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^{13}C NMR Spectra of Monosubstituted Tungsten Carbonyl Complexes. NMR Trans Influence in Octahedral Tungsten(0) Compounds

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^{13}C NMR data and CO stretching force constants of 23 anionic and neutral tungsten pentacarbonyl complexes, $W(CO)_5L$, are compiled. Changes of the ^{13}C chemical shift of the carbonyl groups are shown to arise mainly from the $[\varrho_{AA} + \sum_{B\neq A}\varrho_{AB}]$ term of the paramagnetic shift contribution. The correlation between $\delta(^{13}C)$ and $k(CO)$ is good even if the ligands L span a wide range in terms of donor/acceptor properties. Strong, single-faced π-acceptor ligands L, however, give rise to an additional downfield shift of the ^{13}C resonance of the CO group trans to L. This is explained as being a result of the breakdown of the cylindrical symmetry of the π-bonding system within the L–W–C–O fragment. On the basis of $^1J(^{183}W-^{13}C)$ of the carbonyl group trans to L, the following trans-influence series of ligands L toward tungsten(0) is established: $Ph_2C > CO >$ olefins $> CN^-$, $P(OR)_3$, $PR_3 > H^-$, CH_3^-, NCS^-, $OC(O)R^-$, py $> RNH_2$, RCN, $SC(S)R^-$, $AsR_3 > SbR_3$, $SH^- > Cl^- > Br^- > I^-$. A comparison between this trans-influence series and those for square-planar Rh(I) and Pt(II) complexes reveals the importance of metal–carbon π bonding in octahedral tungsten carbonyl complexes as a mechanism to strengthen the σ interaction.

Introduction

The trans influence of a ligand L in a coordination compound containing the linear fragment L–M–L′ is defined as the ability of the ligand L to weaken the bond to the trans ligand L′. As opposed to the trans effect, which describes the enhancement of the rate of substitution of L′ caused by L, the trans influence is concerned exclusively with ground-state properties of the coordination compound.[1,2]

It has been suggested by Syrkin[3] as early as 1948 and recently explained by Shustorovich[4] that a ligand L forms a strong, short bond to the metal by demanding a high degree of *n*s and $(n-1)$d character from the metal for this bond. Thus, for the bond to the trans ligand L′, less s and d character and more p character remain resulting in an increase of the M–L′ bond length.

The trans influence has mostly been studied by X-ray crystallography, vibrational spectroscopy, and nuclear magnetic resonance.[1] Whereas X-ray techniques certainly give the most direct information on bond lengths and bond strengths, most work has for experimental simplicity been carried out by using metal–ligand stretching frequencies or one-bond spin–spin coupling data. The latter appears to be a justified approach since one-bond coupling constants are directly related to the s character of the hybrid orbitals used by both atoms for this bond.[1] It should be emphasized, however, that the above mentioned techniques are sensitive to different parameters and thus the trans-influence series derived from them are not necessarily the same.

Most NMR work on the trans influence has been carried out on square-planar complexes of Rh(I) and Pt(II) with $^1J(^{103}Rh-^{31}P)$,[5] $^1J(^{195}Pt-^{13}C)$,[6] $^1J(^{195}Pt-^{15}N)$,[7] and $^1J(^{195}Pt-^{31}P)$[8] as probes. The trans-influence series derived from various platinum compounds are all quite similar. There are, however, distinct differences between platinum and rhodium.[5] Thus, it is clear that the trans influence is not an intrinsic property of a ligand but rather depends on the metal and its oxidation state as well.

Recently we discovered a trans-influence series for ligands L in tungsten(0) carbonyl complexes

$$CO > Ph_3P > Ph_3As > Ph_3Sb$$

based on $^1J(^{183}W-^{31}P)$ data for *trans*-$W(CO)_4(PR_3)(L)$ compounds.[9] While the trend within the group 5 ligands was the same as in square-planar Pt(II) compounds, CO turned out to have a particularly strong trans influence in tungsten(0) complexes, much stronger even than organophosphines and phosphites. The question of to what extent the observed metal dependence—$CO < PR_3$ for Pt(II), $CO \simeq PR_3$ for Rh(I), and $CO > PR_3$ for W(0)—might be a peculiarity of the CO ligand prompted us to study the trans influence of a larger range of ligands in tungsten(0) complexes in order to gain additional insight into the still intriguing problem[10] of the trans influence in coordination compounds of the transition metals. Since the range of ligands that can be accommodated trans to a phosphine in tungsten tetracarbonyl derivatives is limited largely to CO, CS, and trivalent compounds of phosphorus, arsenic, and antimony, we turned to ^{13}C NMR spectra of the monosubstituted tungsten carbonyl complexes $W(CO)_5L$ in order to evaluate the trans influence of a larger range of ligands L toward tungsten(0).

