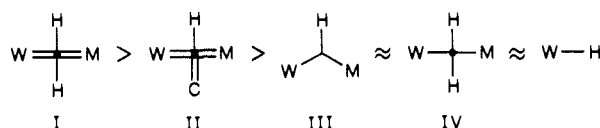


Proton NMR Spectroscopic Criteria for Elucidating the Structures of Bimetallic Organotungsten Hydrides in Solutions. Crystal and Molecular Structures of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ ¹

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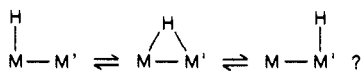
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Abstract: The crystal and molecular structures of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) have been established by a single-crystal, X-ray crystallographic analysis. The compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a = 8.542$ (1) Å, $b = 6.607$ (2) Å, $c = 5.838$ (1) Å, $\alpha = 94.64$ (2)°, $\beta = 108.06$ (1)°, and $\gamma = 98.70$ (2)°. The most chemically interesting feature of the molecular structure of the centrosymmetric dimer is the tungsten-tungsten separation of 2.9032 (9) Å which is indicative of substantial metal-metal bonding in the bridging $\text{W}_2(\mu\text{-H})_2$ unit. The ¹H NMR spectrum of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ confirms that its solid-state molecular structure persists in solutions and that it is static on the NMR time scale with respect to hydride ligand exchange. Furthermore, this spectrum indicates that for a given electronic environment in bimetallic complexes of this type $^1J_{\text{H}_{\text{terminal}}-^{183}\text{W}} \approx ^1J_{\text{H}_{\text{bridging}}-^{183}\text{W}} > ^2J_{\text{H}-^{183}\text{W}}$, the latter parameter generally being <20 Hz. Estimates of $^1J_{\text{H}_{\text{terminal}}-^{183}\text{W}}$ in various families of bimetallic organotungsten hydrides (i.e., those containing Cp_2W , $\text{CpW}(\text{CO})_3$, $\text{W}(\text{CO})_5$, and $\text{CpW}(\text{NO})_x$ ($x = 1$ or 2) groups) are obtainable from the ¹H NMR spectra of appropriate monomeric complexes. The $J_{\text{H}-^{183}\text{W}}$ evident in the ¹H NMR spectrum of a particular bimetallic tungsten hydride can then be analyzed in terms of the expected $^nJ_{\text{H}-^{183}\text{W}}$ ($n = 1$ or 2) values in order to ascertain the static or fluxional nature of the bimetallic complex, the types of fluxional processes operative if it is indeed nonrigid with respect to hydride exchange, and, on occasion, the approximate time scales involved for these processes. Within each family of complexes, the magnitude of ¹H-¹⁸³W coupling decreases in the order



and appears to reflect the valence s-electron density at the tungsten center. The bridging systems are thus best viewed as single units held together by delocalized bonding which extends over all atoms involved in the bridging system. To convey this view, the "fused" representation of W-H bonding shown for these systems is advocated.

While endeavoring to establish the molecular structures of bimetallic hydride complexes in solutions, investigators have long been plagued with ascertaining the modes of attachment of each of the hydride ligands to the metal centers.³ Specifically, they have invariably had to answer the following two questions about each complex: (1) Are the H atoms attached in a terminal or bridging fashion? and (2) Even if the physical properties of the complex in solution suggest the presence of a bridging H ligand, is this a truly static linkage or is it a time-averaged structure reflecting the occurrence of rapid fluxional processes such as



When one of the metals involved is tungsten (¹⁸³W, $I = 1/2$, natural abundance = 14.4%), the principal tool that has been employed to attempt to answer these questions is ¹H NMR spectroscopy. Arguments concerning the nature of W-H linkages in bimetallic compounds have been made on the basis of both the chemical shifts of the hydride resonances and the magnitudes of the ¹H-¹⁸³W coupling constants observed in the solution ¹H NMR spectra of these species. However, there has been a considerable degree of uncertainty on the part of various investigators as to how these NMR parameters are affected by the terminal/bridging nature

of the H ligands as well as by the other ligands present in the complex. In this paper, we present ¹H NMR data that eliminate much of this uncertainty.

We recently reported the synthesis and characterization of several organometallic hydrido nitrosyl complexes of tungsten, including the novel bimetallic compounds, $[\text{CpW}(\text{NO})\text{H}]_2$, $[\text{CpW}(\text{NO})\text{H}_2]_2$, and $[\text{CpW}(\text{NO})\text{H}\{\text{P}(\text{O}^i\text{Pr})_3\}]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).⁴ During the course of this work, it also became necessary for us to answer the two questions posed above for these dimeric species. Fortunately, our task was considerably simplified by the unique nature of one of these species, namely $[\text{CpW}(\text{NO})\text{H}]_2$. As we inferred previously⁴ and have since verified by subsequent work described in this paper, this bimetallic complex contains both bridging and terminal hydride ligands that are static. It is thus correctly represented as $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. Moreover, the distinctive ¹H NMR spectral parameters of this complex have enabled us to develop criteria with which to reinterpret numerous ¹H NMR spectra of bimetallic organotungsten hydrides reported in the literature. In so doing, we have deciphered the static or fluxional characters of a number of such species, some of whose molecular structures in solution have not been known with certainty for over 20 years. Furthermore, we have found that the magnitudes of experimentally observed ¹H-¹⁸³W coupling constants permit reasonable estimates of the types of fluxional processes operative and, on occasion, the approximate time scales involved. Finally, we have demonstrated that within certain, well-defined families of compounds the dependence of the magnitude of $^1J_{\text{H}-^{183}\text{W}}$ on the nature of the W-H link can often be rationalized in terms of straightforward bonding arguments.

(1) Organometallic Nitrosyl Chemistry. 29. For part 28, see: Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* 1986, 108, 317.

(2) (a) The University of British Columbia (b) Simon Fraser University.

(3) *Transition Metal Hydrides*; Muettterties, E. L., Ed.; Marcel Dekker: New York, 1971; and references contained therein.

(4) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* 1985, 4, 1263.

Table I. Crystal Data

formula	C ₅ H ₇ NO _W
formula wt	280.97
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i>	8.542 (1) Å
<i>b</i>	6.607 (2) Å
<i>c</i>	5.838 (1) Å
α	94.64 (2)°
β	108.06 (1)°
γ	98.70 (2)°
<i>V</i>	306.73 Å ³
<i>Z</i>	2
ρ calcd	3.042 g cm ⁻³
μ	191.3 cm ⁻¹

Table II. Data Collection and Refinement

diffractometer	Enraf-Nonius CAD4-F
radiation	Mo K α , graphite monochromator
λ of radiatn	0.70930 Å (α_1); 0.71359 Å (α_2)
scan mode	coupled ω - 2θ
scan width	(1.3 + 0.35 tan θ)° in ω
scan speed	3.30–0.82° min ⁻¹ in ω
background	scan extended by 25% on each side
2θ range	0–45°
size of crystal	0.27 × 0.42 × 0.06 mm
total no. reflctns	798
obsd reflctns ^a	753
no. variables	73
final $R_F^{b,c}$	0.032
final $R_w^{d,e}$	0.043
GOF ^{e,c}	2.01
ρ (wt scheme)	0.0004

^aReflections with $I > 2.3\sigma(I)$. ^b $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$.
^cObserved reflections only. ^d $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
^eGOF = $[\sum w(|F_o| - |F_c|)^2/(\text{no. observations} - \text{no. variables})]^{1/2}$.

We now wish to report these findings in detail. Because of the central importance of [CpW(NO)H]₂(μ -H)₂, we shall first present the results of a single-crystal X-ray crystallographic analysis of this compound.

Experimental Section

General procedures routinely employed in these laboratories have been described in detail previously.⁴ Single crystals of [CpW(NO)H]₂(μ -H)₂ suitable for X-ray crystallographic analysis were grown by slow evaporation under N₂ of a saturated CH₂Cl₂ solution of the complex at room temperature.

Crystal Structure Analysis. A single crystal of [CpW(NO)H]₂(μ -H)₂ was selected and sealed in a thin-walled glass capillary under dry N₂. X-ray photographs taken with Cu radiation confirmed that the crystal was of adequate quality. The crystal was mounted on an Enraf-Nonius CAD4-F diffractometer, and accurate cell dimensions and the orientation matrix were determined by least-squares analysis of the setting angles of 25 reflections with 29° < 2θ < 34° which were accurately centered. Crystal data are given in Table I.

The intensities of a unique data set ($h, -9 \rightarrow 9; k, 0 \rightarrow 7; l, -6 \rightarrow 6$) were collected as outlined in Table II. Two standard reflections, measured after every 100 reflections, showed intensity variations of <2% and no systematic trends. The data were thus not rescaled, but an absorption correction ($T = 0.052 - 0.333$) was applied to the data.⁵

The structure was solved by standard heavy-atom techniques which located all non-hydrogen atoms. Least-squares refinement of these atoms with anisotropic temperature factors and with the cyclopentadienyl H atoms fixed at calculated positions ($r_{C-H} = 0.95$ Å; $U_H =$ average U_{eq} of Cp C atoms) yielded $R = 0.032$. At this stage, attempts were made to locate the hydride ligands. The positions of the cyclopentadienyl and nitrosyl ligands indicated the presence of one terminal H and one bridging H per W atom. The largest peak in an inner-data difference map ($\rho_{max} = 1.5$ (2) e Å⁻³) was a diffuse band of positive electron density lying parallel to the W–W vector, and the second largest feature ($\rho_{max} = 1.0$ (2) e Å⁻³) was in the general area expected for a terminal hydride ligand. However, the interpolated peak maxima gave unreasonable distances for W–H bonds⁶ in both cases. Hydride positions were estimated by placing

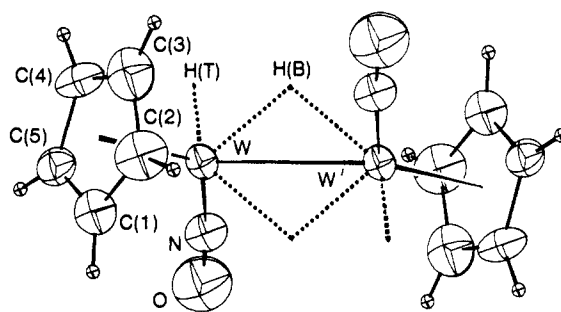


Figure 1. View of the molecular structure of [CpW(NO)H]₂(μ -H)₂. Thermal ellipsoids enclose 50% probabilities. Cyclopentadienyl H atoms are shown as spheres with arbitrarily small radii, and bonds to the hydride ligands are indicated by the broken lines. H(B) and H(T) are shown in observed (but unrefined) positions.

