

borane has not been assigned; however, the absorption at  $1885\text{ cm}^{-1}$  verifies the presence of hydrogen in bridging positions.<sup>3</sup> The spectrum of the sample was examined two times during a 1-hr period and in this time no evidence of additional deuterium migration into bridging positions was observed.

Terminal substitution of deuterium in the 6,9 positions is clearly evident from the  $^{11}\text{B}$  nmr spectrum shown in Figure 1a. The spectrum of normal  $\text{B}_{10}\text{H}_{14}$  is also shown (Figure 1b) for comparison purposes.

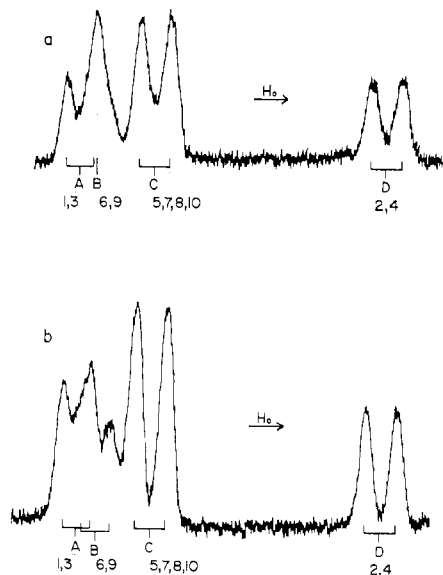


Figure 1.—(a) The  $^{11}\text{B}$  nmr spectrum of a 0.3 M solution of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$  in heptane. (b) The  $^{11}\text{B}$  nmr spectrum of a 0.3 M solution of  $\text{B}_{10}\text{H}_{14}$  in heptane.

Due to the solvent dependence of the  $^{11}\text{B}$  nmr spectrum of  $\text{B}_{10}\text{H}_{14}$ ,<sup>16</sup> both spectra were measured in heptane in order to show most clearly the separation of the 1,3 and 6,9 resonances. The spectrum of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$  consists of a low-field doublet, A ( $\delta -11.7$  ppm;  $J = 156$  Hz), an overlapped singlet, B ( $\delta -9.3$  ppm), a doublet, C ( $\delta +0.2$  ppm;  $J = 152$  Hz), and a high-field doublet, D ( $\delta 37.6$  ppm;  $J = 151$  Hz), of relative areas 2:2:4:2, respectively. Based on spectral assignments which have been published previously,<sup>17,18</sup> resonances A, B, C, and D can be assigned to the 1,3, 6,9, 5,7,8,10, and 2,4 boron atoms, respectively. Comparison of resolution of each doublet in the spectrum of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$  with the corresponding doublets in the spectrum of unsubstituted  $\text{B}_{10}\text{H}_{14}$  indicates that a very small amount of deuterium scrambling into the 5,7,8,10 positions has occurred. However, no measurable amount of deuterium is present in the 1,3 or 2,4 positions.

The preparation of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$  in the above sequence of reactions depends on the fact that in  $\text{B}_{10}\text{H}_{10}\text{D}_5^-$  rapid equilibration of hydrogen and deuterium atoms between bridge and 6,9 terminal positions occurs.<sup>7</sup> However, only minimal scrambling of deuterium into 5,7,8,10 terminal positions is evident. When

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(18) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc., London*, 402 (1964), and references cited therein.

the  $\text{B}_{10}\text{H}_{10}\text{D}_5^-$  is allowed to react with DCl, hydrogen evolution occurs in a reaction which does not give rise to a species in which deuterium scrambling into 5,7,8,10 positions occurs. The exact nature of this reaction is not established at this time.

