Transition-metal Chemical Shifts in Complexes of Molybdenum(0) and Tungsten(0)

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Molybdenum-95 and tungsten-183 n.m.r. spectra have been measured by direct observation and by multiple-resonance methods respectively for 65 related derivatives of $[Mo(CO)_6]$ and $[W(CO)_6]$ with (mainly) phosphorus ligands. The chemical shifts of the two nuclei are remarkably parallel, those for ^{183}W being *ca.* 1.7 times more sensitive to changes in chemical environment than those for ^{95}Mo. The chemical shifts are temperature-dependent, and trends in them can be largely accounted for by variations in the mean electronic excitation energy. The metal–phosphorus spin-coupling constants are very predictable. Molybdenum-95 linewidths in many cases are quite small, and can be broadly explained by the use of a point-charge model.

The natural distribution of isotopes with favourable properties for study by nuclear magnetic resonance (n.m.r.) has impeded detailed comparisons of trends in transition-metal magnetic shielding throughout the Periodic Table.[1] In particular, there is currently no instance where extensive data are available which make it possible to survey and compare chemical shift tendencies within the same group. Even in the relatively promising cases of ^{59}Co and ^{103}Rh the types of compound which have been studied to date have largely been different for the two elements, and this has precluded any valid comparison of the results. Similar considerations apply to other groups of the Periodic Table.

In this paper we report measurements of ^{95}Mo and ^{183}W chemical shifts in a range of octahedral complexes of the elements in the zero oxidation state which have been selected to provide direct comparisons between the behaviour of the two elements. Previously there have been a number of preliminary reports of ^{95}Mo chemical shifts,[2-8] as well as systematic studies of ^{183}W, although of different types of compound.[9-16]

The direct study by n.m.r. spectroscopy of many elements has been greatly facilitated by the introduction of versatile multinuclear Fourier-transform spectrometers capable of being tuned easily to a wide range of different frequencies. Nonetheless, some nuclei have such poor receptivities that it still may be advantageous to use indirect multiple-resonance methods of detection for the study of compounds in which there is observable spin coupling to a nucleus of relatively high receptivity. This is especially true of the only naturally occurring magnetic isotope of tungsten, ^{183}W ($I = \frac{1}{2}$, abundance = 14.3%, sensitivity 0.0044 of that of ^{13}C, receptivity 0.058 relative to ^{13}C) which requires very long accumulation times for direct observation of even concentrated solutions. By contrast ^{1}H-$\{^{183}W\}$, ^{19}F-$\{^{183}W\}$, and ^{31}P-$\{^{183}W\}$ double-resonance experiments have yielded tungsten chemical shifts in a few minutes per compound.[10-12,16] In the present work we have used ^{31}P-$\{^{183}W, ^{1}H_{noise}\}$ multiple-resonance experiments performed on a modified Fourier-transform spectrometer to determine tungsten chemical shifts and splitting patterns in a range of complexes of tungsten(0) with carbonyl and phosphorus-containing ligands, and have also determined the tungsten chemical shift of tungsten hexacarbonyl itself by means of a ^{13}C-$\{^{183}W\}$ experiment.

With molybdenum the situation is different, and its two magnetic isotopes (^{95}Mo, $I = \frac{5}{2}$, natural abundance = 15.7%, receptivity 2.88 times ^{13}C; ^{97}Mo, $I = \frac{5}{2}$, natural abundance = 9.5%, receptivity 1.84 times ^{13}C) have very different nuclear quadrupole moments, that of ^{97}Mo being *ca.* 11 times that of ^{95}Mo, so that ^{97}Mo linewidths can be greater than ^{95}Mo linewidths by a factor of 100 or more, depending upon the correlation time for molecular tumbling. Thus ^{95}Mo is much more suitable to study than ^{97}Mo, and a recent report of ^{95}Mo linewidths ranging from 4 to 110 Hz even in species with less than T_d symmetry has indicated that ^{95}Mo spectroscopy has considerable potential. In fact, the nuclear quadrupole moment of ^{95}Mo can be beneficial in many cases since it permits rapid acquisition of data, and we find that pulsing rates well in excess of ten per second are often satisfactory. At the beginning of this work some ^{31}P-$\{^{95}Mo, ^{1}H_{noise}\}$ experiments were used [17] to obtain ^{95}Mo data indirectly, but these were found to be extremely time-consuming and not particularly precise; direct observation was much more satisfactory, and the range of molybdenum chemical shifts is such that ^{95}Mo spectra can yield valuable structural information even when the linewidths exceed 100 Hz.

Experimental

Molybdenum-95 spectra were recorded on concentrated CH_2Cl_2 solutions contained in spinning tubes (outside diameter 10 mm) on a JEOL FX90Q multinuclear spectrometer operated in pulsed Fourier-transform mode at an observing frequency of 5.85 MHz under conditions of full proton decoupling. For most samples the rate of quadrupolar-induced longitudinal relaxation was sufficient to permit a pulse repetition rate of 20 pulses s^{-1} or faster, and normally 1 000—10 000 transients (total time 50—500 s) gave a satisfactory signal-to-noise ratio in the transformed spectra. Typically, a spectral width of 10 kHz was used and the free induction decay was acquired in about 1 000 data points, zero filling then being used to produce transformed spectra in 4 096 real and 4 096 imaginary data points. The magnetic field was stabilized by the ^{2}H signal from an external D_2O sample built into the probe, and drift was typically ±1 data point, *i.e.* ±2.5 Hz or ±0.5 p.p.m. for periods of several hours. Although the ^{95}Mo chemical shifts in the Tables are given relative to a saturated solution of $[Mo(CO)_6]$ in tetrahydrofuran (thf) at 40 °C, it was generally found convenient to use a neat liquid sample of $[Mo(CO)_5\{P(OPr^i)_3\}]$ as a secondary reference, since this gave a sharp ($W_{\frac{1}{2}} < 12$ Hz) signal of excellent signal-to-noise ratio with only a few pulses.