Table III. Atomic Coordinates and Isotropic Equivalent Thermal Parameters of the Non-Hydrogen Atoms of [CpW(NO)H]₂(μ -H)₂

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
W	0.17165 (5)	0.04140 (6)	0.16400 (8)	2.44
N	0.2563 (14)	-0.1300 (16)	0.0122 (19)	3.3
O	0.3282 (17)	-0.2363 (18)	-0.0860 (23)	6.0
C(1)	0.3499 (17)	0.3538 (19)	0.2323 (26)	3.7
C(2)	0.2024 (22)	0.4023 (20)	0.2673 (29)	4.8
C(3)	0.1876 (20)	0.3124 (24)	0.4711 (32)	4.7
C(4)	0.3226 (20)	0.2090 (24)	0.5598 (23)	4.3
C(5)	0.4247 (16)	0.2425 (21)	0.4117 (23)	3.5

^a $B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$, where U_n are the principal axes of the thermal ellipsoid in Å².

Table IV. Important Interatomic Distances (Å) and Angles (deg) for [CpW(NO)H]₂(μ -H)₂^{a,b}

W–W'	2.9032 (9)	N–O	1.218 (16)
W–N	1.753 (11)	C(1)–C(2)	1.41 (2)
W–C(1)	2.297 (12)	C(2)–C(3)	1.40 (3)
W–C(2)	2.366 (13)	C(3)–C(4)	1.41 (2)
W–C(3)	2.386 (15)	C(4)–C(5)	1.41 (2)
W–C(4)	2.352 (12)	C(5)–C(1)	1.38 (2)
W–C(5)	2.326 (12)		
W'–W–N	99.5 (4)	C(5)–C(1)–C(2)	109.3 (13)
W'–W–CP	127.8	C(1)–C(2)–C(3)	106.3 (13)
N–W–CP	126.6	C(2)–C(3)–C(4)	109.2 (14)
W–N–O	174.3 (10)	C(3)–C(4)–C(5)	106.6 (13)
		C(4)–C(5)–C(1)	108.5 (12)

^aPrimes indicate atoms related to those given in Table II by the transformation $-x, -y, -z$. ^bCP is the centroid of C(1)–C(5): (0.2974, 0.3040, 0.3884).

H(B) in the plane of W, W' and the largest peak with symmetric W–H distances of 1.88 Å and then by extending the vector between W and the second peak to give W–H(T) = 1.73 Å.⁶ As estimated, both H(B) and H(T) lie within the bounds of their broad parent peaks, but attempts to refine them were unsuccessful. They are shown in Figure 1 but have not been included in the structure factor calculations.

Refinement throughout was by full-matrix least-squares minimizing the function $\sum w(|F_o| - |F_c|)^2$. Neutral-atom scattering factors with anomalous dispersion corrections were used.⁷ Computer programs were run on a VAX 11-750 computer.⁸ A weighting scheme of the form $w = [(\sigma(F_o))^2 + pF_o^2]^{-1}$, where $\sigma(F_o)$ is from the counter statistics, was introduced and p varied so as to give the minimum variation of $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ and $\sin \theta/\lambda$. In the final cycle of refinement all shift/error ratios were <0.01. Major peaks in a final full-data difference electron-density map were located close to the W atom and all had intensities <1.9(3) e Å⁻³.

Final fractional coordinates of the non-hydrogen atoms and their isotropic equivalent thermal parameters are presented in Table III, and

(7) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(8) (a) Larson, A. C.; Gabe, E. J. *Computing in Crystallography*; Schenk, H.; Olthof-Hazekamp, R.; Van Koningsveld, H.; Bassi, G. C., Eds.; Delft University Press: Holland, 1978; p 81. (b) Larson, A. C.; Lee, F. L.; Le Page, Y.; Gabe, E. J. *The N.R.C. VAX Crystal Structure System*; Chemistry Division, National Research Council: Ottawa, Canada, 1984.

(5) De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

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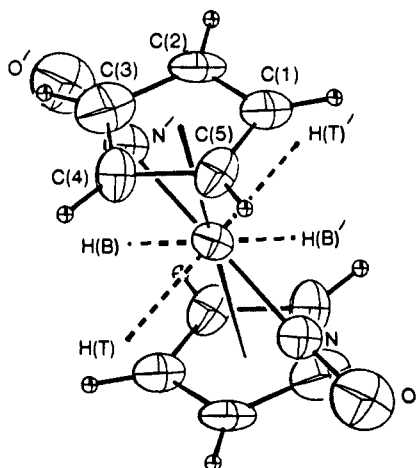


Figure 2. Perspective view of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ down the W-W axis.

interatomic distances and angles are collected in Table IV. Coordinates of the hydrogen atoms, anisotropic thermal parameters, least-squares planes, and structure factors are given in Tables V-VIII and are deposited as Supplementary Material. Figure 1 is a SNOPI diagram⁹ of the solid-state molecular structure of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ with the atoms being labeled as shown.

Results and Discussion

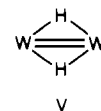
Crystal and Molecular Structures of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. The crystal structure of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ consists of the packing of discrete molecular units separated by normal intermolecular contact distances. Each molecular unit, two views of which are shown in Figures 1 and 2, consists of a centrosymmetric dimer of the form $\text{Cp}(\text{NO})(\text{H})\text{W}(\mu\text{-H})_2\text{W}(\text{H})(\text{NO})\text{Cp}$. The geometries of the cyclopentadienyl rings (Table IV) are as expected, as are the dimensions of the Cp-W linkages (Cp centroid-W = 2.019 Å).¹⁰ The WNO groups are essentially linear ($174(1)^\circ$), the short W-N (1.753 (11) Å) and long N-O (1.218 (16) Å) bond lengths indicating the existence of considerable back-bonding from the electron-rich metal centers to the nitrosyl ligands.¹¹ These features are consistent with the relatively low nitrosyl-stretching frequency (1599 cm^{-1}) evident in the IR spectrum of the compound in CH_2Cl_2 .⁴

The most chemically interesting features of the molecular structure of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ involve the W_2H_4 grouping. The tungsten-tungsten separation of 2.9032 (9) Å is less than that of the W-W single bond (3.222 (1) Å) in $[\text{CpW}(\text{CO})_3]_2$ ¹² and somewhat greater than the Mo≡Mo triple bond (2.448 (1) Å) in the most closely related species, $[\text{CpMo}(\text{CO})_2]_2$.^{13,14} Indeed, this W-W bond length resembles the 3.0162 (11) Å separation found in the valence isoelectronic anion, $[\{\text{W}(\text{CO})_4\}_2(\mu\text{-H})_2]^{2-}$,¹⁶ thereby indicating the presence of substantial metal-metal bonding in $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (vide infra). The positions of the Cp and NO groups in this complex (Figure 1) indicate the presence

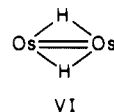
of one terminal hydride ligand on each tungsten center. Taken together with the ¹H NMR evidence⁴ and the crystallographic center of symmetry, this observation also implies the existence of two bridging hydride ligands between the tungsten atoms. These conclusions are given qualified support by the electron-density difference maps (see Experimental Section), but neither the bridging nor terminal hydride atom positions can be successfully refined. Nevertheless, the plane defined by W, H(B), W', and H'(B) lies staggered between N'O' and H(T) (Figure 2) as would be expected on the basis of simple steric considerations, thus lending additional credence to the assigned locations of the bridging hydride ligands, H(B) and H'(B). By analogy with the solid-state structure of $[\{\text{W}(\text{CO})_4\}_2(\mu\text{-H})_2]^{2-}$,¹⁶ we believe that H(B) and H'(B) are indeed equidistant from the two tungsten centers and that the bridging systems are regular.

As we reported previously, $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ exists in solutions as a mixture of two isomers, designated as A and B, the isomer ratio A:B being ~1.3:1 at 20 °C.⁴ Isomer A exhibits an AA'XX' ¹H NMR spectrum (exclusive of the ¹⁸³W satellites) whereas B displays an A₂MX pattern. Careful inspection of the solid-state structure determined (Figures 1 and 2) reveals that it will exhibit an AA'XX' ¹H NMR spectrum and is therefore isomer A. Furthermore, it is a meso complex which is the diastereomer of one of the possible molecular structures that we proposed earlier for this complex.⁴ Isomer B is thus probably a mixture of the two chiral stereoisomers of A. Finally, since a crystal of isomer A was subjected to X-ray crystallographic analysis, the possibility arises that in the solid state $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ may exist solely as this isomer and that isomer B is formed only upon dissolution of the compound in various solvents. We believe that this is an unlikely scenario since the relative proportions of A and B are the same in both CDCl_3 and C_6D_6 . Hence, it is more likely that A and B (which do not interconvert in solutions on the NMR time scale)⁴ are both formed during the initial synthesis of the complex and that it is mere chance that a crystal of A was selected for X-ray analysis.

Rationales of the Bonding in the $\text{W}_2(\mu\text{-H})_2$ Unit of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. We previously formulated the bridging system in $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ as



the formal W=W double bond being invoked so that each metal center could attain the favored 18 valence electron configuration.⁴ Identical bridging systems have also been proposed by others for the valence isoelectronic complexes $[\{\text{W}(\text{CO})_4\}_2(\mu\text{-H})_2]^{2-}$,^{16a} and $[\text{CpW}(\text{CO})_2]_2(\mu\text{-H})_2$.¹⁷ However, the only related system to have been subjected to detailed theoretical analysis to date is the



linkage in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$.¹⁸ On the basis of Fenske-Hall molecular orbital calculations and the gas-phase ultraviolet photoelectron spectrum of $(\mu\text{-H})_2\text{Os}_3(10)_{10}$, Sherwood and Hall¹⁸ concluded that the major part of the bonding in the $\text{Os}_2(\mu\text{-H})_2$ system is composed of two three-center, two-electron Os-H-Os bonds with an additional "t_{2g}-t_{2g}" bonding interaction between the metal centers. Because of the significant metal-metal bonding and hydrogen-hydrogen anti-bonding interactions implicit in such a description and our observation (vide infra) that the $\text{W}_2(\mu\text{-H})_2$ system has a considerably different effect on ¹J_{H-183W} than would be expected from its representation as primarily two three-center,

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(10) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.

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(13) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535.

(14) The solid state molecular structure of $[\text{CpW}(\text{CO})_2]_2$ has not yet been reported. However, it is quite probable that its W=W bond length is similar to the Mo≡Mo distance in its molybdenum analogue.¹⁵

(15) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

(16) (a) X-ray structure: Churchill, M. R.; Chang, S. W.-Y. *Inorg. Chem.* **1974**, *13*, 2413. (b) Neutron structure: Wei, C.-Y.; Marks, M. W.; Bau, R.; Kirtley, S. W.; Bisson, D. E.; Henderson, M. E.; Koetzle, T. F. *Ibid.* **1982**, *21*, 2556.

