derivatives are more soluble than W(CO)<sub>6</sub> and the expected doublets were obtained in rapid fashion. The dipole-dipole interaction which results from the 100% abundant <sup>31</sup>P nucleus interacting with <sup>183</sup>W undoubtedly leads to a relaxation time for these derivatives which is substantially shorter than for the magnetically well-insulated tungsten nucleus in W(CO)<sub>6</sub>. A 1.5 M solution of (OC)<sub>5</sub>WPPh(CH=CH<sub>2</sub>)<sub>2</sub> gave a good spectrum (Fig. 1) from 16 pulses.

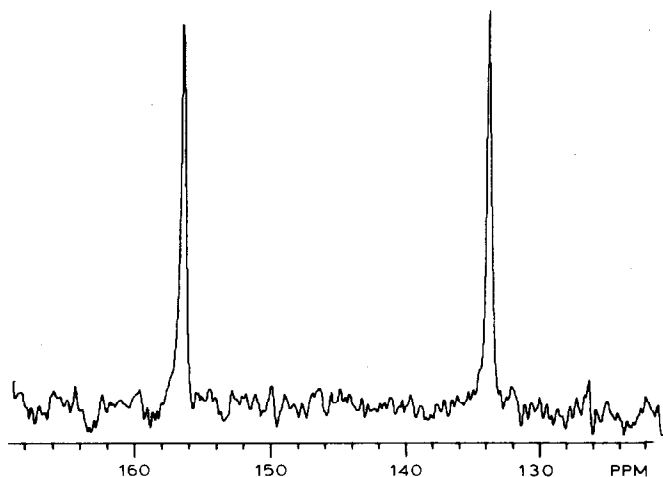


Fig. 1. <sup>183</sup>W NMR Spectrum of (OC)<sub>5</sub>WPPh(CH=CH<sub>2</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The chemical shift scale is with respect to W(CO)<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> with positive values to higher frequency.

TABLE 1

CHEMICAL SHIFTS ( $\delta$ , ppm) AND COUPLING CONSTANTS FOR TUNGSTEN COMPLEXES<sup>a</sup>

Complex	$\nu(^{183}\text{W})$ (MHz)	$\delta$ from W(CO) <sub>6</sub>	<i>J</i> (WP)
W(CO) <sub>6</sub>	4.151866	—	—
(OC) <sub>5</sub> WPPh(CH=CH <sub>2</sub> ) <sub>2</sub>	4.152468	145	236.7
(OC) <sub>5</sub> WPPh <sub>2</sub> CH=CH <sub>2</sub>	4.152580	172	238.8
(OC) <sub>5</sub> WPPh <sub>3</sub>	4.152739	210	244.5

<sup>a</sup> Resonant frequency of aqueous Na<sub>2</sub>WO<sub>4</sub> was 10.422612 MHz or 3446  $\delta$  downfield of W(CO)<sub>6</sub>.

Addition of Cr(acac)<sub>3</sub> (50 mmol) allowed substantially shorter recycle times to be used without detectable broadening of the tungsten resonance or a shift in its frequency. A 1.0 M solution of (OC)<sub>5</sub>WPPh<sub>2</sub>CH=CH<sub>2</sub> and a 0.6 M solution of (OC)<sub>5</sub>WPPh<sub>3</sub> gave good spectra from 644 and 744 pulses, respectively.

Data for the complexes are shown in Table 1. Chemical shifts are reported

relative to  $W(CO)_6$  [6]. Tungsten-phosphorus coupling constants are in agreement with literature values. All of the phosphine complexes are deshielded relative to  $W(CO)_6$  with the better  $\pi$ -acceptor ligands giving most deshielding [ $PPh_3 > PPh_2CH=CH_2 > PPh(CH=CH_2)_2$ ]. Trends in  $^{183}W$  chemical shifts are often complicated and the various contributing factors have been discussed [6].

We conclude that  $^{183}W$  NMR spectra may be obtained by rapid and routine procedures if the conditions listed above can be met. Use of a relaxation agent is particularly important with limited quantities of compound or limited solubility to allow collection of the maximum number of transients in the minimum amount of time.

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- 7 Calculated resonant frequency in a field in which the protons of TMS would resonate at exactly 100 MHz.
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