crystals in the trap at −125 °C. SF_5–OCN can be separated by gas chromatography on a 4-m squalan chromosorb column at 45 °C, yielding 0.2 g of SF_5–OCN (10%). The purified SF_5–OCN contains less than 3% of Cl–CN and melts at −82 °C. The ^{19}F NMR spectrum exhibits an ab_4 pattern with $\delta_a = 51.7$, $\delta_b = 66.5$, and $J_{ab} = 147$ Hz. The ^{14}N NMR spectrum consist of one signal at $\delta = -194$ with $\upsilon_{1/2} = 57$ Hz. The IR spectrum (gas, 10 mbar) shows absorption bands at 2283 (m), 1111 (m), 944 (vs), 879 (vs), 736 (w), and 607 (s) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 2284 (vs, p), 1118 (w, dp), 945 (w, p), 875 (w, p), 736 (vs, p), 643 (m, p), and 605 (w, p) cm^{-1}. The mass spectrum (m/e) indicates the presence of the following ions: $(M - F)^+$, 6.3; SF_5^+, 89.6; SF_4^+, 15.6; SF_3^+, 100; $CNOF^+$, 59.4.

Electron Diffraction. A sample of SF_5–OCN was transported to Tübingen, West Germany, in liquid nitrogen. The scattering intensities were recorded with a Balzers gas diffractograph[33] at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The sample reservoir was kept at −50 °C and inlet system and nozzle were at room temperature. The camera pressure did not exceed 2×10^{-5} mbar during the experiment. Two photographic plates for each camera distance were analyzed by the usual procedures,[34] and the averaged molecular intensities for the scattering ranges 1.4–17 and 8–35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figure 2.[35]

Acknowledgment. We are grateful for financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of electron diffraction scattering intensities (2 pages). Ordering information is given on any current masthead page.

---

(33) Oberhammer, H. In *Molecular Structures by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(34) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

(35) Numerical values for the total scattering intensities are included as supplementary material.

Contribution from the Department of Chemistry
Yale University, New Haven, Connecticut 06511

A ^{183}W NMR Study of Mononuclear Tungsten(VI) Methyl Complexes Containing Terminal Oxo, Sulfido, and Imido Ligands

Yinong Ma, Peter Demou, and J. W. Faller*

Received May 25, 1990

The ^{183}W chemical shifts of a number of organometallic oxo–, sulfido–, and imido–tungsten(VI) complexes have been measured by indirect detection using $^1H\{^{183}W\}$ double-resonance and $^1H\{^1H,^{183}W\}$ triple-resonance techniques. The shielding trends within a series of ligands, including O^{2-}, S^{2-}, PhN^{2-}, Cl^-, Br^-, $\eta^2\text{-}O_2^{2-}$, and $\eta^2\text{-}S_2^{2-}$, are discussed with respect to ligand polarizability and bond multiplicity. The tungsten(VI) nuclei become more deshielded with increasing ligand polarizability and bond multiplicity. The ^{183}W chemical shifts of $Cp^*W({=}O)X_2Me$ complexes show an inverse halogen dependence, as expected from relative polarizability arguments.

Introduction

In our exploration of the chemistry of high oxidation state tungsten and molybdenum organometallics, ^1H NMR spectroscopy proved to be of limited value in some situations. Examination of compounds such as $Cp^*W({=}O)(\eta^2\text{-}O_2)Me$ and its sulfur analogues by ^1H NMR provides only two singlets, which are indicative, but not unequivocally characteristic, of a particular set of ligands. We anticipated that NMR data on the metal nuclei would provide better characterization of new complexes. In order to evaluate the diagnostic utility of ^{183}W chemical shifts for structural determination in these systems, we have compiled the data for a selected group of complexes. We have examined the relative importance of factors contributing to the magnetic shielding of tungsten nuclei in these complexes so as to provide some useful criteria for predicting chemical shifts for a given set of ligands.