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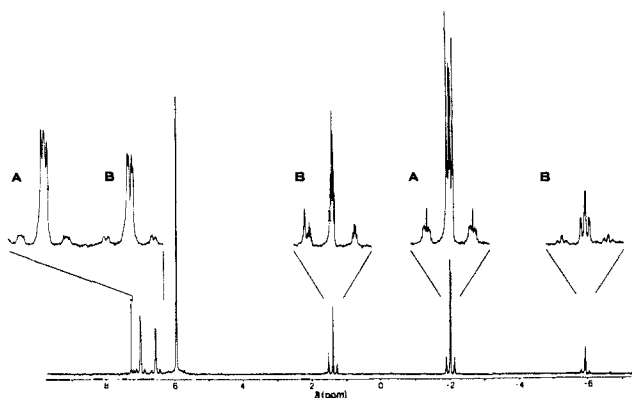
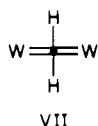


Figure 3. The 400-MHz ^1H NMR spectrum of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ in CDCl_3 at 20°C .

two-electron W–H–W bridges, we now believe that the planar $\text{W}_2(\mu\text{-H})_2$ entity is best considered as a single four-center unit. To reflect this multicenter bonding interaction, we propose to represent the bridging system in $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ as



Such an interaction results in a formal tungsten–tungsten bond order somewhat greater than one, a fact reflected by the W–W separation observed in the solid-state molecular structure of the complex (vide supra). That the $\text{W}_2(\mu\text{-H})_2$ interaction is quite strong is also suggested by the rigidity of the bimetallic complex in solutions.⁴ Finally, the VII linkage in $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ is also probably aided by the presence of the NO ligands which are known to be strong π -acids.¹¹ Like the CO groups in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$,¹⁸ the nitrosyl ligands can, in principle, remove W–W π^* antibonding electron density and thereby increase the net metal–metal bonding. Obviously, the confirmation of these inferences concerning the factors which contribute to the $\text{W}_2(\mu\text{-H})_2$ linkage must await a theoretical analysis of the intramolecular bonding in $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. This analysis will also reveal whether the VII grouping involves four electrons (as for the $\text{Os}_2(\mu\text{-H})_2$ group in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$)¹⁸ or six electrons (as required by the familiar 18 valence electron rule).

The ^1H NMR Spectrum of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. Although this spectrum of our bimetallic hydrido complex has been analyzed in some detail previously,⁴ its salient features merit being briefly reviewed at this time because of their importance with respect to the spectral features of the other bimetallic organotungsten hydrides discussed in this paper.

The ^1H NMR spectrum of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ in CDCl_3 (Figure 3) contains two sets of hydride resonances for isomer A (at δ 6.99 and -2.05) and three sets for isomer B (at δ 6.55, 1.39, and -5.94). The lowfield hydride signals for each isomer are due to the terminally bonded H(T) ligands, and the remaining hydride signals are due to the bridging H(B) ligands, as evidenced by the intensities of the ^{183}W satellites associated with each hydride signal. Observed values for $^1J_{\text{H}-^{183}\text{W}}$ and $^2J_{\text{H}-^{183}\text{W}}$ coupling constants are in the range of 90–100 Hz and 13–15 Hz, respectively (Table XIII). On the NMR time scale, both isomers A and B are stereochemically rigid, a reasonable estimate for the minimum lifetime of isomer B with respect to intramolecular H(T) and H(B) exchange being $\tau \approx 70$ ms since $\Delta\nu = ^2J_{\text{H}-\text{H}} \approx 3$ Hz.¹⁹

The ^1H NMR spectrum of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ thus indicates that for a given electronic environment in bimetallic complexes of this type, (1) the magnitude of one-bond $^1\text{H}-^{183}\text{W}$ coupling is independent of whether the hydride ligand is attached in a

Table IX. Approximate $^1\text{H}-^{183}\text{W}$ Coupling Constants Expected for Various Stereochemically Rigid Organotungsten Hydrides

family of compts	nature of W–H linkage		n	approximate expected
	conventnl reprsntn	fused ^a reprsntn		$^nJ_{\text{H}-^{183}\text{W}}$ (Hz)
Cp_2W	W–H	W–H	1	75
			1	65
			2	20
			1	100
$\text{CpW}(\text{CO})_3$	W–H	W–H	1	75
			1	40
			1	80
			1	55
$\text{W}(\text{CO})_5$	W–H	W–H	1	40
			1	55
			2	15
			1	60
$\text{CpW}(\text{NO})_2$	W–H	W–H	1	40
			1	200
$\text{CpW}(\text{NO})^b$	W–H	W–H	2	20
			1	50–90
			1	70–100
			1	55

^aThe rationale behind the use of the fused representation for the various W–H linkages is presented in the text. ^bBecause of the variety of other ligands coordinated to the $\text{CpW}(\text{NO})$ fragment, this family of compounds exhibits more variation in the expected $^nJ_{\text{H}-^{183}\text{W}}$ values.

terminal or bridging fashion; (2) one-bond $^1\text{H}-^{183}\text{W}$ coupling is greater than two-bond coupling; and (3) the resonances due to bridging hydrides appear upfield of those due to terminal hydrides. These results, particularly (1), coupled with the spectral features of appropriate monomeric tungsten hydrides, now enable us to reanalyze the ^1H NMR spectra of a number of bimetallic tungsten hydride complexes that have been reported in the literature over the years.

^1H NMR Spectroscopic Criteria for Elucidating the Structures of Bimetallic Organotungsten Hydrides in Solutions. For a W_2H spin system, the ^1H NMR spectrum should consist of an equally spaced, five-peak pattern having an integrated intensity ratio of 0.5:1.2.3:74.4:12.3:0.5 regardless of whether the system involves a static, bridged W–H–W linkage or is undergoing rapid H–W–W \rightleftharpoons W–W–H fluxionality.²⁰ The fundamental difference between the two cases is that in the static case $J_{\text{obsd}} = ^1J_{\text{H}(\text{B})-^{183}\text{W}}$ whereas in the fluxional case $J_{\text{obsd}} = 1/2 (^1J_{\text{H}(\text{T})-^{183}\text{W}} + ^2J_{\text{H}(\text{T})-^{183}\text{W}})$ as indicated in Figure 4. Analyses of heterobimetallic spin systems of the type WHM afford similar conclusions, although for these systems only a three-line ^1H NMR pattern (intensity ratio = 7.7:85.6:7.7) due to coupling with ^{183}W is expected. Reasonable estimates of the three $^1\text{H}-^{183}\text{W}$ coupling constants involved in all

(19) Calculated by employing the equation $\tau = (\sqrt{2}\pi\Delta\nu)^{-1}$, where $\Delta\nu$ is the difference in energy states of the exchanging system (e.g., J , ΔJ or $\Delta\delta$ (Hz)); see Bryant, R. G. *J. Chem. Ed.* **163**, 60, 933.

(20) Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116.

Table X. Tungsten Hydride ^1H NMR Parameters for Cp_2W Derivatives

complex	T^a ($^\circ\text{C}$)	solv	W-H interaction ^b	δ^c (ppm)	$^nJ_{\text{H}-^{183}\text{W}}$		ref
					n	J^c (Hz)	
Cp_2WH_2		C_6H_6		-12.28	1	73.2	21, 22
$[\text{Cp}_2\text{WH}_3]^+$		conc HCl		H_A , -6.44	1	47.8 ^d	21
				H_B , -6.08	1	NR	
$\text{Cp}_2\text{W}(\text{H})\text{Ph}$		C_6D_6	W-H	-11.1	1	80	23
$\text{Cp}_2\text{W}(\text{CH}_3)_2$		C_6D_6	W-CH ₃	0.24	2	6.0	24
$\text{Cp}_2\text{WH}_2\cdot\text{W}(\text{CO})_5$		THF		-15.2	1	63.0	22
$\text{Cp}_2\text{WH}_2\cdot\text{Mo}(\text{CO})_5$		THF		NR	2	19.2	
$\text{Cp}_2\text{MoH}_2\cdot\text{W}(\text{CO})_5$		THF		NR	1	65.8	22
$[(\text{CpWH})_2(\mu\text{-H})\{\mu(\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)\}]^+$		CD_3CN		-16.0 ^e	2	19.6	45
$[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Pt}(\text{PEt}_3)(\text{Ph})]^+$	-30	CD_2Cl_2		H_A , -14.1	1	99.1	26
				H_B , -17.1	1	101.1	
$[\text{Cp}_2\text{HW}(\mu\text{-H})\text{Pt}(\text{PEt}_3)_2(\text{Ph})]^+$	-20	CD_2Cl_2		-18.7 ^e			59.7
$[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Rh}(\text{PPh}_3)_2]^+$		CD_2Cl_2		-18.11 ^e			107
$[\text{CpW}(\mu, \sigma: 1\text{-}5\text{-}\eta\text{-C}_5\text{H}_4)(\mu\text{-H})_2\text{IrH}(\text{PPh}_3)_2]^+$		CD_2Cl_2		H_A , -16.41	1	92	28
				H_B , -18.28	1	~90	
				H_C , -24.55	2	NO	
$[\text{CpW}(\text{H})(\mu, \sigma: 1\text{-}5\text{-}\eta\text{-C}_5\text{H}_4)(\mu\text{-H})\text{IrH}(\text{dppe})(\text{PPh}_3)]^+$		CD_2Cl_2		-15.88 ^e			38
$\text{Cp}_2\text{WH}_2\cdot\text{AlEt}_3$		C_6H_6		-12.43	1	~72	29
$\text{Cp}_2\text{WH}_2\cdot\text{ZnCl}_2\cdot\text{DMF}$		DMF		-13.0	1	76.0	30

^a Ambient temperatures unless indicated otherwise. ^b The W-H bonding interactions are discussed in detail in the text. ^c NO = not observed (i.e., the cited paper specifically states that no ^1H - ^{183}W coupling was observed). NR = not reported (i.e., no mention whatsoever is made of this parameter). ^d This coupling constant may be too low by a factor of 2 (cf. ref 22). ^e The complex is fluxional on the NMR time scale at the indicated temperature and all hydride H's are equivalent.

these cases are obtainable by analysis of the ^1H NMR spectra of appropriate monomeric hydrido-tungsten complexes and by application of the principles derived from our analysis of the spectral features of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (vide supra). Having these estimates of $^1J_{\text{H}(\text{T})-^{183}\text{W}}$, $^1J_{\text{H}(\text{B})-^{183}\text{W}}$, and $^2J_{\text{H}(\text{T})-^{183}\text{W}}$ in hand (See Table IX), we are then in a position to judge whether a particular bimetallic organotungsten hydride is static or fluxional in solution (with respect to the exchange of H ligands between metal centers) on the NMR time scale if the appearance of its ^1H NMR spectrum does not resolve this question unambiguously. Furthermore, if the bimetallic complex is judged to be fluxional, the magnitude of $J_{\text{H}-^{183}\text{W}}$ observed enables us to make reasonable estimates of the types of fluxional processes operative and, on occasion, their approximate time scales.