The ^{31}P-$\{^{183}W, ^{1}H_{noise}\}$ multiple-resonance experiments were performed on concentrated solutions in spinning tubes (outside diameter 10 mm) on a modified JEOL FX60 spectrometer, operating at a measuring frequency of 24.2 MHz. Standard conditions were used to record the ^{31}P spectra and a small amount of C_6D_6 added to the sample normally provided an internal locking signal. A GenRad model 1061 frequency synthesizer whose fundamental frequency was controlled by the spectrometer quartz-crystal oscillator provided radiofrequency (r.f.) power at the ^{183}W resonance frequency of *ca.* 2.48 MHz; this power was transmitted *via* a tuned power amplifier and a rejection circuit tuned to 59.8 MHz (the proton-decoupling frequency) to an extra set of coils wound concentrically with the normal proton-decoupler coils in the probe of the spectometer. The maximum value of $\gamma(^{183}W)B_2/2\pi$ available at the sample with this arrangement was *ca.* 200 Hz. For the ^{13}C-{^{183}W} double-resonance experiments the normal $^{13}C,^{1}H$ dual probe was used, power at the ^{183}W resonance frequency being transmitted to the proton-decoupler coils *via* a matching arrangement similar to that described previously.[18] This gave a maximum value of $\gamma(^{183}W)B_2/2\pi$ of *ca.* 25 Hz.

In many cases the ^{183}W satellites in the proton-decoupled ^{31}P spectra were obtained at a satisfactory signal-to-noise ratio with a single pulse, and it then proved convenient to operate the spectrometer in the 'LINE' mode whereby a fresh transformed spectrum was displayed on the cathode ray oscilloscope at intervals of 5—7 s, and then to adjust the output from the synthesizer manually during the search for the ^{183}W resonance frequency. For weaker samples however, and for the ^{13}C-{^{183}W} experiments on [W(CO)$_6$], an automated technique was used in which a PET microcomputer was programmed to adjust the frequency from the synthesizer in a sequential manner after appropriate numbers of transients had been acquired and stored automatically on magnetic tape for later read-out.

The compounds were prepared by literature methods or simple adaptations of them. Substituted molybdenum carbonyl complexes with unidentate ligands were synthesized by the reaction under dinitrogen of [Mo(CO)$_6$] and a stoicheiometric amount of the appropriate ligand in refluxing diglyme (2,5,8-trioxanonane) [compounds (2), (6)—(8), (12), (14), and (15)], 1,2-dimethoxyethane [(5), (9), (13), and (16)], or light petroleum (b.p. 100—120 °C) [(3), (4), and (10)]. The progress of the reaction was monitored by the disappearance of the [Mo(CO)$_6$] carbonyl stretch at 1 990 cm^{-1} in the i.r. spectrum of the reaction solution. Solid products were purified by recrystallization from $CHCl_3$–MeOH; liquids and low-melting solids were distilled under reduced pressure. The tungsten complexes (29)—(36) and compound (11) were synthesized as described previously [12] by the photochemically induced reaction between the hexacarbonyl and the appropriate ligand. The molybdenum complexes (54)—(56) and (58)—(61) were made by the photochemical reaction between [Mo(CO)$_6$] and the ligand, but were not isolated in pure form.

The following complexes were prepared as described in the references: compounds (17)—(19) and (37)—(39);[19] (20), (22), (40), and (42)—(44);[20] (21) and (41);[21] (24) and (46);[22] (25);[23] (47);[24] (26), (27), and (48)—(52);[25] (53);[26] (57) and (64);[27] and (35), (36), (62), (63), and (65).[12]

Compounds (23) and (45), [Mo(CO)$_4${CH_2=C(PPh$_2$)$_2$}] (M = Mo or W), were prepared as follows. The ligand [28] CH_2=C(PPh$_2$)$_2$ (1.0 g, 2.5 mmol) and hexacarbonyl [M(CO)$_6$] (2.5 mmol) were refluxed in diglyme (50 cm^3) under dinitrogen overnight. The solution was cooled and then filtered, and the diglyme removed under reduced pressure. Addition of MeOH (10 cm^3) to the residue gave yellow crystals in both cases. Yield 78% for M = W, 71% for M = Mo (Found: C, 59.5; H, 3.6; P, 10.2. Calc. for [Mo(CO)$_4${CH_2=C(PPh$_2$)$_2$}]: C, 59.6; H, 3.6; P, 10.3. Found: C, 51.8; H, 3.1; P, 8.8. Calc. for [W(CO)$_4${CH_2=C(PPh$_2$)$_2$}]: C, 52.0; H, 3.2; P, 9.0%).