Owing to the extremely low sensitivity of ^{183}W, the ^{183}W chemical shifts reported have been limited to a very small number.[1] In the past, the low NMR sensitivity of ^{183}W to detection had been overcome by employing double-resonance and triple-resonance techniques provided that resolvable coupling existed between ^{183}W and other relatively more sensitive nuclei such as ^1H, ^{19}F, and ^{31}P.[2-6] Although detection has been made easier in recent years with the introduction of more sensitive spectrometers and modern FT pulse experiments,[7] the more traditional techniques still remain useful, particularly for small quantities. In our preparation and characterization of high oxidation state organometallic tungsten(VI) complexes, we have noted that W(VI) complexes with alkyl ligands have fairly large couplings between ^{183}W and the α-H on the alkyl groups; values of $^2J_{W-H}$ vary from 4 to 11 Hz.[8] These relatively large $^2J_{W-H}$ have afforded ready access to the ^{183}W chemical shifts in these complexes upon application of double-resonance techniques. The variations in ^{183}W chemical shifts effected by ligand substitution will be presented in the context of providing some guidelines for interpretation of the observed shifts.

Experimental Section

Preparations of all the complexes used in this work except for $Cp^*W({=}O)({=}NPh)Me$ and $Cp^*W({=}O)Br_2Me$ have been described elsewhere.[8,9] The NMR sample of the complex $Cp^*W({=}O)({=}NPh)Me$ was prepared in situ by mixing $Cp^*W({=}O)Cl_2Me$ and a slight excess of aniline. The compound is extremely moisture sensitive, as is the case with most of the known imido complexes. As a result, no attempt at isolation was made. The presence of the imido complex was verified by mass spectroscopy of the sample mixture, which contained both the product $Cp^*W({=}O)({=}NPh)Me$ and $Cp^*W({=}O)_2Me$, the latter resulting from partial hydrolysis. The $Cp^*W({=}O)Br_2Me$ complex was prepared by stirring a diethyl ether solution of $Cp^*W({=}O)_2Me$ with an excess of Me_3SiBr overnight, which resulted in a yellow crystalline precipitate. The procedure is essentially similar to the preparation of the chloride analogue described in the literature.[9]

The ^{183}W resonance frequencies were obtained on a Bruker WM-500 spectrometer using $^1H\{^{183}W\}$ double resonance for most compounds and triple resonance in the case of $CpW({=}O)Me_3$, where ^1H decoupling of

---

(1) Minelli, M.; Enemark, J.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

(2) Klein, M. P.; Happe, J. *Bull. Am. Phys. Soc.* **1961**, *6*, 104.

(3) McFarlane, W.; Noble, A.; Winfield, J. *J. Chem. Soc. A* **1971**, 948.

(4) Green, P. J.; Brown, T. H. *Inorg. Chem.* **1971**, *10*, 206.

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

(6) Andrew, G. T.; Colquhoun, I. J.; McFarlane, W.; Grim, S. O. *J. Chem. Soc., Dalton Trans.* **1982**, 2353. John Enemark, personal communication for Na_2WO_4.

(7) (a) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760. (b) Brevard, C.; Schimpf, R. *J. Magn. Reson.* **1982**, *47*, 528.

(8) (a) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609. (b) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. (c) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1989**, *368*, 45. (d) Faller, J. W.; Kucharczyk, R. R.; Ma, Y. *Inorg. Chem.* **1990**, *29*, 1662.

(9) Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

Table I. ^{183}W Resonance Frequencies (Hz) and $^2J_{W-H}$ (Hz) of Cp*WMe Complexes[a]

compd	^{183}W resonance freq	$\lvert ^2J_{W-H} \rvert$
$(\eta^5\text{-}C_5H_5)W(CO)_3Me$	20 763 806	3.7
$(\eta^5\text{-}C_5Me_5)W(CO)_3Me$	20 769 873	3.5
$(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}O_2)Me$	20 815 121	8.4
$(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2)Me$	20 819 817	7.4
$(\eta^5\text{-}C_5Me_5)W({=}O)({=}NPh)Me$	20 820 320	5.4
$(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$	20 824 213	10.8
$(\eta^5\text{-}C_5Me_5)W({=}O)Me_3$	20 826 851	6.0
$(\eta^5\text{-}C_5Me_5)W({=}O)Cl_2Me$	20 836 252	5.7
$(\eta^5\text{-}C_5Me_5)W({=}O)Br_2Me$	20 837 952	6.1
$(\eta^5\text{-}C_5Me_5)W({=}S)(\eta^2\text{-}S_2)Me$	20 845 977	6.0
$(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$	20 847 525	8.4
$(\eta^5\text{-}C_5Me_5)W({=}S)Cl_2Me$	20 863 388	4.8
$(\eta^5\text{-}C_5Me_5)W({=}S)_2Me$	20 871 959	7.7