The systems whose reported ^1H NMR spectra we have reanalyzed are grouped according to families in Tables X-XIII. These groupings contain most of the bimetallic tungsten hydrides and related monomeric complexes to be found in the chemical literature at present. In addition to the chemical formula of each complex and the relevant ^1H NMR data, we have also included in these listings static representations of the tungsten-hydrogen bonding interactions in each complex since they are central to many of the arguments presented in the ensuing paragraphs. These "fused" bonding representations are not, however, intended to reflect the structural dynamics of the complex in solution. In the following discussion, all coupling constants are assumed to have the same sign although, as yet, no determinations of such signs appear to have been reported.

(a) **Cp_2W Derivatives (Table X).** This family of compounds

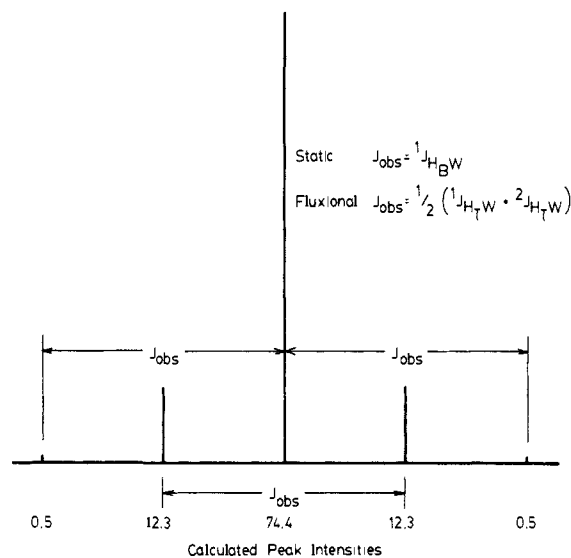










Figure 4. Expected ^1H NMR pattern for static and fluxional W-H systems, the outer lines being drawn twice their actual size for clarity.





provides the most unambiguous series of organotungsten hydrides for examination. Analysis of the ^1H NMR parameters presented in Table X for the Cp_2W derivatives which are unquestionably rigid³¹ in solution on the NMR time scale lead to the approximate $^nJ_{\text{H}-^{183}\text{W}}$ values listed in Table IX for this family of compounds.

Table XI. Tungsten Hydride ^1H NMR Parameters for $\text{CpW}(\text{CO})_3$ Derivatives

complex	T^a ($^\circ\text{C}$)	solv	W-H interaction ^b	δ^c (ppm)	$^nJ_{\text{H}-^{183}\text{W}}$		J_{obsd} (Hz)	ref
					n	J (Hz)		
$\text{CpW}(\text{CO})_3\text{H}$	-70	C_6H_{12}	W-H	-7.33	1	37.7	32	
		CDCl_3	W-H	-7.3	1	36.7 ^d	33	
<i>cis</i> - $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$	-38	C_7D_8	W-H	-8.32	1	48.0	34	
<i>trans</i> - $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$	-38	C_7D_8	W-H	-7.51	1	48.0	34	
$\text{CpW}(\text{PMe}_3)\text{H}_2$		C_6D_6	W-H	-3.95	1	42.5	35	
$\text{CpW}(\text{PMe}_3)_2(\eta^2\text{-C}_5\text{H}_8)\text{H}$		C_6D_6	W-H	-7.35	1	40	35	
$[(\text{CpW}(\text{CO})_3)_2(\mu\text{-H})]^+$		conc H_2SO_4		-24.77	1	38.6 ^e	36	
$[(\text{CpW}(\text{CO})_3)(\mu\text{-H})(\text{CpMo}(\text{CO})_3)]^+$		conc H_2SO_4		-22.88	1	38.0 ^d	36	
$[\text{CpW}(\text{CO})_2]_2(\mu\text{-H})(\mu\text{-OMe})$	-80	$(\text{CD}_3)_2\text{CO}$		-10.56	1	57.4	37	
$[(\text{CpW}(\text{CO})_2)_2(\mu\text{-H})(\mu\text{-MeCCMe})]^+$		$(\text{CD}_3)_2\text{CO}$		-18.5	1	32	38	
$[\text{CpW}(\text{CO})_2](\mu\text{-H})(\mu\text{-CHMe})[\text{Pt}(\text{PMe}_3)_2]$	-30	CD_2Cl_2		-7.77	1	53	39	
isomer ii	-30	CD_2Cl_2		-8.29	1	56	39	
$\text{Cp}(\text{CO})_2\text{WCH}(\text{PMe}_3)\text{-CHCOMe}$	-20	CD_2Cl_2		2.49	2	3.2	40	
$[(\text{Ph}_3\text{PC}_5\text{H}_4)\text{W}(\text{CO})_3\text{H}]^+$		CF_3COOH	W-H	2.01	2	4.5	41	
$[\text{CpW}(\text{CO})_2]_2(\mu\text{-H})_2$	-30	$(\text{CD}_3)_2\text{CO}$		-7.15	1	36	41	
$[(\eta^5\text{-C}_5\text{Me}_5)\text{W}(\text{CO})_2]_2(\mu\text{-H})_2$		$(\text{CD}_3)_2\text{CO}$		-13.24	1	83.1 ^e	17	
$\text{CpW}(\text{CO})_3(\text{SnMe}_3)$		C_6H_6	$(\eta^5\text{-C}_5\text{H}_5)\text{W}$ W-Sn-CH ₃	-9.30	1	82.8	17	
				NR	2	1.4	42	
				0.52	3	~0.6	42	

^a Ambient temperatures unless indicated otherwise. ^b The W-H bonding interactions are discussed in detail in the text. ^c NR = not reported (i.e., the cited paper makes no mention whatsoever of this parameter). ^d ^{183}W satellites were reported to constitute ~14% of the total integrated area of the resonance. ^e ^{183}W satellites were reported to constitute ~24% of the total integrated area of the resonance.

Table XII. Tungsten Hydride ^1H NMR Parameters for $\text{W}(\text{CO})_5$ Derivatives

complex	T^a ($^\circ\text{C}$)	solv	W-H interaction ^b	δ (ppm)	$^nJ_{\text{H}-^{183}\text{W}}$		J_{obsd} (Hz)	ref
					n	J (Hz)		
$[\text{HW}(\text{CO})_5]^-$		CD_3CN	W-H	-4.2	1	53.4	43	
$[\text{HW}(\text{CO})_4(\text{P}(\text{OMe})_3)]^-$		CD_3CN	W-H	-4.5	1	54	44	
$[\text{HW}(\text{CO})_4(\text{PMe}_3)]^-$		CD_3CN	W-H	-3.6	1	54	44	
$[\text{W}(\text{CO})_5(\mu\text{-H})]^-$		THF		-12.52	1	41.9 ^c	45	
$[\text{W}(\text{CO})_5(\mu\text{-H})\{\text{Mo}(\text{CO})_5\}]^-$		THF		-12.37	1	42.3	45	
$[\text{W}(\text{CO})_5(\mu\text{-H})\{\text{Cr}(\text{CO})_5\}]^-$		THF		-15.43	1	~40	45	
$[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3]_2(\mu\text{-H})^-$		CD_3CN		-11.9	1	45.2	46a	
$[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})\{\text{Cr}(\text{CO})_5\}]^-$		CD_3CN		-14.4	1	38.4	44	
$[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})\{\text{W}(\text{CO})_5\}]^-$		CD_3CN		-12.2	1	42, 45.6 ^d	44	
$[\text{W}(\text{CO})_3(\text{NO})\{\text{P}(\text{OMe})_3\}(\mu\text{-H})\{\text{W}(\text{CO})_5\}]^-$		CDCl_3		-12.50	1	39.5	47	
$[\text{W}(\text{CO})_5(\mu\text{-H})\{\text{AuPPH}_3\}]^-$		CD_2Cl_2		-2.69	1	46	48	
$[\text{W}(\text{CO})_5(\mu\text{-H})\{\text{Cp}_2\text{Ta}(\text{CO})\}]^-$		C_6D_6		-15.48	1	42.5	49	
$[\text{W}(\text{CO})_5\{\text{Fe}(\text{CO})_4\text{H}\}]^-$		THF	W-Fe-H	-11.8	2	15.0	50	
$[\text{W}(\text{CO})_3](\mu\text{-CO})(\mu\text{-}\eta^2\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-dppm})[\text{Re}(\text{CO})_3]$	-20	CD_2Cl_2		-3.69	1	48	51	
$[(\text{W}(\text{CO})_4)_2(\mu\text{-H})_2]^{2-}$		$(\text{CD}_3)_2\text{CO}$		-4.0	1	62 ^{c,e,f}	46	
$\text{W}(\text{CO})_5(\text{PMePh}_2)$		CH_2Cl_2	W-P-CH ₃	2.21	3	2.1	42	

^a Ambient temperatures unless indicated otherwise. ^b The W-H bonding interactions are discussed in detail in the text. ^c ^{183}W satellites were reported to constitute ~24% of the total integrated area of the resonance. ^d Two separate $^1\text{H}-^{183}\text{W}$ coupling constants are observable due to the asymmetry of the complex. ^e See text for discussion of this species. ^f Redetermined value.

These approximate coupling constants may then be utilized to ascertain the solution molecular structures of the various fluxional species in this family in the following manner.

The observed $^1\text{H}-^{183}\text{W}$ coupling constant of 45 Hz for the $[(\text{CpWH})_2(\mu\text{-H})\{\mu(\eta^5\text{-C}_5\text{H}_4-\eta^5\text{-C}_5\text{H}_4)\}]^+$ cation in CD_3CN at

ambient temperatures is consistent with the system undergoing terminal-terminal hydrogen exchange, i.e.