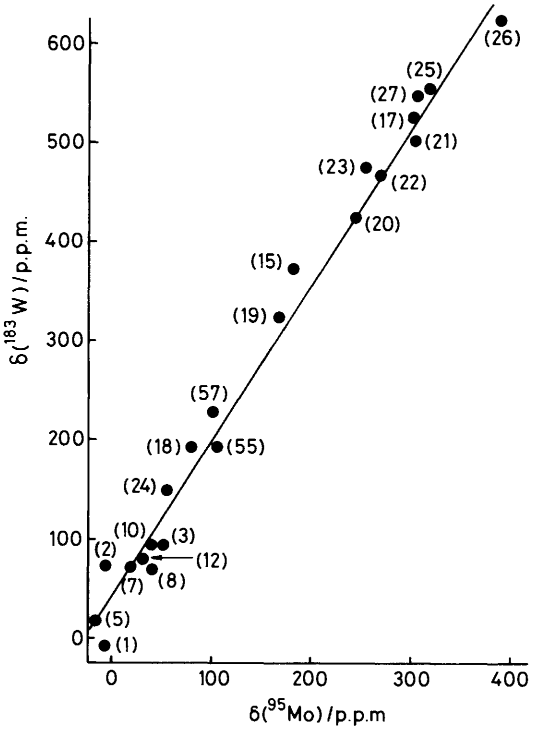

Figure 1. Tungsten-183 *versus* molybdenum-95 nuclear magnetic shieldings in corresponding molecules. The numbers of the plotted points refer to the molybdenum compounds in the Tables

Results and Discussion

Although the most commonly used and suitable references for ^{95}Mo and ^{183}W chemical shifts in general are MoO_4^{2-} and WO_4^{2-} respectively, it is convenient for the present work to refer all the data to [Mo(CO)$_6$] and [W(CO)$_6$], and this has been done in Tables 1—3 which summarize the results. In fact, [Mo(CO)$_6$] has a chemical shift of 1 856 p.p.m. to low frequency of neutral aqueous molybdate,[3] and we find the chemical shift of [W(CO)$_6$] is 3 505 p.p.m. to low frequency of sodium tungstate.[13] The most striking feature of the results is the very close parallel between molybdenum and tungsten shieldings in corresponding compounds as illustrated by Figure 1. Furthermore, this plot can also accommodate without significant deviation several other molybdenum and tungsten chemical shifts available from the literature [6,12] including those for [M(CO)$_3$(η^5-C_5H_5)X] (M = Mo or W; X = Cl, Br, or I) which require relatively little extrapolation. However, for MoO_4^{2-} and WO_4^{2-} which lie several thousand p.p.m. beyond the range of Figure 1 the fit is not so good, the calculated extrapolated ^{95}Mo chemical shift being 2 140 p.p.m., which may be compared with the experimental value of 1 856 p.p.m. It is thus clear that a knowledge of either the ^{95}Mo or the ^{183}W chemical shift in a particular type of compound can permit the calculation of the other with fair accuracy, and this should be of considerable value to the preparative chemist.

Heavy-metal shieldings are normally dominated [29] by the paramagnetic term of Ramsey's treatment which is given approximately by equation (1), where ΔE is an average energy

$$\sigma^P = -(2e^2\hbar^2/3m^2c^2\Delta E)(\langle r^{-3}\rangle_{np}P_i + \langle r^{-3}\rangle_{nd}D_i) \quad (1)$$

Table 1. Molybdenum-95 n.m.r. data for substituted complexes of molybdenum hexacarbonyl

(*a*) Monosubstituted $[\mathrm{Mo(CO)_5L}]$

No.	L	$\delta(^{95}\mathrm{Mo})$ [a]	$^1J(^{95}\mathrm{Mo}-^{31}\mathrm{P})$ [b]	$W_{\frac{1}{2}}(^{95}\mathrm{Mo})$ [c]	$\delta(^{31}\mathrm{P})$ [d]	Conditions
(1)	CO	0	—	12 ± 1	—	thf, 40 °C
(2)	$\mathrm{PBu_3}$	-7 ± 5 [e]	130 ± 2	—	$+12.4$	$\mathrm{CH_2Cl_2}$, 24 °C
(3)	$\mathrm{P(NMe_2)_3}$	$+53 \pm 1$	173 ± 2	15 ± 2	$+145.3$	$\mathrm{CH_2Cl_2}$, 40 °C
(4)	$\mathrm{PPh(NEt_2)_2}$	$+55 \pm 1$	159 ± 3	25 ± 2	$+195.6$	$\mathrm{CH_2Cl_2}$, 40 °C
(5)	$\mathrm{P(OMe)_3}$	-5 ± 1	217 ± 2	12 ± 2	$+161.2$	$\mathrm{CH_2Cl_2}$, 40 °C
(6)	$\mathrm{P(OEt)_3}$	$+5 \pm 10$ [e]	214 ± 2	—	$+155.9$	neat, 24 °C
(7)	$\mathrm{P(OPr^i)_3}$	$+25 \pm 1$	215 ± 2	20 ± 2	$+153.5$	$\mathrm{CH_2Cl_2}$, 40 °C
(8)	$\mathrm{P(OPh)_3}$	$+43 \pm 1$	236 ± 2	20 ± 2	$+154.3$	$\mathrm{CH_2Cl_2}$, 40 °C
(9)	$\mathrm{P(OCH_2)_3CEt}$	-2 ± 1	227 ± 2	20 ± 2	$+138.4$	$\mathrm{CH_2Cl_2}$, 40 °C
(10)	$\mathrm{PPh(OMe)_2}$	$+40 \pm 10$ [e]	183 ± 2	—	$+176.4$	$\mathrm{CH_2Cl_2}$, 24 °C
(11)	$\mathrm{C_5H_{10}NH}$ [f]	$+433 \pm 3$	—	50 ± 5	—	$\mathrm{CH_2Cl_2}$, 40 °C