Experimental Section

Materials. Solvents were purified by standard procedures and were distilled and stored under nitrogen before use. Tungsten hexacarbonyl and the ligands were commercial products and were used without further purification. All syntheses were carried out in standard Schlenk ware under an atmosphere of nitrogen.

Spectroscopic Measurements. Infrared spectra were obtained from dilute solutions in 0.1-mm CaF_2 cells by using a Perkin-Elmer 283 instrument, which was frequently calibrated with the gas-phase spectra of CO and H_2O. ^{13}C NMR spectra were recorded with a Bruker WH 90 instrument operating at 22.64 MHz with proton noise decoupling. Approximately 1 M solutions in an appropriate deuterated solvent containing 20 mg of $Cr(acac)_3$ as a shiftless relaxation reagent were employed in 10-mm sample tubes. A digital resolution of 0.75 Hz was used routinely, and approximately 200 000 pulses were required to bring out the ^{183}W satellites of the trans CO resonances. When C–H couplings were of interest, the spectra were run in standard 5-mm sample tubes on a Bruker WM 400 operating at 100.61 MHz. At

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Table I. ^{13}C NMR Data and CO Stretching Force Constants[a] of Monosubstituted Tungsten Carbonyl Complexes, $W(CO)_5L$

no.	L	solvent	cis CO		trans CO		k(cis), mdyn/Å	k(trans), mdyn/Å
			δ	J, Hz	δ	J, Hz		
1	H^-	CD_3CN	205.9	124.0	210.3	149	15.06	14.07
2	CH_3^-	CD_2Cl_2	206.9	124.7	209.1	149.2	15.04	13.79
3	Ph_2C[b]	$(CD_3)_2CO$	195.1	127.0	215.0	102.5	16.08	15.87[c]
4	CO[b]	$CDCl_3$	191.0	124.5	191.0	124.5	16.41	16.41[d]
5	CN^-	$(CD_3)_2CO$	197.6	124.3	200.2	139.0	15.53	14.58
6	DMF[e]	$CDCl_3$	193.4	125.0	202.7	134.8	16.41	16.39
7	$C_6H_{11}NH_2$	$CDCl_3$	198.3	130.9	201.2	153.0	15.75	15.09
8	C_5H_5N	C_6D_6	199.2	131.6	202.7	150	15.78	15.11
9	CH_3CN	C_6D_6	195.9	129.4	199.2	154	15.94	15.20
10	SCN^-	$CDCl_3$	197.5	128.7	201.1	150	15.59	14.38
11	Me_3P	$CDCl_3$	197.0	125.0	200.0	145	15.81	15.56
12	$(Me_2N)_3P$	C_6D_6	197.6	125.0	199.0	139.3	15.79	15.45
13	$(MeO)_3P$[f]	neat	196.5	125.1	199.5	139.1	15.84	15.64[g]
14	Ph_3P	$CDCl_3$	197.2	125.7	199.0	140	15.88	15.46
15	$(PhO)_3P$	$CDCl_3$	194.0	125.4	196.5	137.7	16.10	15.86
16	Ph_3As	$CDCl_3$	196.7	125.7	199.0	155	15.90	15.49
17	Ph_3Sb	$CDCl_3$	196.1	124.3	198.2	162	15.92	15.51
18	$CH_3C(O)O^-$	$(CD_3)_2CO$	201.5	131.0	206.0	149.8	15.41	13.99
19	SH^-	$CDCl_3$	200.3	126.5	203.4	161.8	15.37	13.92
20	$HC(S)S^-$	$(CD_3)_2CO$	200.1	128	204.8	155	15.55	14.37
21	Cl^-	$(CD_3)_2CO$	199.6	128.0	201.4	164.7	15.51	14.06
22	Br^-	$(CD_3)_2CO$	198.6	127.2	201.5	170.6	15.53	14.07
23	I^-[b]	$(CD_3)_2CO$	197.1	127.0	201.6	175.8	15.58	14.15

[a] CO force constants were calculated from the infrared frequencies given in the Experimental Section and by using the Cotton-Kraihanzel approach.[30] [b] Reference 31. [c] Reference 32. [d] Reference 30. [e] Dimethyl fumarate. [f] Reference 33. [g] Reference 17.

the high field strength of this instrument no relaxation problems were encountered even without the addition of $Cr(acac)_3$. In all cases the deuterium signal of the solvent was used as internal lock; Me_4Si and the solvent signals served as internal standards.