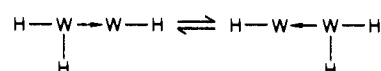
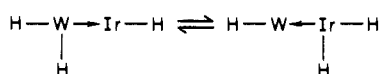


Table XIII. Tungsten Hydride ^1H NMR Parameters for $\text{CpW}(\text{NO})_x$ ($x = 2$ or 1) Derivatives

complex	T^a ($^\circ\text{C}$)	solv	W-H interaction ^b	δ (ppm)	$^n J_{\text{H}-^{183}\text{W}}$		J_{obsd} (Hz)	ref	
					n	J (Hz)			
$\text{CpW}(\text{NO})_2\text{H}$		C_6D_6	W-H	2.67	1	200^f		53	
$[\text{CpW}(\text{NO})_2(\mu\text{-H})]^+$		CD_3NO_2		-8.33			114.2 ^d	20	
$[\text{CpW}(\text{NO})_2(\mu\text{-H})][\text{CpMo}(\text{NO})_2]^+$		CD_3NO_2		-8.92			123.6 ^f	20	
$\text{CpW}(\text{NO})\text{H}[\text{P}(\text{O}^i\text{Pr})_3]$		CDCl_3	W-H	-2.04	1	54		4	
<i>trans</i> - $\text{CpW}(\text{NO})\text{H}_2[\text{P}(\text{O}^i\text{Pr})_3]$		CDCl_3	H-W-H	-1.82	1	88		4	
$[\text{CpW}(\text{NO})\text{I}]_2(\mu\text{-H})_2$		CDCl_3		-1.21 ^{d,e}	1	88.3		4	
						1	70.8		
$[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$									
isomer A		CDCl_3		H_A , 6.99	1	95 ^f		4	
					H_X , -2.05	2	~ 13		
					1	93 ^{d,g}			
isomer b		CDCl_3		H_A , 6.55	1	99 ^f		4	
					H_M , 1.39	2	~ 15		
					H_M , 1.39	1	92 ^d		
					H_X , -5.94	1	96 ^d		
$[\text{CpW}(\text{NO})[\text{P}(\text{O}^i\text{Pr})_3]_2(\mu\text{-H})_2$		C_6D_6		1.32			55 ^d	4	
$\text{Cp}(\text{NO})(\text{Cl})\text{W}[\text{CHCHC}(\text{O})\text{Me}]$	-20	CD_2Cl_2		7.64	2	8.8		54	

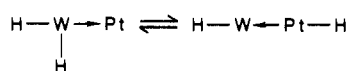
^a Ambient temperatures unless indicated otherwise. ^b The W-H bonding interactions are discussed in detail in the text. ^c Redetermined value. ^d ^{183}W satellites were reported to constitute $\sim 24\%$ of the total integrated area of the resonance. ^e The ^{183}W satellites form an AA'X system; see text for a discussion of this species. ^f ^{183}W satellites were reported to constitute $\sim 14\%$ of the total integrated area of the resonance. ^g $J_{\text{obsd}} = 1/2(^1J_{\text{H}_X-^{183}\text{W}} + ^1J_{\text{H}_X'-^{183}\text{W}})$.

for which $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = 1/6(3 \times ^1J_{\text{H}-^{183}\text{W}} + 3 \times ^2J_{\text{H}-^{183}\text{W}}) = 1/6(3 \times 65 \text{ Hz} + 3 \times 20 \text{ Hz}) = 42.5 \text{ Hz}$, a reasonable agreement. Such an exchange probably proceeds via a symmetrically bridged W-H-W intermediate, but the intermediate does not possess a significant lifetime on the NMR time scale and is thus undetectable. A similar exchange mechanism, i.e.

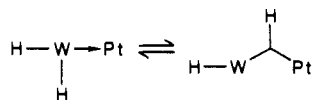


may be invoked for the $[\text{CpW}(\text{H})(\mu, \sigma: 1-5-\eta\text{-C}_5\text{H}_4)(\mu\text{-H})\text{IrH}(\text{dppe})(\text{PPh}_3)]^+$ cation in CD_2Cl_2 at room temperature to account for its observed $J_{\text{H}-^{183}\text{W}}$ of 38 Hz. For both these cases an approximate maximum lifetime for the exchanging species can be calculated to be $\tau \approx 5 \text{ ms}$, since $\Delta\nu = \Delta J \approx (65 - 20) = 45 \text{ Hz}$.¹⁹ The same type of calculation can be done for all the exchanging species discussed in this paper.

The fluxionality of the $[\text{Cp}_2\text{HW}(\mu\text{-H})\text{Pt}(\text{PEt}_3)_2(\text{Ph})]^+$ cation in CD_2Cl_2 at -20°C is clearly different from that exhibited by the complexes considered in the preceding paragraph since its $J_{\text{H}-^{183}\text{W}}$ value is 59.7 Hz. This observation may be accounted for reasonably well by invoking either of the exchange mechanisms depicted below, i.e., either

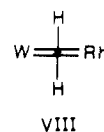


for which $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = 1/4(3 \times ^1J_{\text{H}(\text{T})-^{183}\text{W}} + ^2J_{\text{H}(\text{T})-^{183}\text{W}}) = 1/4(3 \times 65 \text{ Hz} + 20 \text{ Hz}) \approx 54 \text{ Hz}$ or

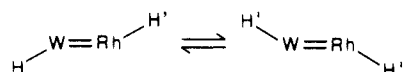


for which $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = 1/4(3 \times ^1J_{\text{H}(\text{T})-^{183}\text{W}} + ^1J_{\text{H}(\text{B})-^{183}\text{W}}) = 1/4(3 \times 65 \text{ Hz} + 65 \text{ Hz}) = 65 \text{ Hz}$ if it is assumed that $^1J_{\text{H}(\text{T})-^{183}\text{W}} \approx ^1J_{\text{H}(\text{B})-^{183}\text{W}}$ as is true for $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$. Both these types of fluxionality are also consistent with the limited variable temperature ^1H NMR data presently available for this complex.²⁶

The ^1H NMR spectrum of the $[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Rh}(\text{PPh}_3)_2]^+$ cation in CD_2Cl_2 at ambient temperatures is particularly interesting in that it indicates both hydride ligands to be equivalent (and therefore fluxional) and displays a large $J_{\text{H}-^{183}\text{W}}$ value of 107 Hz. As can be seen from Table IX and from a general inspection of Tables X-XIII, a tungsten hydride interaction that can be written (in static form) as I always shows a $^1\text{H}-^{183}\text{W}$ coupling constant considerably greater than that for its monomeric parent. The observation of such a large coupling for this



linkage immediately tells us what type of fluxionality must be occurring. If this compound were undergoing



fluxionality, then $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = 1/2(^1J_{\text{H}(\text{T})-^{183}\text{W}} + ^2J_{\text{H}(\text{T})-^{183}\text{W}}) = 1/2(100 + 20) = 60 \text{ Hz}$, a long way from the observed value. On the other hand, if the exchange process involves the two hydride ligands maintaining direct interaction with both metal centers (e.g., by spinning about the metal-metal axis), then $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = 1/2(^1J_{\text{H}(\text{B})-^{183}\text{W}} + ^1J_{\text{H}(\text{B})-^{183}\text{W}}) = 1/2(100 + 100) = 100 \text{ Hz}$, very much in accord with observation. An identical conclusion was reached by the original investigators.^{27,28}

(21) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. J. *Chem. Soc.* **1961**, 4854.

(22) Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1968**, *90*, 3276.

(23) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc. A* **1971**, 1508.

(24) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

(25) Green, M. L. H.; Otero, A. *J. Organomet. Chem.* **1980**, *202*, 421.

(26) Albinati, A.; Naegeli, R.; Togni, A.; Venanzi, L. M. *Organometallics* **1983**, *2*, 926.

(27) Alcock, N. W.; Howarth, O. W.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1160.

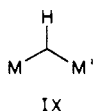
(28) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1982**, 541.

on the basis of variable temperature ^1H NMR studies.

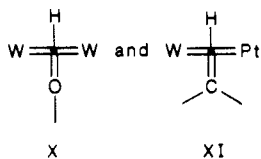
One final feature concerning the data presented in Table X merits discussion at this point. That feature is that there is very little information to be gained from the chemical shifts of the individual resonances due to the hydride ligands. The chemical shifts of the signals due to static hydrides terminally bonded to Cp_2W range from -6 to -15 ppm whereas those due to static, bridging hydrides range from -14 to -18 ppm. Although this agrees with the generally observed trend of bridging hydrides exhibiting signals upfield of those due to terminal H ligands,^{58a} the fact remains that the overlapping of these two regions means that the chemical shift of just a single signal cannot be employed with certainty to ascertain the terminal or bridging nature of a particular hydride ligand. This conclusion also applies to the other families of organotungsten hydrides yet to be considered.

(b) $\text{CpW}(\text{CO})_3$ Derivatives (Table XI). Although the magnitudes of the $^1\text{H}-^{183}\text{W}$ coupling constants observed for this family of compounds are smaller than those for the Cp_2W derivatives just considered, a similar type of analysis is nevertheless possible. The model complex, $\text{CpW}(\text{CO})_3\text{H}$, exhibits $^1J_{\text{H}-^{183}\text{W}}$ of ~ 37 Hz which increases to 48 Hz upon replacement of one of the CO ligands by the strongly basic PMe_3 . This is presumably a manifestation of the increased s-electron density at the metal center in the latter complex (vide infra). As for the Cp_2W -containing compounds, involvement of derivatives of this family in VII interactions markedly increases $^1J_{\text{H}-^{183}\text{W}}$, e.g., ~ 83 Hz for $[\text{CpW}(\text{CO})_2]_2(\mu\text{-H})_2$.

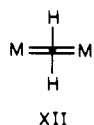
The complexes represented in Table XI as having 3-center, 2-electron



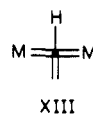
bonds fall into two categories, unsupported and supported. In the first of these, the two cations which contain such an unsupported linkage, i.e., $[\{\text{CpW}(\text{CO})_3(\mu\text{-H})\}\{\text{CpM}(\text{CO})_3\}]^+$ ($\text{M} = \text{W}$ or Mo), exhibit $^1\text{H}-^{183}\text{W}$ coupling constants similar in magnitude to those observed for the monomeric species. If these systems were fluxional, then $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = \frac{1}{2}(^1J_{\text{H}-^{183}\text{W}} + ^2J_{\text{H}-^{183}\text{W}}) = \frac{1}{2}(40 + 15) = 27.5$ Hz if it is assumed that two-bond $^1\text{H}-^{183}\text{W}$ coupling in these systems is of the same order of magnitude as that found for the Cp_2W derivatives. Hence, the observation of coupling of magnitude expected for a monomer suggests that the $[\{\text{CpW}(\text{CO})_3(\mu\text{-H})\}\{\text{CpM}(\text{CO})_3\}]^+$ cations in solution are static with respect to hydride ligand exchange. In the second category are complexes in which the formally electron-deficient III bridge is supported by another bridging ligand. The complexes in Table XI shown as containing



bridging systems exhibit $^1\text{H}-^{183}\text{W}$ coupling constants some 20 Hz greater than those for the unsupported bridge systems. However, these coupling constants are still some 25 Hz less than that observed for the VII grouping in this family. To reflect these facts, we believe that these two supported, planar bridging systems are best viewed as single, four-center groupings as the fused representations imply. This also visually suggests the similarity of these linkages to the



bridge, which Sherwood and Hall have described as being fundamentally the same, although the



interaction was shown to be weaker.¹⁸ Interestingly, this intuitively agrees with the observed trend in coupling constants. When the bridge incorporates a perpendicular acetylene to give



in $[\{\text{CpW}(\text{CO})_2(\mu\text{-H})(\mu\text{-MeCCMe})\}]^+$ for example, the $^1\text{H}-^{183}\text{W}$ coupling constant reverts to that of an unsupported bridge, suggesting that the removal of planarity from the supported bridge results in a $\text{W}-\text{H}-\text{W}$ interaction that is essentially the same as an unsupported one. Since the unsupported III linkages appear to be static in solution, we believe that the supported linkages are rigid as well.