(*b*) Disubstituted $[\mathrm{Mo(CO)_4L_2}]$ [g]

No.	L	$\delta(^{95}\mathrm{Mo})$ [a]	$^1J(^{95}\mathrm{Mo}-^{31}\mathrm{P})$ [b]	$W_{\frac{1}{2}}(^{95}\mathrm{Mo})$ [c]	$\delta(^{31}\mathrm{P})$ [d,h]
(12)	$\mathrm{P(OMe)_3}$	$+29 \pm 1$	215 ± 2	25 ± 2	$+165.0$
(13)	$\mathrm{P(OPh)_3}$ [i]	$+78 \pm 20$	?	700 ± 50	$+161.1$
(14)	$\mathrm{PPh_2(OMe)}$	$+179 \pm 1$	161 ± 2	30 ± 3	$+156.4$
(15)	$\mathrm{PMe_2Ph}$ [i]	$+186 \pm 1$	130 ± 2	22 ± 2	$+19.5$
(16)	$\mathrm{C_5H_{10}NH}$ [f]	$+779 \pm 5$	—	115 ± 10	—
(17)	$\mathrm{Ph_2PCH_2PPh_2/2}$	$+304 \pm 4$	110 ± 10	80 ± 10	$+1.5$
(18)	$\mathrm{Ph_2PCH_2CH_2PPh_2/2}$	$+80 \pm 3$	134 ± 5	50 ± 5	$+55.3$
(19)	$\mathrm{Ph_2PCH_2CH_2CH_2PPh_2/2}$	$+167 \pm 2$	127 ± 3	30 ± 2	$+20.4$
(20)	$\mathrm{Ph_2PCH_2PPr^i{}_2/2}$	$+244 \pm 2$	117 ± 20	150 ± 20	$+1.9$, $+23.9$
(21)	$\mathrm{Ph_2PCH_2PBu^t{}_2/2}$	$+304 \pm 2$	117 ± 5	50 ± 20	$+2.8$, $+43.0$
(22)	$\mathrm{Ph_2PCH_2PPr^iPh/2}$	$+268 \pm 2$	124 ± 5	50 ± 20	$+1.6$, $+12.2$
(23)	$\mathrm{CH_2{=}C(PPh_2)_2/2}$	$+278 \pm 3$	125 ± 10	140 ± 10	$+26.4$
(24)	*cis*-$\mathrm{Ph_2PCH{=}CHPPh_2/2}$	$+55 \pm 1$	134 ± 2	30 ± 3	$+63.9$
(25)	$\mathrm{HC(PPh_2)_3/2}$ [j]	$+318 \pm 3$	127 ± 10	100 ± 10	*j*
(26)	$\mathrm{Ph_2P(S)CH_2PPh_2/2}$ [k]	$+388 \pm 20$	?	400 ± 40	$+55.5$, $+37.9$
(27)	$\mathrm{Ph_2P(S)CH_2PPr^i{}_2/2}$ [k]	$+311 \pm 20$	?	400 ± 40	$+55.5$, $+60.5$

[a] In p.p.m. to high frequency of a saturated solution of $[\mathrm{Mo(CO)_6}]$ in tetrahydrofuran (thf) at 40 °C for which $\Xi(^{95}\mathrm{Mo}) = 6.504\,836$ MHz. [b] In Hz. In complexes with two inequivalent phosphorus atoms the separate values of $^1J(^{95}\mathrm{Mo}-^{31}\mathrm{P})$ were not resolved. [c] Linewidth in Hz at half-height of the ^{95}Mo resonance. [d] In p.p.m. ±0.1 p.p.m. to high frequency of 85% $\mathrm{H_3PO_4}$. [e] Measured by $^{31}\mathrm{P}-\{^{95}\mathrm{Mo},{}^1\mathrm{H}_{\mathrm{noise}}\}$ multiple resonance. [f] Piperidine. [g] In $\mathrm{CH_2Cl_2} + \mathrm{C_6D_6}$ (lock) at 24 °C except where otherwise stated. [h] When two values are given the first applies to the first phosphorus atom in column 2. [i] At 40 °C. [j] The ^{95}Mo spectrum is a triplet, confirming that only two phosphorus atoms are co-ordinated. The ^{31}P spectrum is of the $\mathrm{A_2B}$ type with $^2J(^{31}\mathrm{P_A}-^{31}\mathrm{P_B}) = 25.6$ Hz and $\delta(^{31}\mathrm{P_A}) = +22.5$ p.p.m., $\delta(^{31}\mathrm{P_B}) = -23.2$ p.p.m. [k] The bidentate ligand is co-ordinated through sulphur and phosphorus.

of electronic excitation from the ground state to states which are mixed in by the magnetic field, $\langle r^{-3}\rangle_{np}$ and $\langle r^{-3}\rangle_{nd}$ are radial expansion terms representing the average inverse cubes of the distances of the relevant *p* and *d* electrons from the nucleus, and P_i and D_i are measures of the degree of electronic imbalance in the relevant *p* and *d* orbitals respectively. Evidence that the $(\Delta E)^{-1}$ term is important for the shielding of transition-metal nuclei is provided by the temperature dependences of their chemical shifts;[1] *e.g.*, up to 3 p.p.m. per °C for ^{59}Co, 1.0 p.p.m. per °C for ^{103}Rh, and 0.7 p.p.m. per °C for ^{195}Pt. In the present work the temperature dependences were measured for five compounds with the following results: (1), 0.29; (2), 0.34; (7), 0.48; (10), 0.38; and (31), 0.37 p.p.m. per °C. These are of comparable magnitude to and of the same sign as those for other second- and third-row transition metals and are thus consistent with variations in $(\Delta E)^{-1}$ playing a significant part in the shielding, since an increase in temperature will increase the accessibility of the electronic excited states. However, it should be pointed out that the molecule (7) with the largest temperature coefficient is also the one with the most flexible substituents, while the most rigid molecule (1) also has the smallest coefficient, so it appears that the observed temperature dependence may also depend upon conformational changes leading to interbond-angle deformation. As is discussed later, this can be expected significantly to affect the metal shielding.