In order to ensure clean labeling, several modifications of the published experimental techniques were used. In the preparation of  $\text{B}_{10}\text{H}_{10}\text{D}_5^-$ , monoglyme was added to the  $\mu\text{-B}_{10}\text{H}_{10}\text{D}_4\text{-NaBD}_4$  mixture in a container large enough so that good mixing was ensured.<sup>12</sup> Also, the reaction was carried out under an  $\text{N}_2$  atmosphere. This procedure minimizes the formation of  $\mu\text{-B}_{10}\text{H}_{10}\text{D}_3^-$  in the reaction. The exchange reactions which were used to replace hydrogen or deuterium in the bridging positions of decaborane were allowed to continue for only 3–5 min. Upon completion of the exchange the decaboranes were immediately extracted into diethyl ether, the ether was flash evaporated, and the product was purified by sublimation. These procedures minimized both scrambling and loss of product due to hydrolysis.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE,  
CHICAGO, ILLINOIS 60680

### Tungsten-183 Chemical Shifts in *cis*- and *trans*-Bis(tributylphosphine)tetracarbonyltungsten

BY PAUL J. GREEN\* AND THOMAS H. BROWN

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The first measurement of a tungsten-183 nuclear resonance in a nonconducting material was the double-resonance determination of tungsten hexafluoride (liquid).<sup>1</sup> Apparently the only other compound measured has been tungsten trioxide (solid)<sup>2</sup> which showed a chemical shift of  $-1000$  ppm from that of tungsten hexafluoride. Because the platinum<sup>3,4</sup> and rhodium<sup>5</sup> resonances in square-planar and octahedral *halide* complexes have exhibited a regular dependence on the geometrical form of the complexes, it seemed that a similar measurement on two isomers of a carbonyl complex might prove useful by comparison. Therefore we have measured the tungsten chemical shifts in the compounds *cis*- and *trans*-( $\text{CO})_4\text{W}((\text{C}_4\text{H}_9)_3\text{P})_2$ .

The preparation and phosphorus-31 spectra of the compounds have been reported by Grim and Wheatland.<sup>6</sup> The method of preparation was the same as

\* To whom correspondence should be addressed at Union Carbide Research Corp., Tarrytown, N. Y.

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(3) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1970 (1968).

(4) W. McFarlane, *Chem. Commun.*, 393 (1968).

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(6) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).

described by those authors. The spectra of the complexes in methylene chloride solution were recorded on a Bruker HFX-90 MHz spectrometer with 5- and 13-mm spinning sample tubes. The experimental method employed was to observe the phosphorus spectrum while applying a small irradiation field which perturbed the  $^{183}\text{W}$  ( $I = 1/2$ , abundance 14.3%) satellites. A capillary of  $\text{H}_3\text{PO}_4$  was used for an external reference. The ligand protons were decoupled during the experiments in order to improve the signal:noise ratio of the spectra.<sup>7</sup> Thus the tungsten shifts are accurate to  $\pm 1$  ppm and the coupling constants to  $\pm 1$  Hz. Also for the tungsten shifts the difference in bulk susceptibility between samples in the two sized tubes was found to be less than 2 ppm when referred to the phosphorus-31 capillary. The tungsten shifts were calculated from our measured frequency and the reported ratio of tungsten to proton frequencies in tungsten hexafluoride and water, respectively.<sup>1</sup>

The tungsten chemical shifts reported in Table I

TABLE I  
NMR DATA FOR TUNGSTEN AND PLATINUM  
COMPLEXES AT ROOM TEMPERATURE

Compound	$\delta(\text{P})^a$ , ppm	$J(\text{P-M})$ , Hz	$\delta(\text{M})^b$ , ppm
<i>cis</i> -(CO) <sub>4</sub> W((C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P) <sub>2</sub>	+10.0	224	+1965
<i>trans</i> -(CO) <sub>4</sub> W((C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P) <sub>2</sub>	+2.6	270	+2021
<i>cis</i> -((C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P) <sub>2</sub> PtCl <sub>2</sub> <sup>c</sup>	-1.4	3508	+4450
<i>trans</i> -((C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P) <sub>2</sub> PtCl <sub>2</sub>	-4.9	2380	+3930