(c) $\text{W}(\text{CO})_2$ Derivatives (Table XII). The obvious parent monomeric complex presently known in this family is $[\text{HW}(\text{C}-\text{O})_5]^-$, and it exhibits $^1J_{\text{H}-^{183}\text{W}}$ of 53.4 Hz. Surprisingly, this parameter does not change significantly upon replacement of a carbonyl ligand by a phosphine or a phosphite. Nevertheless, when these entities engage in 3-center, 2-electron III linkages, there is a decrease in the observed $^1\text{H}-^{183}\text{W}$ coupling constant to 38–45 Hz. At first glance, this would appear to be indicative of the occurrence of terminal-terminal hydrogen exchange (as for the analogous Cp_2W derivatives discussed earlier). In such a situation, $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = \frac{1}{2}(^1J_{\text{H}-^{183}\text{W}} + ^2J_{\text{H}-^{183}\text{W}}) = \frac{1}{2}(54 + 15) = 34.5$ Hz, assuming again that $^2J_{\text{H}-^{183}\text{W}}$ is of magnitude similar to that observed in the other families of hydridotungsten complexes. However, the static nature of $[\{\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})\}\{\text{W}(\text{CO})_5\}]^-$ is established unambiguously by the observation of two distinct $^1\text{H}-^{183}\text{W}$ coupling constants, a fact attributed to the presence of an asymmetric hydride bridge spanning the two tungsten centers.⁴⁴ Furthermore, variable-temperature ^1H NMR studies of $[\text{W}(\text{CO})_5(\mu\text{-H})\{\text{AuPPh}_3\}]$ have also confirmed the absence of hydride ligand exchange in this bimetallic compound.⁴⁸

(29) Storr, A.; Thomas, B. S. *Can. J. Chem.* **1971**, *49*, 2504 and references therein.

(30) Aripovskii, A. V.; Bulychev, B. M.; Krividin, L. B.; Polyakova, V. B. *Zhur. Neorg. Khim.* **1981**, *26*, 2109.

(31) This rigidity refers only to exchange of hydride ligands between various metal centers.

(32) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

(33) Faller, J. W.; Anderson, A. S.; Chen, C.-C. *J. Chem. Soc. D* **1969**, 719.

(34) (a) Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1969**, *19*, 115. (b) Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *Ibid.* **1970**, *24*, 445.

(35) Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1467.

(36) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(37) Alt, H. G.; Eichner, M. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205.

(38) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *258*, C37.

(39) Awang, M. R.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1426.

(40) Alt, H. G.; Thewalt, U. *J. Organomet. Chem.* **1984**, *268*, 235.

(41) Kotz, J. C.; Pedrotty, D. G. *J. Organomet. Chem.* **1970**, *22*, 425.

(42) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

(43) Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(44) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662.

(45) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

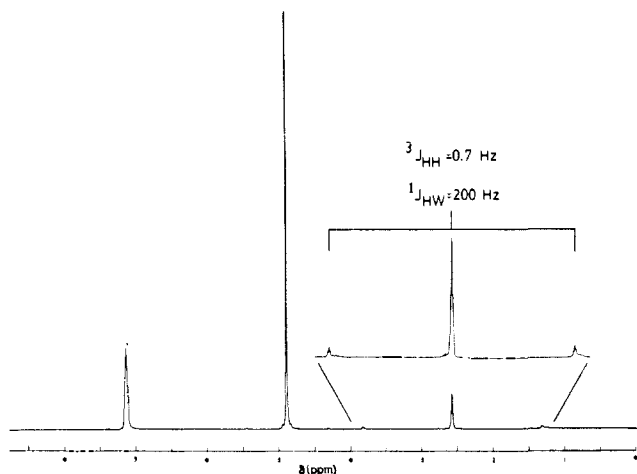


Figure 5. The 80-MHz ^1H FT NMR spectrum of $\text{CpW}(\text{NO})_2\text{H}$ in C_6D_6 .

By analogy, it seems likely that all the other analogous species listed in Table XII are also rigid. This apparent contravention of the principles that we have established in earlier families may possibly be explained by the fact that the parent in this case is a monoanion, while the parents in the other cases are all neutral molecules. The anionic nature of $[\text{HW}(\text{CO})_5]^-$ would undoubtedly result in increased s-electron density at the metal center over what would be expected in a neutral species, and this may be the cause of the unexpectedly large value of $^1J_{\text{H}-^{183}\text{W}}$. The most appropriate parent for this family may therefore be $(\eta^2\text{-H}_2)\text{W}(\text{CO})_5(\text{PCy}_3)_2$ (Cy = cyclohexyl). Unfortunately, probably because of dipolar broadening, ^{183}W satellites of the $\eta^2\text{-H}_2$ resonance were not observed.⁵⁵ If coupling to ^{183}W is ever observed, we predict that the magnitude of the coupling constant will be in the vicinity of 40–45 Hz. Because of the well-known isolobal analogy between AuPPh_3 and H ,⁵⁶ the above-mentioned $[\text{W}(\text{CO})_5](\mu\text{-H})[\text{AuPPh}_3]$ (perhaps better described as $(\eta^2\text{-HAuPPh}_3)\text{W}(\text{CO})_5$) may therefore be the best parent "monomer".

The $[\{\text{W}(\text{CO})_3\}\{\text{Fe}(\text{CO})_4\text{H}\}]^-$ anion is quite an interesting species. It was originally formulated as $[\{\text{W}(\text{CO})_3\}(\mu\text{-H})\{\text{Fe}(\text{CO})_4\}]^-$ ^{50a} but was later reformulated as having "considerable Fe–H terminal character" on the basis of its solid-state molecular structure.^{50b} In solution, some bridging character was attributed to the hydride ligand because of "the distinctive highfield position of the hydride resonance (–1.8 ppm) and a definite (albeit small, 15.0 Hz) W–H coupling".^{50b} As we have noted earlier, the chemical shift is not a particularly useful criterion to invoke in these situations. Since the observed coupling constant is of the magnitude expected for $^2J_{\text{H}-^{183}\text{W}}$, we believe that direct W–H interaction in $[\{\text{W}(\text{CO})_3\}\{\text{Fe}(\text{CO})_4\text{H}\}]^-$ is so slight as to be negligible.⁵²

Previous investigators have reported $^1J_{\text{H}-^{183}\text{W}}$ values for $[\{\text{W}(\text{CO})_4\}_2(\mu\text{-H})_2]^{2-}$ of 32 Hz^{16b} and 30.4 Hz.^{46a} These values struck us as being too low for what would be expected for a VII grouping

(46) (a) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296. (b) We have redetermined the ^1H NMR spectrum of $[\text{n-Bu}_4\text{N}][\{\text{W}(\text{CO})_4\}_2(\mu\text{-H})_2]$ in $(\text{CD}_3)_2\text{CO}$. The salt was prepared by a minor modification of the procedure reported by Churchill, M. R.; Chang, S. W.-Y.; Berch, M. L.; Davison, A. *J. Chem. Soc., Chem. Commun.* **1973**, 691.

(47) Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey, B. R.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4491.

(48) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2497.

(49) Leblanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.

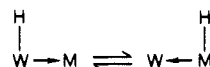
(50) (a) Arndt, L.; Delord, T.; Darenbourg, M. Y. *J. Am. Chem. Soc.* **1984**, *106*, 456. (b) Tooley, P. A.; Arndt, L. W.; Darenbourg, M. Y. *Ibid.* **1985**, *107*, 2422.

(51) Jeffery, J. C.; Orpen, A. G.; Robinson, W. T.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 396.

(52) The original investigators of this system have also recently adopted this view: (a) Arndt, L. W.; Darenbourg, M. Y.; Fackler, J. P.; Lusk, R. J.; Marler, D. O.; Youngdahl, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7218. (b) Arndt, L. W.; Darenbourg, M. Y.; Delord, T.; Bancroft, B. T. *Ibid.* **1986**, *108*, 2617. (c) See, also: Halpin, C. F.; Hall, M. B. *Ibid.* **1986**, *108*, 1695.

(vide supra). Consequently, we have redetermined this parameter and have found it to be 62 Hz^{46b} (i.e., twice the published value), a magnitude more in line with the trends in ^1H – ^{183}W coupling constants found for the other families of organotungsten hydrides (Table IX).

(d) $\text{CpW}(\text{NO})_x$ ($x = 2$ or 1) Derivatives (Table XIII). These compounds may conveniently be divided into dinitrosyl and mononitrosyl species. Contrary to the original report,^{53a} the ^1H NMR spectrum of the parent dinitrosyl hydride, $\text{CpW}(\text{NO})_2\text{H}$, (Figure 5) exhibits $^1J_{\text{H}-^{183}\text{W}}$ of 200 Hz,^{53b} by far the largest value yet observed for this parameter. On the other hand, the binuclear cations $[\{\text{CpW}(\text{NO})_2\}(\mu\text{-H})\{\text{CpM}(\text{NO})_2\}]^+$ ($\text{M} = \text{Mo}$ or W) exhibit couplings approximately one-half that of the parent monomer. This fact immediately implies the occurrence of terminal–terminal H exchange in the bimetallic systems, i.e.,

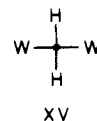


for which $J_{\text{H}-^{183}\text{W}}(\text{predicted}) = \frac{1}{2}(^1J_{\text{H}-^{183}\text{W}} + ^2J_{\text{H}-^{183}\text{W}}) = \frac{1}{2}(200 + 15) = 107.5$ Hz, a value not far from those observed. A reasonable estimate for the minimum lifetime of each isomer containing a terminal M–H bond is $\tau \approx 1.2$ ms, since $\Delta\nu = \Delta J \approx 185$ Hz.¹⁹

The monomeric mononitrosyl compounds listed in Table XIII display considerably smaller ^1H – ^{183}W coupling constants. Nevertheless, these values are larger than those found for the analogous $\text{CpW}(\text{CO})_3\text{H}$ derivatives (Table XI). The fact that *trans*- $\text{CpW}(\text{NO})\text{H}_2\{\text{P}(\text{O}^i\text{Pr})_3\}$ exhibits a larger coupling than $\text{CpW}(\text{NO})\text{H}\{\text{P}(\text{O}^i\text{Pr})_3\}$ is again probably a manifestation of the greater s-electron density at the metal center of the former compound. This inference is consistent with the electronic changes expected when a terminal H ligand is formally replaced by the more electronegative I ligand.