The slope of the plot of Figure 1 should be given by equation (2).[30] Electronic spectra for many complexes of

$$\frac{\Delta\delta(^{183}\mathrm{W})}{\Delta\delta(^{95}\mathrm{Mo})} = \frac{\Delta E(\mathrm{Mo})}{\Delta E(\mathrm{W})}\left[\frac{\langle r^{-3}\rangle_{6p\mathrm{W}}P_i(\mathrm{W}) + \langle r^{-3}\rangle_{6d\mathrm{W}}D_i(\mathrm{W})}{\langle r^{-3}\rangle_{5p\mathrm{Mo}}P_i(\mathrm{Mo}) + \langle r^{-3}\rangle_{5d\mathrm{Mo}}D_i(\mathrm{Mo})}\right] \quad (2)$$

molybdenum and tungsten indicate that the ratio $\Delta E(\mathrm{Mo})/\Delta E(\mathrm{W})$ is very close to unity,[31] so that this part of equation (2) cannot account for the experimentally observed slope of 1.7. Values of the radial expansion terms are apparently not available but are likely to run parallel for the *p* and *d* orbitals; comparison with main-group elements suggests[32] a ratio of *ca.* 2.5 : 1, but this will be substantially reduced by the lanthanide contraction, probably to considerably less than 1.7 : 1 since the covalent radii of tungsten and molybdenum are in the ratio of 1.01 : 1. The electronic imbalance terms will be modified by the extent of π back-bonding involving the metal *d* orbitals and thus somewhat reduced back-bonding in the tungsten complexes could lead to greater electronic imbalance and hence to larger P_i and D_i terms. At a more qualitative level, it can be stated that tungsten chemical shifts are more sensitive to changes in chemical environment than are molybdenum ones, this probably reflecting a correspond-

Table 2. Tungsten-183 n.m.r. data for substituted complexes of tungsten hexacarbonyl

(*a*) Monosubstituted [W(CO)$_5$L]

No.	L	δ(^{183}W) [a]	^1J(^{183}W–^{31}P) [b]	δ(^{31}P) [c]	Conditions
(28)	CO	0	—	—	thf, 55 °C
(29)	PBu$_3$	+74.2 ± 0.5	230.6 ± 0.3	−6.1	CH$_2$Cl$_2$, 24 °C
(30)	P(NMe$_2$)$_3$ [d]	+98.0 ± 0.5	310 ± 5	+129.9	CH$_2$Cl$_2$, 24 °C
(31)	P(OMe)$_3$	+13.7 ± 0.5	386.4 ± 0.4	+138.0	neat
(32)	P(OPr^i)$_3$	+73.0 ± 0.5	380.8 ± 0.3	+129.9	CH$_2$Cl$_2$, 24 °C
(33)	P(OPh)$_3$	+72.7 ± 0.5	414.8 ± 0.2	+131.5	CH$_2$Cl$_2$, 24 °C
(34)	PPh(OMe)$_2$ [d]	+97.3 ± 0.5	330 ± 4	+153.1	C$_6$H$_6$, 24 °C

(*b*) *cis*-Disubstituted [W(CO)$_4$L$_2$] [e]

No.	L	δ(^{183}W) [a]	^1J(^{183}W–^{31}P) [b]	δ(^{31}P) [c]
(35)	P(OMe)$_3$	+81.4 ± 0.5	+379.0 ± 0.2	+141.5
(36)	PMe$_2$Ph [d]	+373.3 ± 1	+225 ± 2.5	−25.8
(37)	Ph$_2$PCH$_2$PPh$_2$/2	+527 ± 1	+201.2 ± 0.2	−23.0
(38)	Ph$_2$PCH$_2$CH$_2$PPh$_2$/2	+192 ± 1	+228.9 ± 0.2	+40.7
(39)	Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$/2	+326 ± 1	+222.2 ± 0.3	−0.1
(40)	Ph$_2$PCH$_2$PPr$^i{}_2$/2	+424 ± 1	+202.6, +193.8 ± 0.2	−23.6, +1.4
(41)	Ph$_2$PCH$_2$PBu$^t{}_2$/$_2$	+504 ± 1	+210.6, +190.4 ± 0.2	−22.0, +23.6
(42)	Ph$_2$PCH$_2$PPr^{i}Ph/2	+469 ± 1	+199.7, +198.0 ± 0.2	−23.9, −11.6
(43)	Ph$_2$PCH$_2$PMe$_2$/2	+505 ± 1	+198.4, +194.7 ± 0.2	−23.2, −53.5
(44)	Ph$_2$PCH$_2$PMePh/2	+497 ± 1	+199.2, +198.7 ± 0.2	−23.3, −39.3
(45)	CH$_2$=C(PPh$_2$)$_2$/2	+477 ± 1	+210 ± 0.2	+7.8
(46)	*cis*-Ph$_2$PCH=CHPPh$_2$/2	+150 ± 1	+233.2 ± 0.2	+49.8
(47)	HC(PPh$_2$)$_3$/2 [f]	+555 ± 2	+208.5 ± 0.3	*f*
(48)	Ph$_2$P(S)CH$_2$PPh$_2$/2	+625 ± 1	−8 ± 1,[g] +239.3 ± 0.5	+59.7, +25.3
(49)	Ph$_2$P(S)CH$_2$PMe$_2$/2	+606 ± 1	?, +234.4 ± 0.2	+59.4, −4.4
(50)	Ph$_2$P(S)CH$_2$PPr$^i{}_2$/2	+551 ± 1	−4 ± 1,[g] +225.1 ± 0.3	+60.4, +49.0
(51)	Ph$_2$P(S)CH$_2$PMePh/2	+600 ± 1	−7.5 ± 1,[g] +237.4 ± 0.3	+59.1, +8.9
(52)	Ph$_2$P(S)CH$_2$PPr^{i}Ph/2	+586 ± 1	−5 ± 1,[g] +236.3 ± 0.3	+59.8, +32.9
(53)	Ph$_2$P(Se)CH$_2$PPh$_2$/2	+574 ± 1	−7 ± 1,[g] +236.3 ± 0.3	+42.3, +27.3