Synthesis. $PPN[W(CO)_5H]$ was prepared from $W(CO)_5$(piperidine) and $(PPN)BH_4$ following Darensbourg's procedure.[11] IR (THF) (cm^{-1}): ν(CO) 2030 vw, 1886 vs, 1854 s. ^{13}C NMR: ^2J(C-H)(cis) = 7.4 Hz, ^2J(C-H)(trans) = 16.8 Hz.

$Et_4N[W(CO)_5CH_3]$ was obtained from $Et_4N[W(CO)_5Br]$ and $LiCH_3$.[12] IR (THF) (cm^{-1}) ν(CO) 2028 w, 1884 vs, 1836 m. ^{13}C NMR: $\delta(CH_3)$ -34.2, ^1J(C-H) = 123 Hz.

$Et_4N[W(CO)_5CN]$[13] was synthesized by halide displacement from $[W(CO)_5Cl]^-$ in a protic solvent, a method previously developed in our laboratory.[14] KCN (0.65 g, 10 mmol) was dissolved in 50 mL of methanol, and 2.45 g (5 mmol) of $Et_4N[W(CO)_5Cl]$ was added and allowed to react at ambient temperature for 1 h. After addition of 1.66 g (10 mmol) of Et_4NCl, dissolved in 10 mL of water, the volume of the solution was reduced in vacuo to 15 mL, and the precipitated product was collected, washed with water, and dried in vacuo. After recrystallization from THF/hexane light yellow needles were obtained in 55% yield. IR (THF) (cm^{-1}): ν(CO) 2055 w, 1919 vs, 1888 m; ν(CN) 2104 vw. ^{13}C NMR: δ(CN) 134.5 ^1J(W-C) = 90 Hz.

$Et_4N[W(CO)_5NCS]$ was prepared similarly from $Et_4N[W(CO)_5Br]$ and KSCN; yield 75%. IR (THF) (cm^{-1}): ν(CO) 2061 w, 1920 vs, 1875 m; ν(CN) 2095 w. ^{13}C NMR: δ(NCS) 135.9. Both ν(CN) and δ(NCS) are typical for N-bonded thiocyanate.[15]

$W(CO)_5$(dimethyl fumarate)[16] was obtained as follows: 2.45 g (5 mmol) of $Et_4N[W(CO)_5Cl]$, 1.40 g (10 mmol) of dimethyl fumarate, and 2.05 g (6 mmol) of $NaBPh_4$ were stirred in 25 mL of dichloromethane at ambient temperature. After 2 h the solution was filtered over a short silica gel column and the filtrate taken to dryness. Excess ligand was removed by sublimation at 40 °C (10^{-3} torr), leaving a 70% yield of essentially pure yellow, crystalline product. IR (CH_2Cl_2) (cm^{-1}): ν(CO) 2098 m, 2000 sh, 1980 vs. ^{13}C NMR: δ(C=C) 56.8, ^1J(C—H) = 167 Hz, $\delta(CO_2R)$ 171.4, $\delta(OCH_3)$ 52.3, ^1J(C—H) = 148 Hz.

$W(CO)_5L$ compounds with L = cyclohexylamine, pyridine, acetonitrile, Ph_3P, Ph_3As, and Ph_3Sb were all prepared from $Et_4N[W(CO)_5Cl]$ as described previously.[14] IR (hexane) (cm^{-1}), ν(CO): L = cyclohexylamine 2071.5 w, 1931 vs. 1919 m; L = pyridine 2072.2 w, 1933.7 vs. 1921.0 m; L = acetonitrile 2078.5 w, 1944.5 vs, 1927.5 m; L = Ph_3P 2072.3 w, 1942.7 vs; L = Ph_3As 2073.3 w, 1944.7 vs; L = Ph_3Sb 2072.0 w, 1947.0 vs. ^{13}C NMR (L = Ph_3P): ^2J(P–C)(cis) = 7.3 Hz, ^2J(P–C)(trans) = 22.1 Hz.