[a] The measurements were made with $CDCl_3$ as solvent, and the ^{183}W frequencies are estimated to be accurate to ±3 Hz. The signs of the coupling constants were not determined. In these experiments, the resonance frequency of TMS in $CDCl_3$ was observed at 500.135 421 MHz when the field was locked on the deuterium resonance of $CDCl_3$.

one set of methyl resonances was required to cleanly observe the ^{183}W satellites. The ^{183}W resonance frequencies were generated by a General Radio 1061 frequency synthesizer locked to the 10-MHz oscillator in the spectrometer's frequency synthesizer. The ^{183}W frequencies were varied while the ^{183}W satellites of the methyl resonances in the ^{1}H NMR spectra were monitored by using a 5 mm diameter ^{1}H-BB inverse probe tuned to 20.805 MHz. A typical measurement was performed as follows: initially, the frequency was changed in increments of 500 Hz with the CW decoupler power set at 2 W; once a near-resonance condition was located, as evidenced by collapsing of the ^{183}W satellites, the decoupler power was gradually attenuated and decreasing frequency increments changed on the frequency synthesizer until the exact ^{183}W resonance frequency was determined. The center of the ^{183}W quartet was taken as the position where the spin-tickling effects on both ^{1}H satellites were the same. Although other techniques, such as INEPT,[7] would allow determination of these frequencies, this modified INDOR approach is rapid, accurate for these systems, and can be carried out with minimum effort.

Results

The ^{183}W resonance frequencies of a number of tungsten methyl complexes were recorded indirectly by monitoring the tungsten satellites of the methyl resonances in the ^{1}H NMR spectra while the tungsten nuclei were decoupled, as described in the Experimental Section. Data are listed in Table I. The data for the complex $CpW(CO)_3Me$ is included for the sake of comparison with the existing literature value. The Ξ values have been calculated and are listed in Table II for the purpose of converting chemical shifts according to the existing reference standard in the literature. In this paper, the complex WF_6 was chosen as the reference and the chemical shifts calculated on the basis of this standard are also listed in Table II. The chemical shift with WF_6 as a reference can be readily correlated approximately with that of WO_4^{2-} as a reference by adding −1117 ppm.[1]

Discussion

Of the three analogous complexes involving oxo, sulfido, and imido, the ^{183}W chemical shift of the imido complex $Cp^*W({=}O)({=}NPh)Me$ is most shielded, by 187 ppm compared to its oxo analogue $Cp^*W({=}O)_2Me$ and by 1307 ppm compared to its sulfido analogue $Cp^*W({=}O)({=}S)Me$. The deshielding of tungsten in replacing oxo by sulfido is consistent with the trend observed for similar transformations, such as MO_4^{2-} to MS_4^{2-} for M = Mo and W.[10] Two independent theoretical studies[11] on the substitution of O^{2-} in MoO_4^{2-} by S^{2-} have analyzed the influence of the substitution on both the diamagnetic and paramagnetic terms in the Ramsey equation, $\sigma = \sigma^{dia} + \sigma^{para}$, where σ is the shielding constant.[12] Their analyses show that σ^{para} is the dominant factor in the changes in total nuclear shielding and the magnitude of σ^{para} correlates with the polarizability of ligands. The relatively small change in shielding as a result of imido replacement of oxo contrasts with the effect of oxo replacement by sulfido and reflects the substantial increase in the polarizability, or softness, of the elements on moving from the second to the third row.