[a] In p.p.m. to high frequency of a saturated solution of [W(CO)$_6$] in thf at 55 °C for which Ξ(^{183}W) = 4.151 878 MHz. [b] In Hz. When two figures are given the first refers to the first-mentioned phosphorus in column 2. [c] In p.p.m. ±0.1 p.p.m. to high frequency of 85% H$_3$PO$_4$. When two figures are given the first refers to the first-mentioned phosphorus in column 2. [d] From W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1976, 1616. [e] In CH$_2$Cl$_2$ + C$_6$D$_6$ (lock) at 24 °C. [f] The ^{183}W spectrum is a triplet, confirming that only two phosphorus atoms are co-ordinated. The ^{31}P spectrum is of the A$_2$B type with ^2J(^{31}P$_A$–^{31}P$_B$) = 26.3 Hz and δ(^{31}P$_A$) = −3.2, δ(^{31}P$_B$) = −23.6 p.p.m. [g] Refers to ^2J(^{183}W–^{31}P) since the bidentate ligand is co-ordinated through phosphorus and the chalcogen.

Table 3. Molybdenum-95 and ^{183}W n.m.r. data for miscellaneous derivatives of molybdenum and tungsten hexacarbonyls

No.	Complex [a]	δ(M) [b]	^1J(M–^{31}P) [c]	$W_{\frac{1}{2}}$(^{95}Mo) [d]	δ(^{31}P) [e]
(54)	*trans*-[Mo(CO)$_4${P(OMe)$_3$}$_2$]	+12 ± 2	235 ± 10	60 ± 20	+174.0
(55)	*fac*-[Mo(CO)$_3${P(OMe)$_3$}$_3$]	+104 ± 1	214 ± 2	10 ± 2	+166.2
(56)	*mer*-[Mo(CO)$_3${P(OMe)$_3$}$_3$]	+75 ± 4	210 ± 20 [f]	200 ± 20	+168.0 [g], +176.2 [h,i]
(57)	*fac*-[Mo(CO)$_3${PPh(CH$_2$CH$_2$PPh$_2$)$_2$}]	+101 ± 2	138 ± 10	30 ± 4	+56.1, +83.1 [j]
(58)	*cis*-[Mo(CO)$_2${P(OMe)$_3$}$_4$]	+196 ± 3	220 ± 10 [f]	100 ± 10	+166.8 [g], +175.5 [h]
(59)	*trans*-[Mo(CO)$_2${P(OMe)$_3$}$_4$]	+177 ± 10	?	1 600 ± 10	+179.6
(60)	[Mo(CO){P(OMe)$_3$}$_5$]	+338 ± 10	240 ± 20 [f]	100 ± 10	+164.2 [g], +174.6 [h,l]
(61)	[Mo{P(OMe)$_3$}$_6$] [k]	+498 ± 1	256 ± 3	15 ± 2	+171.6
(62)	*trans*-[W(CO)$_4${P(OMe)$_3$}$_2$]	+56.0 ± 0.5	417.5 ± 0.3	—	+147.6
(63)	*fac*-[W(CO)$_3${P(OMe)$_3$}$_3$]	+193 ± 1	373.6 ± 0.3	—	+143.5
(64)	*fac*-[W(CO)$_3${PPh(CH$_2$CH$_2$PPh$_2$)$_2$}]	+228 ± 1	223.4 ± 0.4 220.9 ± 0.4 [j]	—	+40.7, +72.3 [j]
(65)	*trans*-[W(CO)$_2${P(OMe)$_3$}$_4$]	+275.5 ± 1	430.6 ± 0.3	—	+150.0

[a] In CH$_2$Cl$_2$ + C$_6$D$_6$ (lock) at 24 °C. [b] See footnote *a* to Tables 1 and 2. [c] In Hz. [d] Width in Hz of ^{95}Mo resonance at half-height. [e] In p.p.m. ±0.1 p.p.m. to high frequency of 85% H$_3$PO$_4$. [f] Mean of two ^{95}Mo–^{31}P coupling constants. [g] Phosphorus *trans* to CO. [h] Phosphorus *trans* to phosphorus. [i] |^2J(^{31}P–^{31}P)| = 44.6 ± 0.2 Hz. [j] First figure refers to first-mentioned phosphorus atom in column 2. [k] In light petroleum at 22 °C. [l] |^2J(^{31}P–^{31}P)| = 48 ± 2 Hz.

ingly greater sensitivity of electronic distribution to such changes. This situation is comparable with that previously found for the triad Si,Sn,Pb,[33] and for the dyad Se, Te [34] where the shielding of the heavier nuclei is again more sensitive to chemical environment than predicted by equation (1).