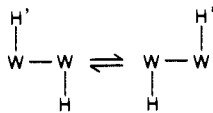
The ^1H NMR spectrum of $[\text{CpW}(\text{NO})\text{IH}]_2$ unequivocally established that the complex is rigid in solution on the NMR time scale and that the hydride ligands are bridging. On the basis of this and other chemical evidence, we previously⁴ formulated this complex as $[\text{CpW}(\text{NO})]_2(\mu\text{-H})_2(\mu\text{-I})_2$. Our greater understanding of ^1H – ^{183}W coupling constants now leads us to reformulate this bimetallic compound as $[\text{CpW}(\text{NO})\text{I}]_2(\mu\text{-H})_2$ with a molecular structure closely akin to that of $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (Figure 1) and containing the familiar VII bridging grouping. Our reasons for doing so are twofold. Firstly, the $^1J_{\text{H}-^{183}\text{W}}$ values exhibited by $[\text{CpW}(\text{NO})\text{I}]_2(\mu\text{-H})_2$ are only slightly less than those displayed by $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$, and the slight decrease is as expected for formal I for H substitution (vide supra). Secondly, involvement of a $\text{CpW}(\text{NO})\text{IH}$ moiety in a VII interaction would be expected to result in increased ^1H – ^{183}W coupling constants relative to those exhibited by related monomeric species, and just such an increase is observed experimentally. Nevertheless, a single-crystal X-ray crystallographic analysis of $[\text{CpW}(\text{NO})\text{I}]_2(\mu\text{-H})_2$ would be desirable to confirm the true nature of its bridging system. Regrettably, the thermal instability of the complex in solution has so far precluded its isolation as crystals suitable for such analysis.

Our previous work with $[\text{CpW}(\text{NO})\{\text{P}(\text{O}^i\text{Pr})_3\}]_2(\mu\text{-H})_2$, which contains a



bridging system, established that in solution the two hydride ligands are exchanging rapidly on the NMR time scale so as to maintain, on average, a *trans* orientation with respect to both phosphite phosphorus atoms.⁴ If they were undergoing rapid terminal–terminal exchange, i.e.

(53) (a) Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250. (b) Redetermined 80-MHz ^1H FT NMR spectrum of $\text{CpW}(\text{NO})_2\text{H}$ (C_6D_6): δ 4.96 (d, 5 H, C_5H_5 , $^3J_{\text{H}-\text{H}} = 0.7$ Hz), 2.67 (sextet, 1 H, W-H , $^1J_{\text{H}-^{183}\text{W}} = 200$ Hz).



then the observed $^1\text{H}-^{183}\text{W}$ coupling constant of 55 Hz would imply $J_{\text{obsd}} = 1/2(^1J_{\text{H}-^{183}\text{W}} + ^2J_{\text{H}-^{183}\text{W}})$, $\therefore 55 \text{ Hz} = 1/2(^1J_{\text{H}-^{183}\text{W}} + 15 \text{ Hz})$, $\therefore ^1J_{\text{H}-^{183}\text{W}} = 95 \text{ Hz}$. This value is higher than those usually found for terminal W-H linkages in this class of compounds (Table IX). Consequently, it is likely that the nonrigidity of $[\text{CpW}(\text{NO})\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\mu\text{-H})_2]$ involves the two bridging hydride ligands undergoing exchange while maintaining direct interaction with both tungsten atoms in a manner analogous to that invoked for $[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Rh}(\text{PPh}_3)_2]^+$ (vide supra).

As noted in passing above, all the nitrosyl complexes listed in Table XIII exhibit $^1\text{H}-^{183}\text{W}$ couplings that are considerably greater than those displayed by analogous carbonyl compounds (Table XI). This feature is probably a manifestation of the fact that NO ligands are much stronger donors of σ electron density than are CO groups.⁵⁷ Such donation by the nitrosyls would be expected to increase the tungsten center's valence s-electron density and, consequently, $J_{\text{H}-^{183}\text{W}}$. In addition to their effect on the $^1\text{H}-^{183}\text{W}$ coupling constants, the NO groups also influence the chemical shifts of the resonances due to the hydride ligands. These signals range from +7 to -2 ppm for static, terminal hydrides and from +1.4 to -6 ppm for static, bridged hydrides, i.e., substantially downfield of those exhibited by most of the other organotungsten hydrides considered in this study. While the general trend of bridging hydride signals being upfield of terminal hydride signals⁵⁸ also holds for the hydrido nitrosyl complexes, the fact remains that the chemical shift of a single hydride resonance per se is not a terribly useful indicator of the bridging or terminal nature of the particular H ligand.⁵⁹

Justification for Using "Fused" Representations of the Tungsten-Hydrogen Bonding. Although the factors that influence the magnitudes of one-bond, metal-hydrogen coupling constants have not as yet been delineated, more general analyses of one-bond, spin-spin couplings have been published.⁶¹ It has been shown that such couplings are dominated by the Fermi contact term which, in turn, is dominated by the polarizability of the bond (i.e., the amount of s character in the linkage) and the valence s-electron densities at the coupled nuclei. In the case of transition-metal-phosphorus coupling, it has been suggested that the polarizability factor predominates.⁶² If similar factors govern one-bond, tungsten-hydrogen couplings, then the most important contributor to the magnitude of $^1J_{\text{H}-^{183}\text{W}}$ should be the amount of s-electron density contributed by tungsten to the W-H linkage since the hydride ligand can only contribute s-character to this bond. In other words, increases in the tungsten's valence s-electron densities should be reflected in increased magnitudes of $^1J_{\text{H}-^{183}\text{W}}$. Indeed, just such a trend is observed for the organotungsten hydrides considered during this study, as has already been noted for particular classes of compounds in the preceding paragraphs.

(54) Alt, H. G.; Hayen, H. I.; Klein, H.-P.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 809.

(55) Kubas, G. L.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J.; *J. Am. Chem. Soc.* **1984**, *106*, 451.

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(58) (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

(b) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

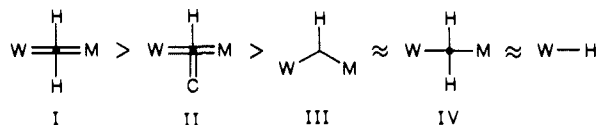
(59) A striking illustration of this fact is provided by the recent report⁶⁰ of $\text{W}_2\text{H}(\text{O}-i\text{-Pr})_4(\mu\text{-C}_6\text{Me}_6)(\mu\text{-CPh})$, a ditungsten complex containing a static, terminal W-H group which exhibits a ^1H NMR resonance 20.42 ppm downfield of Me_4Si . This resonance is approximately 10 ppm downfield from the $\text{W}_2(\mu\text{-H})$ hydride signals exhibited by alkoxides of the type $[\text{W}_2(\mu\text{-H})(\text{O}-i\text{-Pr})_7]_2$ and $\text{NaW}_2(\mu\text{-H})(\text{O}-i\text{-Pr})_2$ diglyme.

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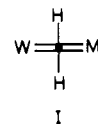
(61) (a) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1. (b) Kowalewski, J. *Annu. Rev. Nucl. Magn. Reson. Spectrosc.* **1982**, *12*, 82.

(62) Pregosin, P. S.; Kunz, R. W. In *NMR, Basic Principles and Progress*; Diehl, P.; Fluck, E.; Kosfeld, R., Eds.; Springer-Verlag: New York, 1979; Vol. 16.

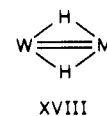
Inspection of the data summarized in Table IX reveals that the magnitudes of $^1J_{\text{H}-^{183}\text{W}}$ depend on the nature of the tungsten-hydrogen interaction and decrease in the order



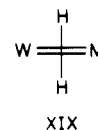
within each family of compounds. The fact that the



bridging system exhibits the largest $^1\text{H}-^{183}\text{W}$ coupling is indicative of it possessing the greatest s-character of all the W-H interactions considered. More importantly, this fact also indicates that such I groupings do not simply involve two separate three-center, two-electron III groups as is implied by their representation as



Consequently, we believe that they are best viewed as constituting a single, four-center unit and have thus represented this interaction as I. [We considered, but rejected, representing these W-H interactions as



since this latter representation could be viewed as involving dihydrogen as a ligand,^{55,63} a connotation that we wanted to avoid.] For similar reasons, we have also employed "fused" representations of II and IV bonding interactions throughout this paper. The advantage of this notation is that each line from an atom in a "fused" representation represents one orbital contributed by that atom to the overall bonding interaction just as in the familiar three-center, three-orbital III interaction. Hence, I indicates a four-center, six-orbital interaction, IV a four-center, four-orbital interaction, and so on. However, the number of electrons involved in each delocalized bonding interaction cannot be directly inferred in all cases. While the III interaction is believed to involve two electrons, the situation regarding I, II, and IV interactions is not so clear-cut. As we outlined earlier in this paper, the I grouping can, in principle, involve from four to six electrons, and similar uncertainties arise with the II and IV systems. Consequently, a proper description of the bonding in these three latter groups must await a detailed theoretical analysis of the intramolecular bonding in representative complexes which contain such groups.

Summary

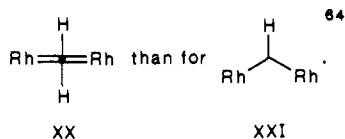
The ^1H NMR spectrum of the unique compound, $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (Figure 3) confirms that its solid-state molecular structure persists in solutions and that it is static on the NMR time scale with respect to the exchange of H ligands between the metal centers. Furthermore, this spectrum indicates that for a given electronic environment in bimetallic complexes of this type $^1J_{\text{H}_{\text{terminal}}-^{183}\text{W}} \approx ^1J_{\text{H}_{\text{bridging}}-^{183}\text{W}} > ^2J_{\text{H}-^{183}\text{W}}$, the latter parameter typically being in the range of 15–20 Hz. Estimates of $^1J_{\text{H}_{\text{terminal}}-^{183}\text{W}}$ (and hence $^1J_{\text{H}_{\text{bridging}}-^{183}\text{W}}$) in various families of bimetallic organotungsten hydrides are obtainable from the ^1H NMR spectra of appropriate monomeric complexes. Comparison of these estimates of $^nJ_{\text{H}-^{183}\text{W}}$ ($n = 1$ or 2) (Table IX) with the $^1\text{H}-^{183}\text{W}$ coupling

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exhibited by a particular bimetallic tungsten hydride then permits the assessment of the static or fluxional nature of the complex if the appearance of its ^1H NMR spectrum does not unambiguously establish its nature (e.g., by the intensities of the ^{183}W satellites associated with each signal). If the complex is indeed fluxional with respect to hydride ligand exchange, the $J_{\text{H}-^{183}\text{W}}$ evident in its ^1H NMR spectrum may be analyzed in terms of the expected $^2J_{\text{H}-^{183}\text{W}}$ values in static isomers to gain some insight into the types of fluxional processes operative. Inferences concerning fluxionality drawn in this manner are usually consistent with the exchange mechanisms indicated by variable temperature ^1H NMR studies. Although it is true that bridging hydride ligands show chemical shifts in areas upfield of those due to terminal ones, the fact that these regions always overlap even in any one particular family means that a particular resonance cannot be used diagnostically to determine the terminal or bridging nature of a particular hydride ligand in a bimetallic organotungsten complex.