Table II. Ξ Values (Hz) of ^{183}W Resonance Frequencies and Chemical Shifts (ppm) for Cp*WMe Complexes in $CDCl_3$

	$\Xi(^{183}W)$[a]	color	$\delta(^{183}W)$[b]
$(\eta^5\text{-}C_5H_5)W(CO)_3Me$[c]	4 151 637	light yellow	−2437.2
$(\eta^5\text{-}C_5Me_5)W(CO)_3Me$	4 152 850	yellow	−2145.7
WF_6[d]	4 161 780		0.0
$(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2O_2)Me$	4 161 897	colorless	28.1
$(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2)Me$	4 162 836	yellow	253.7
$(\eta^5\text{-}C_5Me_5)W({=}O)({=}NPh)Me$	4 162 937	colorless	277.9
$(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$	4 163 715	colorless	464.9
$(\eta^5\text{-}C_5Me_5)W({=}O)Me_3$	4 164 242	colorless	591.6
$(\eta^5\text{-}C_5Me_5)W({=}O)Cl_2Me$	4 166 122	yellow	1043.3
$(\eta^5\text{-}C_5Me_5)W({=}O)Br_2Me$	4 166 462	yellow	1125.0
$(\eta^5\text{-}C_5Me_5)W({=}S)(\eta^2\text{-}S_2)Me$	4 168 067	purple	1510.5
$(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$	4 168 376	yellow	1584.9
$(\eta^5\text{-}C_5Me_5)W({=}S)Cl_2Me$	4 171 548	orange	2347.1
$(\eta^5\text{-}C_5Me_5)W({=}S)_2Me$	4 173 262	red	2758.8

[a] The Ξ value of TMS is defined as 100.000 000 MHz. The Ξ value provides the frequency at which a nucleus will resonate when the field is such that TMS resonates at exactly 100 MHz. The values given here are approximately ±1 Hz. [b] Positive values are downfield from WF_6, the Ξ value of which[5] has been used to calculate the $\delta(^{183}W)$ values. [c] The $\Xi(^{183}W)$ value of $CpW(CO)_3Me$ calculated according to our measurement is in reasonable agreement with the early literature value (4 151 630 ± 3 Hz) measured in benzene by McFarlane et al.[5] [d] To retain the precision inherent in INDOR, the chemical shifts are referenced to WF_6, as used in ref 5. Approximate chemical shifts relative to tungstate can be calculated by adding −1117 ppm to δ relative to WF_6. Shifts relative to $W(CO)_6$ in $CDCl_3$ or 2 M Na_2WO_4 in D_2O can be computed from the tabulated Ξ values by using the reference of $\Xi[W(CO)_6]$ = 4 151 878 Hz or $\Xi[Na_2WO_4]$ = 4.166 39 MHz.[6]

The change in the nuclear shielding for a particular ligand exchange can vary considerably; e.g. it is 841 ppm[10c] for WO_4^{2-}/WO_3S^{2-} and 1304 ppm for $Cp^*W({=}O)Cl_2Me/Cp^*W({=}S)Cl_2Me$. The substitution of two oxo ligands by two sulfido groups, forming $Cp^*W({=}S)_2Me$ from $Cp^*W({=}O)_2Me$, causes a deshielding of 2294 ppm, which falls between the values of 1787 and 2905 ppm for the analogous differences between $[WO_4]^{2-}$ and $[WO_2S_2]^{2-}$ [10c] and between $[W({=}O)_2(C_5H_{10}NO)_2]$ and $[W({=}S)_2(C_5H_{10}NO)_2]$,[13] respectively. Some consideration of these seemingly random variations is appropriate. The substitution of one oxo ligand by sulfido has a deshielding effect of 1120 ppm in comparing $Cp^*W({=}O)_2Me$ ($\nu_{W{=}O,avg}$ = 928.5 cm^{-1}) with $Cp^*W({=}O)({=}S)Me$, 1174 ppm for $Cp^*W({=}O)({=}S)Me$ ($\nu_{W{=}O}$ = 930 cm^{-1}) with $Cp^*W({=}S)_2Me$, 1257 ppm for $CP^*W({=}O)(\eta^2\text{-}S_2)Me$ ($\nu_{W{=}O}$ = 944 cm^{-1}) with $Cp^*W({=}S)(\eta^2\text{-}S_2)Me$, and 1304 ppm for the $Cp^*W({=}O)Cl_2Me$ ($\nu_{W{=}O}$ = 945 cm^{-1}) with $Cp^*W({=}S)Cl_2Me$. A noteworthy feature is observed in these comparisons, i.e. the higher the $\nu_{W{=}O}$ of the starting complex, the more deshielded the tungsten by the substitution of O^{2-} by S^{2-}. It appears that in complexes having W=S of higher bond orders, which are reflected in the higher W=O stretching frequencies of their parent oxo groups, the tungsten nuclei are more deshielded than those of lower bond order. In the case of $Cp^*W({=}O)_2Me$, the tungsten nucleus is deshielded by 578 ppm when the oxo ligand is replaced by two chloride ligands, while in a similar replacement involving $Cp^*W({=}O)({=}S)Me$, the tungsten nucleus is deshielded by as much as 762 ppm. The only difference between these two