$W(CO)_5PMe_3$ was obtained photochemically from $W(CO)_6$.[17] IR (hexane) (cm^{-1}): ν(CO) 2069.0 w, 1948.5 m, 1939.0 vs. ^{13}C NMR: ^2J(P–C)(cis) = 7.5 Hz, ^2J(P–C)(trans) = 19 Hz; $\delta(CH_3)$ 21.5, ^1J(P–C) = 29 Hz, ^1J(C–H) = 129 Hz.

$W(CO)_5P(OPh)_3$[18] was prepared in the same way. IR (hexane) (cm^{-1}): ν(CO) 2082.5 m, 1967.5 s, 1958.5 vs. ^{13}C NMR: ^2J(P–C)(cis) = 9.6 Hz, ^2J(P–C)(trans) = 45 Hz.

$W(CO)_5P(NMe_2)_3$[19] was obtained as follows: 1.35 g (3.7 mmol) of $W(CO)_5NCCH_3$ and 1 mL (6 mmol) of $P(NMe_2)_3$ were dissolved in 40 mL of hexane, and the resultant mixture was set aside for 3 days. The slightly turbid yellow solution was filtered, evaporated to 20 mL, and cooled to −30 °C, whereupon the product separated in large yellow crystals in 74% yield. IR (hexane) (cm^{-1}): ν(CO) 2067.3 m, 1942.0 vs, 1933.0 vs.[20] ^{13}C NMR: ^2J(P–C)(cis) = 8.8 Hz, ^2J(P–C)(trans) = 26.0 Hz; $\delta(CH_3)$ 37.8.

$Et_4N[W(CO)_5OC(O)CH_3]$ was synthesized from $Et_4N[W(CO)_5Br]$ and $TlOC(O)CH_3$.[22] IR (THF) (cm^{-1}): ν(CO) 2055 vw, 1906 vs, 1849 s. ^{13}C NMR: δ(OCO) 176.2, $\delta(CH_3)$ 23.0.

$PPN[W(CO)_5SH]$. Angelici's procedure[23] was employed to prepare this compound. IR (cm^{-1}): ν(CO) 2049 vw, 1905 vs, 1845 m. ^1H

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NMR (CH_2Cl_2): δ(SH) −3.30, ^2J(W–H) = 3 Hz.

$Et_4N[W(CO)_5SC(S)H]$. Dithioformate complexes of chromium and tungsten were recently obtained via CS_2 insertion into the M–H bond of the corresponding pentacarbonyl hydrides.[24] The following procedure also gave acceptable yields. A solution of 1.76 g (5 mmol) of $W(CO)_6$ in 300 mL of ethanol was irradiated with a medium-pressure mercury arc (Philips HPK 125) until the infrared spectrum indicated complete conversion to $W(CO)_5EtOH$. $KHCS_2$[25] (1.16 g, 10 mmol) was added, the volume of the solution was reduced to 50 mL, and the product was precipitated by addition of 50 mL of 0.1 M aqueous Et_4NBr and further evaporation to 60 mL. After recrystallization from THF/hexane orange microcrystals were obtained in 69% yield. IR (THF) (cm^{-1}): ν(CO) 2054 w, 1920 vs, 1875 s. ^{13}C NMR: $\delta(HCS_2)$ 239.8, ^1J(C–H) = 171 Hz. ^1H NMR (acetone-d_6): $\delta(HCS_2)$ 11.73, ^3J(W–H) = 5 Hz.

$Et_4N[W(CO)_5Hal]$ complexes were prepared from $W(CO)_6$ and $Et_4N(Hal)$.[26] IR (THF) (cm^{-1}), ν(CO): Hal = Cl 2062 vw, 1912 vs, 1854 s; Hal = Br 2059 vw, 1915 vs, 1855 s; Hal = I 2058.5 vw, 1918.0 vs, 1860.5 s.

Results

The ^{13}C NMR parameters and CO stretching force constants of the cis and trans carbonyl groups of 23 anionic and neutral derivatives $W(CO)_5L$ are presented in Table I. Other spectroscopic data are listed in the Experimental Section. While a number of chemical shift data and even ^1J(W–C) for the cis carbonyls are available from the literature,[27-29] most researchers have not detected ^1J(W–C)(trans). The data in Table I represent the values obtained in our laboratory except where reference is made to the literature.