Figure 2 shows the effect upon the ^{95}Mo shielding of increasing *n* from 0 to 6 in the series [Mo(CO)$_{6-n}${P(OMe)$_3$}$_n$]. A very similar curve is given by tungsten. The general appearance of this curve cannot be attributed to changes in the electron-imbalance term since as has been well established in the case of tin [33] this leads to a concavity of the opposite sense, irrespective of which substituent [*i.e.* P(OMe)$_3$ or CO] is considered to have the greater electron-withdrawing ability. Furthermore, in those cases where there is geometrical isomerism, the isomer expected to have the greater orbital-electron imbalance (*viz.* for *n* = 2, the *trans*; for *n* = 3, the

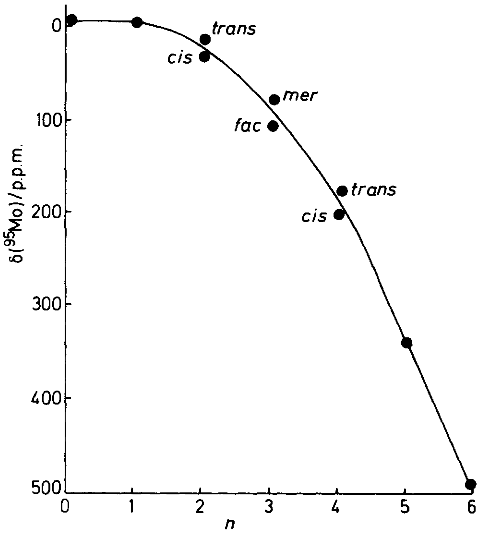

Figure 2. Plot of molybdenum-95 chemical shift against *n* for all members of the series $[Mo(CO)_{6-n}\{P(OMe)_3\}_n]$

mer; for $n = 4$, the *trans*) always has the more- rather than the less-shielded metal atom. This is, however, understandable if changes in ΔE are the governing factor, and is also in accord with observations of ^{195}Pt chemical shifts in *cis* and *trans* isomers.[35] It is of interest in this connection that, unusually, ^{119}Sn shielding in $SnMe_{4-n}\{Fe(CO)_4\}_n$ and certain other similar series with tin–transition metal bonds displays a similar pattern of variation, and this has been attributed to variations in the extent of d_π–d_π overlap leading to changes in $(\Delta E)^{-1}$ for tin and hence to changes in the shielding.[36]

The series of monosubstituted derivatives (5)—(9) and (31)—(33) demonstrate that relatively minor changes in a substituent at a site remote from the metal atom can have a small but not negligible effect upon the shielding. It seems likely that differences in the bulk of the ligands which will put constraints upon the interbond angles at the metal atom may play a major part here. This effect is clearly apparent in the chelate complexes (17)—(25) and (37)—(47). Molecular models show that when the metal is part of a four-membered ring the P–M–P interbond angle will be constrained to be substantially less than its ' natural ' value of 90°, whereas when there is a five-membered ring this P–M–P interbond-angle strain will be reduced. In comparison with the presumably unstrained situations in the *cis*-disubstituted unidentate complexes (15; M = Mo) and (36; M = W), the metal in the complexes with a four-membered chelate ring experiences significantly decreased shielding (*ca.* 100 p.p.m. for Mo, 160 p.p.m. for W), whereas when there is a five-membered ring the shielding is substantially increased. With a still larger ring (where the P–M–P interbond angle should be unstrained) there appears to be little effect upon the shielding. This behaviour can be compared with well established effects of ring size upon ^{31}P shielding in chelate complexes,[19] and also with known trends in tin[37] and lead[38] shielding which are related to deformations of interbond angles.

The experimental ratio of the metal–phosphorus coupling constants $^1J(^{183}W-^{31}P)/^1J(^{95}Mo-^{31}P)$ in corresponding compounds is 1.76 : 1, and yields a ratio for the reduced coupling constants $^1K(WP)/^1K(MoP)$ of 2.76 : 1. The magnitude of this ratio is as expected and can be attributed almost wholly to the smaller value of $\psi(0)_{5s}{}^2$ for molybdenum. The small sizes of any deviations in particular cases from this average