---

(10) (a) Lutz, O.; Nolle, A.; Kronek, P. *Z. Naturforsch.* **1976**, *31A*, 454; **1977**, *32A*, 505. (b) Gheller, S. F.; Gazzana, P. A.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Rodgers, J. R.; Snow, M. R. *Inorg. Chim. Acta* **1981**, *54*, L131. (c) Gheller, S. F.; Hamley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519.

(11) (a) Combariza, J. E.; Enemark, J. H.; Barfield, M. *J. Am. Chem. Soc.* **1989**, *111*, 7619. (b) Nakatsuji, H.; Sugimoto, M. *Inorg. Chem.* **1990**, *29*, 1221.

(12) Ramsey, N. F. *Phys. Rev.* **1950**, *77*, 567. Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

(13) McDonell, A. C.; Vasudevan, S. G.; O'Connor, M. J.; Wedd, A. G. *Aust. J. Chem.* **1985**, *38*, 1017.

replacements is that the former has generated an oxo group with a higher bond order as compared to those of the substrate molecule and the latter has increased the bond order of a sulfido group. Apparently, the softer sulfido group exerts more influence on the deshielding of the tungsten even with such a minor change in bond order. Therefore, the magnitude of deshielding not only depends on the type of ligand replacement, but also depends to a significant extent on synergistic effects on deshielding caused by variations in the bonding of the other ligands. Consequently, one cannot anticipate a simpler linear substituent effect equation as found, for example, in ^{13}C shifts of alkanes. Hence, one should be extremely cautious when estimating shielding effects in one complex on the basis of a ligand replacement in another complex if the environment produced by the other ligands is not comparable in both complexes.

Another point of interest is that a ^{95}Mo NMR study of similar chloride replacements in a dioxo-Mo(VI) series has revealed that all of these substitutions resulted in increased shielding of the Mo nuclei.[14] The shielding of molybdenum nuclei in this Mo(=O)$_2$(S$_2$CNR$_2$)$_2$ series may be affected by reduced overlap between the sulfur lone pairs and one unoccupied d orbital as a result of the formation of MO≡O in the Mo(=O)Cl$_2$(S$_2$CNR$_2$)$_2$ complexes.

The ^{183}W chemical shift of Cp*W(=O)Br$_2$Me reflects deshielding of the tungsten center when compared to that of the chloride analogue Cp*W(=O)Cl$_2$Me. Such a shielding trend is sometimes called an "inverse halogen dependence", a term introduced by Kidd along with the term "normal halogen dependence" for the opposite trend.[15] Another pair of W(VI) complexes, WF$_6$ and WCl$_6$, with known ^{183}W chemical shifts, also displays an inverse halogen dependence. As noted for the Mo(VI) complexes by Minelli et al.,[14] an inverse halogen dependence is very likely a general feature of W(VI) complexes. A limited number of six-coordinate Mo(IV) complexes represent the only other class of complexes with known ^{95}Mo chemical shifts showing this feature.[1,10c] Note that all of these compounds have two things in common: their coordination spheres are unsaturated, and they have either d^0 or d^2 configurations. It appears that d^6, d^8, and d^{10} configurations give rise to normal halogen dependence.[1,11b,15,16] Some workers suggest that the crossover from inverse to normal halogen dependence occurs when the d orbitals become more than half-filled.[11b,16] Nevertheless, although some coordinatively saturated d^4 Mo(II) complexes show the normal halogen dependence (e.g., CpMo(CO)$_3$X), others show inverse dependence (e.g., HB(Me$_2$pz)$_3$Mo(NO)X$_2$).[1] Therefore, one is led to the conclusion that this inverse halogen dependence is an intrinsic characteristic of high oxidation state metals.