Discussion

A. Chemical Shifts. The screening constant for a particular nucleus may be expressed as the sum of three contributions:

$$\sigma = \sigma(\text{dia}) + \sigma(\text{para}) + \sigma(\text{other atoms})$$

The chemical shift ranges of nuclei other than protons are thought to arise from changes in σ(para). A detailed treatment of this term has been given by Karplus and Pople.[34]

$$\sigma_p{}^A = -\frac{e^2\hbar^2}{2m^2c^2\Delta E}\langle r^{-3}\rangle_{2p}[Q_{AA} + \sum_{B\neq A} Q_{AB}]$$

Here, ΔE is an average excitation energy, $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube of the distance from the nucleus of a carbon 2p electron, and Q_{AA} and Q_{AB} contain the elements of the charge density, bond order matrix.

Probably most useful for an assessment of the relative importance of the various effects contributing to $\delta(^{13}C)$ of substituted metal carbonyls is the observation of *opposite* trends in $\delta(^{13}C)$ and $\delta(^{17}O)$.[35] Specifically, if a donor L in a substituted metal carbonyl is replaced by a better donor L′ the ^{17}O nuclei are *shielded* whereas the ^{13}C nuclei are *deshielded*.[36]

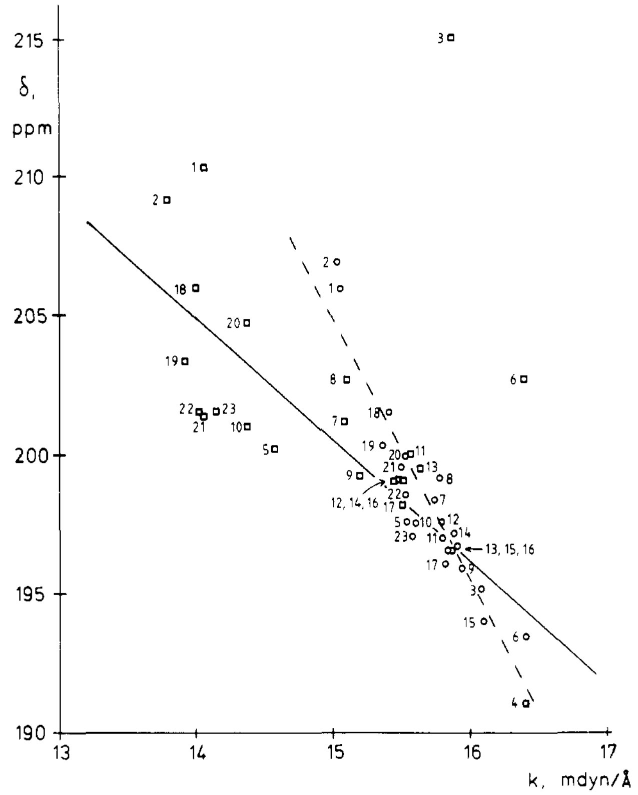

Figure 1. Plot of ^{13}C chemical shifts vs. CO stretching force constants of the carbonyl groups in the compounds $W(CO)_5L$. The data of the cis carbonyls (○) yield the least-squares line (- - -) $\delta = -9.522k + 347.75$, correlation coefficient 0.94. The trans carbonyls (□), excluding compounds **3** and **6** (see text), yield the least-squares line (—) $\delta = -4.417k + 266.83$, correlation coefficient 0.82.

Various explanations have been given to account for this perhaps surprising behavior. Thus, it was suggested that with increasing π donation from the metal to the CO groups the positive charge on carbon would increase whereas on oxygen it would decrease, thus leading to a contraction of the carbon 2p orbitals and to an expansion of the oxygen 2p orbitals.[35c,d] This would be in contradiction to chemical as well as spectroscopic observations. From a study of the rate of attack of organolithium reagents on the CO ligands of $M(CO)_5L$ complexes, Darensbourg and Darensbourg have shown that the positive charge on carbon decreases with decreasing CO stretching force constants, i.e. increasing donor strength of L.[38] Jolly et al. measured the carbon and oxygen 1s binding energies of a larger number of substituted metal carbonyls and found that with increasing donor strength of L the positive charge on *both* carbon and oxygen decreases, the effect actually being larger on carbon than on oxygen.[39]

The downfield shift of the ^{13}C resonances with increasing metal-to-CO π bonding, which is manifested in usually good correlations between $\delta(^{13}C)$ and the carbonyl stretching force constants,[33,40] has mostly been explained as being due to a