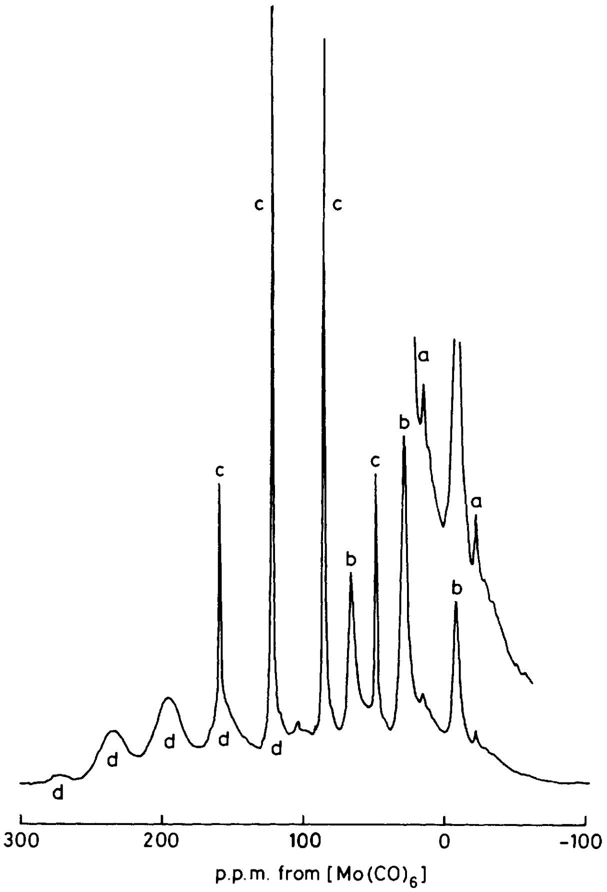

Figure 3. Molybdenum-95 n.m.r. spectrum at 5.85 MHz of an unseparated mixture from the photochemical reaction between trimethyl phosphite and molybdenum hexacarbonyl in a 4 : 1 molar ratio in thf. Peak assignments: a, $[Mo(CO)_5\{P(OMe)_3\}]$; b, *cis*-$[Mo(CO)_4\{P(OMe)_3\}_2]$; c, *fac*-$[Mo(CO)_3\{P(OMe)_3\}_3]$; d, *cis*-$[Mo(CO)_2\{P(OMe)_3\}_4]$

coupling-constant ratio indicate that the tungsten and molybdenum hybridizations and electronic charges are very similar in corresponding compounds. Interestingly, for $^1K(MC)$ in $[M(CO)_6]$ the ratio is 2.88 : 1.

Figure 3 shows the ^{95}Mo spectrum of an unseparated mixture from the reaction between $[Mo(CO)_6]$ and $P(OMe)_3$, and illustrates dramatically the wide variations in ^{95}Mo linewidths which can occur in these systems. It also emphasizes that $W_{\frac{1}{2}}$ is an additional parameter of considerable diagnostic value. For example, in this figure it is immediately apparent from the linewidths just which lines form part of the triplet arising from *cis*-$[Mo(CO)_4\{P(OMe)_3\}_2]$, and which are part of the quartet from *fac*-$[Mo(CO)_3\{P(OMe)_3\}_3]$. By contrast, the ^{31}P spectrum of the same mixture was very complex, since several of the overlapping spin systems present are markedly second order, and was only satisfactorily analyzed *after* the ^{95}Mo spectrum had given the relative proportions of the various components.

The ^{95}Mo linewidths will be dominated by quadrupolar relaxation and thus provide a guide to the degree of electronic asymmetry at the ^{95}Mo nucleus, and to the rate of molecular tumbling in solution. Although a point-charge model will be a very crude approximation for these complex molecules, it can nonetheless be used to provide a satisfactory qualitative description of the ^{95}Mo linewidths for the different species. This approach has been used previously with considerable success to account for niobium-93 linewidths in mixed

$NbCl_6^-$–$NbBr_6^-$ species.[39] For the series of octahedral species $[Mo(CO)_{6-n}\{P(OMe)_3\}_n]$ (n = 0–6) the point-charge model predicts [40] that the electric field gradient at molybdenum will be zero for n = 0 and 6, and also (perhaps surprisingly) for the *fac* isomer when n = 3. In accordance with this, these three molecules do indeed give sharp lines, the finite residual widths (*ca.* 10 Hz) being mainly attributable to molecular deformations which perturb the idealized geometry. The symmetry of the *fac* isomer is also approximated to by arenemolybdenum tricarbonyl derivatives, and in conformity with this we and others [4] have found the ^{95}Mo linewidth to be only 5 Hz in $[Mo(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$, indicative of an essentially zero electric field gradient at molybdenum in this species also. For the other members of the octahedral series, (5), (12), (54), (56), (58), (59), and (60), the point-charge model predicts the electric field gradients to be in the ratio 9 : 16 : 36 : 27 : 16 : 36 : 9. In the case that the molecular tumbling in solution is isotropic the ^{95}Mo longitudinal relaxation rates and hence linewidths should then be proportional to the products of these field gradients and the molecular volumes. This is borne out by the results. Thus (5) with a small field gradient and a small molecular volume gives fairly sharp lines, whereas (60), which in principle has the same field gradient but a much larger molecular volume, also has broader resonance lines. In a similar way, the greater linewidth for (59) compared with (54) can also be attributed to the larger volume and hence slower rate of tumbling in the former molecule. The foregoing treatment is clearly inexact because: (*i*) the point-charge model can only be an approximation in molecules of this complexity, and the effective electronegativities and hence charges of the substituents may differ in different molecules; (*ii*) d_π bonding has been ignored; (*iii*) the molecular tumbling will not be isotropic; and (*iv*) there will be both dynamic and static deformations of the idealized geometry, especially when the molecule contains several bulky substituents. Nonetheless, it does provide a reasonable description of the overall pattern of differential linewidths that is observed.

We conclude that ^{95}Mo and ^{183}W n.m.r. spectroscopy both have much to offer the synthetic chemist, especially as results for one nucleus are generally applicable to the other, and as the general trends of chemical shifts and coupling constants can be roughly accounted for in terms of currently available models. For ^{95}Mo direct observation is undoubtedly the best method of measurement, and also yields invaluable information on linewidths and hence molecular symmetry; for ^{183}W indirect methods of detection are still important, although the increasing availability of sensitive spectrometers operating at high magnetic fields is making direct observation more attractive.

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