Replacement of the peroxo group of Cp*W(=O)(η^2-O$_2$)Me by a persulfido group, η^2-S$_2$, deshields the tungsten by 226 ppm, which would be expected on the basis of the increased polarizability. Attempts to synthesize the 1,1'-diphenylhydrazo analogue, Cp*W(=O)(η^2-N$_2$Ph$_2$)Me, by reacting Cp*W(=O)Cl$_2$Me and 1,1'-diphenylhydrazine have only led to the formation of the imido complex, Cp*W(=O)(=NPh)Me. On the basis of the observed shielding trend of =NPh > =O > =S, one would reasonably expect such a η^2-hydrazo complex, if it were isolated, to be shielded relative to the peroxo species.

Conclusions

The variations in ^{95}Mo and ^{183}W chemical shifts of these higher formal oxidation state molybdenum and tungsten complexes may seem counterintuitive when compared with more familiar proton and carbon NMR shifts. Accordingly, in situations where changes in diamagnetic contributions dominate, a more electronegative substituent would tend to reduce the charge on a nucleus and cause it to be deshielded. In situations such as those discussed here with high oxidation state early transition metals, it is the paramagnetic contributions which vary most significantly on replacement of ligands.[11] *Consequently, in these situations an increase in electron density on the metal can result in decreased shielding*—contrary to the expectation based on diamagnetic contributions alone. Although little theoretical work has been carried out on tungsten chemical shifts, there tends to be a linear correlation of ^{183}W with ^{95}Mo shifts in comparable compounds, $\Delta(\delta^{95}\text{Mo})/\Delta(\delta^{183}\text{W}) \sim 1.7$, suggesting similar explanations for both.[10c,11] The paramagnetic contributions largely reflect the separation between filled and unfilled molecular orbitals with substantial d character. If one wishes to qualitatively appreciate the effects of ligand substitutions on chemical shift, one needs to focus on factors that modify the separations between MO's with metal character. One observes that factors which tend to increase "back-bonding", such as increased softness of the ligand or lower ligand electronegativity, correlate with decreased shielding.

One must take care, however, not to equate the correlation with the origin of the effect. These very features that describe ground-state electronic distributions are the same ones that influence the energy separations between occupied and unoccupied MO's, which are the essence of the theoretical explanation of the paramagnetic contribution. In this context, one must consider the relationship of orbital energies in the metal fragment that is retained and both the filled and unfilled orbital energies in the ligand that is replaced.

In practical situations one may not be prepared (or be willing) to carry out an MO analysis to predict a shift for an unknown compound. In terms of reliable trends, for higher oxidation state tungsten complexes one can expect decreased shielding with increased softness of the ligands. The amount of change for substitution of an O by S, $\Delta(\text{O} \rightarrow \text{S})$, in the series from WO$_4^{2-}$ to WS$_4^{2-}$ is approximately 900 ppm.[10c] The value for a given replacement, however, can vary significantly depending on the other ligands, as we have discussed earlier. It would appear that in many cases the softer the other ligands, the greater will be $\Delta(\text{O} \rightarrow \text{S})$.

Thus, the sequential replacement shift differences $\Delta(\text{O} \rightarrow \text{S})$ for WO$_4^{2-}$, WO$_3$S^{2-}, WO$_2$S$_2^{2-}$, WOS$_3^{2-}$, and WS$_4^{2-}$ of 841, 946, 973, and 1009 ppm, reflect the increased softness of the remaining ligands. Similar trends appear in the compounds discussed here, e.g. the $\Delta(\text{O} \rightarrow \text{S})$ values for Cp*W(=O)$_2$Me, Cp*W(=O)(=S)Me, and Cp*W(=S)$_2$Me are 1120 and 1257 ppm. For complexes of similar structure, reference to Table II or other compilations of data[1] allows estimation of a shift for a given ligand replacement, $\Delta(\text{L} \rightarrow \text{L}')$; however, one must be cognizant of the effect of the relative softness of the other ligands on the magnitude of $\Delta(\text{L} \rightarrow \text{L}')$.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

---

(14) Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1111.

(15) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1979**, *10A*, 1.

(16) (a) Mason, J. *Chem. Rev.* **1987**, *87*, 1299. (b) Dechter, J. J. *Prog. Inorg. Chem.* **1985**, *33*, 393.