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decrease in ΔE. Although the various occupied and unoccupied molecular orbitals of a metal carbonyl complex certainly do not contribute in exactly the same way to ΔE for both the ^{13}C and ^{17}O resonances, one would hardly expect opposite trends. One would then be left with the conclusion that for the ^{13}C resonances the changes in ΔE are predominant in determining σ(para), whereas the ^{17}O chemical shifts are dominated by changes in the charge on oxygen. This quite unsatisfactory situation prompted us to reconsider the $[Q_{AA} + \sum_{B\neq A}Q_{AB}]$ term as a source of the variations of both the ^{13}C and ^{17}O chemical shifts. Model calculations for two limiting cases with (a) no metal-to-carbon π bonding and (b) substantial metal-to-carbon π bonding indeed indicated that this term may well be responsible for a downfield contribution to the ^{13}C resonance and at the same time for an upfield contribution to the ^{17}O resonance with increasing metal-to-carbon π bonding.[41]

For good acceptor ligands, L, such as CO or $P(OPh)_3$, the ^{13}C chemical shifts of the carbonyl groups of the compounds $W(CO)_5L$ are at high field as expected, whereas strong donors such as acetate, methyl, or hydride cause large downfield shifts. A plot of the chemical shifts vs. the Cotton–Kraihanzel force constants of the CO groups is shown in Figure 1. Even for this large range of ligands the correlation is still good for the cis carbonyl resonances, but less so for the trans resonances. To some extent the deviations may be due to pecularities of the force constant calculation. k(trans) is mainly determined by the frequency of the $A_1^{(1)}$ mode, which in many cases is not well separated from the E mode and which also is very solvent dependent. Thus, it is not surprising that for ionic compounds, which had to be recorded in THF solutions, the points fall well below the expected straight line. Bodner et al. have shown that although there exists a good correlation between $\delta(^{13}C)$ of the cis CO's of compounds $M(CO)_5L$ (M = Cr, Mo) and $\delta(^{13}C)$ of analogous nickel complexes $Ni(CO)_3L$, the correlation is not as good for the trans CO's. On the other hand there is still a good correlation between the trans CO chemical shifts of analogous chromium and molybdenum compounds.[42] Thus, it seems that some other effects also contribute to $\delta(^{13}C)$ of the trans carbonyl groups.

There are two compounds for which the deviation from the correlation between k(CO) and $\delta(^{13}C)$ is exceptionally large: the diphenyl carbene complex and the dimethyl fumarate derivative both have trans CO resonances at unexpectedly low fields. If the $k(CO)/\delta(^{13}C)$ correlation would hold, the trans CO carbons should be more shielded by about 18 and 8 ppm, respectively. The diphenylcarbene complex is also exceptional in having a very deshielded ^{17}O resonance of the axial CO.[37] It is perhaps not incidental that these two compounds contain strong "single-faced" π acceptors[43] as the unique ligand L. As a result the tungsten d_{xz} and d_{yz} orbitals (z being the direction of the L–W–CO(trans) bonds) are no longer degenerate. This in turn lifts the degeneracy of the π orbitals of the trans carbonyl group leading in effect to a breakdown of its cylindrical symmetry. Under these circumstances σ_p^{zz} does not vanish any more[41] but makes an additional downfield contribution to the paramagnetic screening tensor *for both* ^{13}C *and* ^{17}O.[44]

B. Two-Bond Coupling Constants $^2J(^{31}P-^{13}C)$. Two-bond coupling constants involving phosphorus in transition-metal complexes are largely determined by the metal, by the stereochemistry of the compound, and by the average electronegativity $\overline{EN}$ of the organic substituents at phosphorus.[46] For bis(phosphine) complexes $W(CO)_4(R_3P)(R'_3P)$, a nearly linear correlation has been found between $\overline{EN}$ and $^2J(P-P)$ with $|^2J(P-P)(trans)]$ always being larger than $|^2J(P-P)(cis)|$.[9] A very similar relationship apparently holds for $^2J(P-C)$ in the pentacarbonyl series,[42] although the range of $^2J(P-C)(cis)$ is too small to allow any definite conclusions. Recent double-resonance experiments also indicate that the signs of $^2J(P-C)$ in tungsten carbonyl complexes[47] are analogous to those of $^2J(P-P)$,[48] i.e. positive for trans couplings and negative for cis couplings.