The magnitudes of $^1\text{H}-^{183}\text{W}$ couplings appear to be influenced primarily by the magnitudes of the valence s-electron densities at the tungsten centers. Within a given family of bimetallic tungsten hydrides, these couplings decrease in the order $\text{I} > \text{II} > \text{III} \approx \text{IV} \approx \text{W} - \text{H}$. This fact suggests that the four groupings in the above series which contain bridging hydride ligands are best viewed as single units held together by delocalized bonding which extends over all atoms involved in the bridging system. To convey this view, we advocate the use of the "fused" representations of the tungsten-hydrogen bonding in these bridging systems as shown. Finally, we note that similar trends appear to exist for the coupling of hydrides to other transition-metal centers e.g., $^1J_{\text{H}-^{103}\text{Rh}}$ is greater for



and hence analyses of the ^1H NMR spectra of other bimetallic hydrides in a manner identical with that outlined in this paper may well prove to be quite fruitful.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and to the University

of British Columbia for the award of a graduate fellowship to J.T.M. We also thank Professor M. B. Hall for valuable discussions.

Registry No. Cp_2WH_2 , 1271-33-6; $[\text{Cp}_2\text{WH}_3]^+$, 51263-09-3; $\text{Cp}_2\text{W}(\text{H})\text{Ph}$, 11077-71-7; $\text{Cp}_2\text{W}(\text{CH}_3)_2$, 39333-53-4; $\text{Cp}_2\text{WH}_2\text{W}(\text{CO})_5$, 104780-32-7; $\text{Cp}_2\text{WH}_2\text{Mo}(\text{CO})_5$, 104780-33-8; $\text{Cp}_2\text{MoH}_2\text{W}(\text{CO})_5$, 104780-34-9; $[(\text{CpWH})_2(\mu\text{-H})\{\mu(\eta^2\text{-C}_5\text{H}_4\text{-}\eta^2\text{-C}_5\text{H}_4)\}]^+$, 76857-70-0; $[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Pt}(\text{PEt}_3)(\text{Ph})]^+$, 85762-71-6; $[\text{Cp}_2\text{HW}(\mu\text{-H})\text{Pt}(\text{PEt}_3)_2(\text{Ph})]^+$, 85762-69-2; $[\text{Cp}_2\text{W}(\mu\text{-H})_2\text{Rh}(\text{PPh}_3)_2]^+$, 73413-09-9; $[\text{CpW}(\mu\text{-}\sigma\text{-}1\text{-}5\text{-}\eta\text{-C}_6\text{H}_4)(\mu\text{-H})\text{IrH}(\text{dppe})(\text{PPh}_3)]^+$, 83221-85-6; $[\text{CpW}(\mu\text{-}\sigma\text{-}1\text{-}5\text{-}\eta\text{-C}_6\text{H}_4)(\mu\text{-H})_2\text{IrH}(\text{PPh}_3)_2]^+$, 83214-92-0; $\text{Cp}_2\text{WH}_2\text{AlEt}_3$, 11084-59-6; $\text{Cp}_2\text{WH}_2\text{ZnCl}_2$, 79736-32-6; $\text{CpW}(\text{CO})_3\text{H}$, 12128-26-6; *cis*- $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$, 31811-36-6; *trans*- $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$, 31852-08-1; $\text{CpW}(\text{PMe}_3)_5$, 95029-85-9; $\text{CpW}(\text{PMe}_3)_2(\eta^2\text{-C}_5\text{H}_8)\text{H}$, 95029-87-1; $[(\text{CpW}(\text{CO})_2)_2(\mu\text{-H})]^+$, 68868-71-3; $[(\text{CpW}(\text{CO})_3)(\mu\text{-H})(\text{CpMo}(\text{CO})_3)]^+$, 68893-52-7; $[\text{CpW}(\text{CO})_2)_2(\mu\text{-H})(\mu\text{-OMe})$, 81628-79-7; $[(\text{CpW}(\text{CO})_2)_2(\mu\text{-H})(\mu\text{-MeCCMe})]^+$, 89199-40-6; $[\text{CpW}(\text{CO})_2](\mu\text{-H})(\mu\text{-CHMe})[\text{Pt}(\text{PMe}_3)_2]$ (isomer 1), 104870-90-8; $[\text{CpW}(\text{CO})_2](\mu\text{-H})(\mu\text{-CHMe})[\text{Pt}(\text{PMe}_3)_2]$ (isomer 2), 104870-91-9; $\text{Cp}(\text{CO})_2\text{WCH}(\text{PMe}_3)\text{CHCOMe}$, 92416-46-1; $[(\text{Ph}_3\text{PC}_5\text{H}_4)\text{W}(\text{CO})_3\text{H}]^+$, 47663-26-3; $[\text{CpW}(\text{CO})_2)_2(\mu\text{-H})_2$, 86307-87-1; $[(\eta^2\text{-C}_6\text{Me}_5)\text{W}(\text{CO})_2)_2(\mu\text{-H})_2$, 86307-89-3; $\text{CpW}(\text{CO})_3(\text{SnMe}_3)$, 12093-29-7; $[\text{HW}(\text{CO})_5]^+$, 7727-36-2; $[\text{HW}(\text{CO})_4\text{IP}(\text{OMe})_3]^-$, 91839-87-1; $[\text{HW}(\text{CO})_4(\text{PMe}_3)]^-$, 82963-31-3; $[\text{W}(\text{CO})_5]_2(\mu\text{-H})^-$, 73740-64-4; $[\text{W}(\text{CO})_5(\mu\text{-H})[\text{Mo}(\text{CO})_5]]^-$, 103310-31-2; $[\text{W}(\text{CO})_5(\mu\text{-H})[\text{Cr}(\text{CO})_5]]^-$, 77110-95-3; $[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})]^-$, 84850-83-9; $[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})[\text{Cr}(\text{CO})_5]]^-$, 82963-40-4; $[\text{W}(\text{CO})_4\text{P}(\text{OMe})_3(\mu\text{-H})[\text{W}(\text{CO})_5]]^-$, 82963-42-6; $[\text{W}(\text{CO})_3(\text{NO})\text{IP}(\text{OMe})_3(\mu\text{-H})[\text{W}(\text{CO})_5]]^-$, 60219-55-8; $[\text{W}(\text{CO})_5(\mu\text{-H})[\text{AuPPh}_3]]^-$, 83601-25-6; $[\text{W}(\text{CO})_5(\mu\text{-H})[\text{Cp}_2\text{Ta}(\text{CO})]]^-$, 85601-17-8; $[\text{W}(\text{CO})_5\{\text{Fe}(\text{CO})_4\text{H}\}]^-$, 101032-82-0; $[\text{W}(\text{CO})_3(\mu\text{-Co})(\mu\text{-C}^2\text{-CH}_2\text{C}_6\text{H}_4\text{Me-}4)(\mu\text{-dppm})[\text{Re}(\text{CO})_3]$, 91864-59-4; $[\text{W}(\text{CO})_4)_2(\mu\text{-H})_2]^{2-}$, 52032-33-4; $\text{W}(\text{CO})_5[\text{PMePh}_2]$, 18534-36-6; $\text{CpW}(\text{NO})_2\text{H}$, 69532-01-0; $[(\text{CpW}(\text{NO})_2)_2(\mu\text{-H})]^+$, 79329-49-0; $[(\text{CpW}(\text{NO})_2)(\mu\text{-H})\text{CpMo}(\text{NO})_2]^+$, 79329-52-5; *trans*- $\text{CpW}(\text{NO})\text{H}_2[\text{P}(\text{O}^i\text{Pr})_3]$, 96429-81-1; $[\text{CpW}(\text{NO})\text{I}]_2(\mu\text{-H})_2$, 104780-35-0; $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (isomer 1), 104870-92-0; $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (isomer 2), 104870-93-1; $[\text{CpW}(\text{NO})\text{IP}(\text{O}^i\text{Pr})_3]_2(\mu\text{-H})_2$, 96444-57-4; $\text{Cp}(\text{NO})(\text{Cl})\text{W}[\text{CHCHC}(\text{O})\text{Me}]$, 92184-47-9; $\text{CpW}(\text{NO})\text{IH}[\text{P}(\text{O}^i\text{Pr})_3]$, 73199-23-2; W , 7440-33-7.

Supplementary Material Available: Tabulations of the atomic coordinates of the hydrogen atoms, the thermal parameters, and the weighted least-squares plane of a cyclopentadienyl ligand (3 pages); observed and calculated structure factors for $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ (6 pages). Ordering information is given on any current masthead page.

The Cyclopropylmethyl Free Radical Clock. Calibration for the Range 30–89 °C

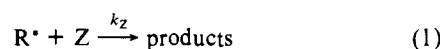
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Abstract: The Arrhenius equation for the ring-opening isomerization of cyclopropylmethyl radicals (R^*) to 3-buten-1-yl radicals (R'^*) for the 303–362 K temperature range was determined by thermolysis of (cyclopropylmethyl)(1-hydroxy-1-methylethyl)diazene in the presence of excess 1,1,3,3-tetramethylisindolin-2-yloxy (Y^*). Rate constants for coupling of R^* with Y^* were assumed to be proportional to diffusion-controlled rate constants (k_d) and rate constants (k_i) for the isomerization were calculated from k_d (corrected) and product ratios ($\text{RY}/\text{R}'\text{Y}$). The temperature dependence of k_i , given by $\log(k_i/\text{s}^{-1}) = (13.9 \pm 0.4) - (7.6 \pm 0.2)/\theta$, is significantly different from that determined by kinetic EPR spectroscopy in the temperature range 128–153 K; $\log(k_i/\text{s}^{-1}) = (11.34 \pm 0.85) - (5.94 \pm 0.57)/\theta$, where $\theta = 2.3RT \text{ kcal mol}^{-1}$.

Rate constants for radical-molecule reactions, eq 1, can be estimated conveniently by means of competition kinetics, provided that R^* undergoes a competitive reaction, often a unimolecular isomerization, eq 2, for which the rate constant is known.¹ Radical

processes for which the absolute rate constants have been de-



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