<sup>a</sup>  $\delta(^{31}\text{P})$  relative to 85%  $\text{H}_3\text{PO}_4$ . <sup>b</sup>  $\delta(^{183}\text{W})$  relative to  $\text{WF}_6(1)$  and  $\delta(^{195}\text{Pt})$  relative to  $\text{H}_2\text{PtCl}_6(\text{soln})$ . <sup>c</sup> Taken from ref 3.

exhibit a few general trends which deserve discussion. First, the tungsten resonances of these carbonyl complexes are found to higher field than those of the higher oxidation state complexes previously measured. This parallels the trend noted for the variation in chemical shift between the different oxidation state compounds of several other transition metal elements.<sup>8</sup> Moreover the magnitude of this effect appears to be about the same size for tungsten as for the lighter elements. Specifically, the manganese-55 resonance in solutions of

(7) For a description of the method see T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, **91**, 3378 (1969).

(8) T. H. Brown and P. J. Green, *Phys. Lett. A*, **31**, 148 (1970).

$\text{Mn}(\text{CO})_5^+$  is 2600 ppm above that of potassium permanganate solution.<sup>9</sup>

It is also interesting to note the tungsten-183 nmr shift difference between the *cis* and *trans* isomers of the carbonyl-phosphine complex studied. Previous attempts to observe manganese<sup>9</sup> or cobalt<sup>10</sup> nmr isomer shift differences in their analogous carbonyl complexes have been unsuccessful; in view of our results this is probably because of the much larger line widths associated with the spectra of those nuclei. For purposes of comparison with the present study the platinum-195 nmr data for *cis*- and *trans*-((C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub><sup>3</sup> have been included in Table I. In that complex the platinum resonance of the *trans* isomer was found 520 ppm to lower field than that of the *cis* isomer. In fact, as mentioned, this is a general trend which has been observed for all the metal halide complexes so far studied. (The isomer shift difference was as small as 40 ppm for the compound ((CH<sub>3</sub>)<sub>2</sub>Se)<sub>2</sub>PtCl<sub>2</sub>.<sup>4</sup>) However, in the present study the tungsten resonance of the *trans* isomer of (CO)<sub>4</sub>W((C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P)<sub>2</sub> is found to *higher* field than that of the *cis* isomer, opposite to that in the halide complexes.

It is perhaps surprising that the trends in the central atom chemical shifts reported in Table I appear to parallel those in the metal-phosphorus coupling constants. Thus in the platinum halide complexes the metal-phosphorus coupling is always larger in the *cis* isomer than in the *trans* isomer while just the opposite is true for the tungsten-carbonyl complexes. The trends in the coupling constant data have already been interpreted<sup>6</sup> as being consistent with the  $\pi$ -bonding model in the complexes. Whether there is a significant relation between the observed trends in the coupling constants and those in the central atom shifts might possibly be resolved by calculations. However, this study gives further evidence of the sensitivity of the metal atom shifts to the differences in chemical bonding between various types of metal complexes.

(9) W. J. Miles, B. B. Garrett, and R. J. Clark, *Inorg. Chem.*, **8**, 2817 (1969).

(10) E. A. C. Lucken, K. Noack, and D. F. William, *J. Chem. Soc. A*, 148 (1967).

## Correspondence

### Geometrical Configuration of the Product Obtained from Ammonia Photoaquation of Chloropentaamminechromium(III) Ion

Sir:

The photochemical behavior of mixed-ligand chromium(III) complexes has been extensively investigated in recent years.<sup>1</sup> The main features which emerge from the body of the available results are as follows: (i) different photoreactions may occur simultaneously (*e.g.*,

(1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970.

photoaquation reactions involving different ligands); (ii) the predominant photoreaction is not necessarily the one which occurs thermally; (iii) the photochemical behavior may be spectroscopic (*i.e.*, the type of photoreaction and the quantum yield may be wavelength dependent). In order to systematize and predict the photochemical behavior of these complexes, two *empirical* rules have been given by Adamson.<sup>2-4</sup> They

(2) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

(3) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(4) A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).