C. One-Bond Coupling Constants $^1J(^{183}W-^{13}C)$(cis). The magnitude of a spin–spin coupling constant across one bond is dominated by the Fermi contact term, which is usually given in its simplified form:

$$^1J(A-B) = \frac{64h}{9}\beta^2\gamma_A\gamma_B\zeta^2\frac{|S_A(0)|^2|S_B(0)|^2}{^3\Delta E}\alpha_A{}^2\alpha_B{}^2$$

γ_x are the gyromagnetic ratios of the nuclei A and B, ζ is a normalizing factor for the valence-bond function describing the A–B bond, $|S_x(0)|^2$ represents the s-electron densities at the nuclei, $^3\Delta E$ is an average singlet–triplet excitation energy, and $\alpha_x{}^2$ are the s characters of the hybrids used for A–B bonding by the atoms A and B.[49] In a series of closely related compounds, it is usually assumed that $|S_x(0)|^2$ and $^3\Delta E$ change very little and variations in $^1J(A-B)$ are largely due to changes in s character of the bonding hybrids.

For our series of compounds $^1J(W-C)$(cis) is remarkably constant. This gives us confidence that the above mentioned assumption about the s-electron densities and $^3\Delta E$ is essentially correct. Although $^1J(W-C)$(cis) varies only by 8 Hz, a few interesting features emerge. $^1J(W-C)$(cis) appears to be determined solely by the atom that occupies the unique coordination site. Thus, for all phosphorus donor complexes covering the entire range from the strongly donating trialkylphosphines to the weakly donating triphenylphosphite, a value of 125 Hz is found. All nitrogen donors regardless of their hybridization at nitrogen are found in the upper range at 130 ± 1.5 Hz. Carbon donors as different as CO, olefins, carbene, or CH_3^- cause the cis coupling constant to lie between 124 and 127 Hz.

D. One-Bond Coupling Constants $^1J(^{183}W-^{13}C)$(trans). The Trans Influence. From the data in Table I the ligands L may be arranged in a series of decreasing trans influence in octahedral tungsten carbonyl complexes, as derived from the increase of $^1J(^{183}W-^{13}C)$ of the axial carbonyl group in $W(CO)_5L$: $Ph_2C > CO >$ olefins $> CN^-, P(OR)_3, PR_3 > H^-, CH_3^-, NCS^-, OC(O)R^-$, py $> RNH_2, RCN, SC(S)R, AsR_3 > SbR_3, SH^- > Cl^- > Br^- > I^-$. This series differs in many respects from those obtained from NMR studies of square-planar complexes of Rh(I) and Pt(II).[5-8] On the basis of $^1J(^{195}Pt-^{31}P)$ of a series of square-planar complexes [(di-

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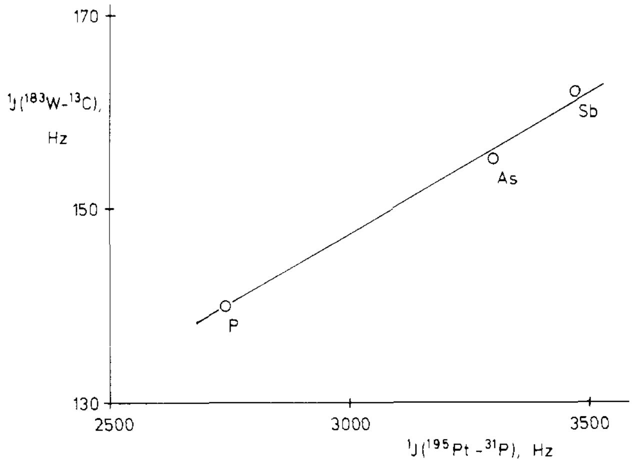

Figure 2. Plot of $^1J(^{183}W-^{13}C)$ of the CO group trans to EPh_3 in $W(CO)_5EPh_3$ vs. $^1J(^{195}Pt-^{31}P)$ of the phosphorus trans to EPh_3 in $[(diphos)Pt(CH_3)EPh_3]^+$.

phos)Pt(CH_3)X$]^{n+}$, Appleton and Bennett derived the following trans-influence series:[8a] $CH_3^- > P(OR)_3, PR_3 > CN^- > SH^-, CO > AsPh_3 > SbPh_3 > py > I^- > OC(O)CH_3^- > Cl^- > NCCH_3$. Other authors have obtained similar though less complete series. Their data indicate that H^- is almost as high in trans influence as CH_3^-,[8c,d] N-bonded NCS^- is similar to Cl^-,[8c] and ethylene equals pentylamine.[50] If we compare this series with our tungsten series, the high trans influence of CO toward tungsten is most conspicuous. The main reason for this certainly is the high π-donor ability of tungsten(0), which contributes largely to the strength of the tungsten–carbon bond and reinforces the σ interaction. The strong W–C bond in turn makes the CO group an ideal probe for a study of the trans influence.[10] If a ligand L trans to a CO group makes less demand for the tungsten 6s orbital, rehybridization will take place to increase the contribution of this orbital to the tungsten–carbon σ bond.

There are several mechanisms by which a ligand can change the hybridization within the linear L–W–CO fragment. From simple perturbation theory, Burdett and Albright[10] arrived at an expression for the bond weakening:

$$\Delta_{\mathrm{ML'}} = 2k^4\frac{S'^2_\sigma}{(\Delta\epsilon')^2}\left[\frac{S'^2_\sigma}{\Delta\epsilon'} - \frac{S_\sigma^2}{\Delta\epsilon}\right]$$

In our case M corresponds to tungsten and L′ to the axial CO ligand, S_σ^2 and S'^2_σ are the overlap integrals of the W–L and W–C σ interactions, respectively, and $\Delta\epsilon$ and $\Delta\epsilon'$ are the energy separations between the donor orbitals of L and CO and the tungsten acceptor orbital. Thus, an increase in $\Delta\epsilon$ or a decrease in S_σ^2 will strengthen the tungsten–carbon bond, allowing for a rehybridization such as to maximize $S'^2_\sigma/\Delta\epsilon'$ for the W–C bond. This is nicely shown by the trans-influence series $Ph_3P > Ph_3As > Ph_3Sb$. According to photoelectron spectroscopy, these ligands have almost identical energies of their lone pairs.[51] However, the C–E–C angle decreases along this series[52] indicating an increase of the s character of the lone pair which thus becomes less available for bonding. This results in a decrease of S_σ^2 and thus in an increase of the W–C(trans) interaction. This mechanism should be essentially independent of the metal, and indeed there exists a linear correlation between ^1J(W–C)(trans) in $W(CO)_5EPh_3$ and ^1J(Pt–P)(trans) in $[(diphos)Pt(CH_3)EPh_3]^+$ (Figure 2). Similarly the weaker trans influence of amines compared to phosphines may be explained. Both types of donors have similar ionization potentials, amines, however, being hard bases interact less strongly with soft transition-metal acids. Thus, it is again a smaller S_σ^2 that is responsible for the lower trans influence of amines.

The much higher importance of π bonding in tungsten(0) compounds as compared to platinum(II) derivatives has already been mentioned. There are a number of other examples to confirm this. Along the series cyclohexylamine, pyridine, and acetonitrile, there seems to be a slight increase in π-acceptor ability as evidenced by the increase of k(trans) of their $W(CO)_5$ complexes. In the same direction the s character of the lone pair at nitrogen increases, accompanied by a decrease in orbital energy. Thus $\Delta\epsilon$ becomes larger, which should result in an increased interaction between the metal and the trans ligand. This is indeed observed in square-planar platinum compounds.[8a] Toward tungsten(0) the three nitrogen donors have quite similar trans influence indicating that the increase of $\Delta\epsilon$ is compensated for by an approximately equal increase in S_σ^2. This increase of σ overlap is brought about by an additional π interaction between the filled tungsten t_{2g} orbitals and the π^* levels of pyridine and acetonitrile, respectively.

Along the same lines, the reversed order of trans influence of CO, CN^-, and CH_3^- (i.e. $CO > CN^- > CH_3^-$ toward W(0) and $CH_3^- > CN^- > CO$ toward Pt(II)) may be explained. First of all, any negatively charged ligand will bind more strongly to the positively charged platinum fragment than to the uncharged $W(CO)_5$ unit. In addition, replacement of oxygen by the less electronegative nitrogen or hydrogen atoms and addition of a unit negative charge substantially increase the energy of the lone pair at carbon, making CN^- and especially CH_3^- much better trans-influence ligands toward platinum. On the other hand, CN^- is only a weak π acceptor and CH_3^- is none at all, as evidenced by the low carbonyl stretching force constants of their $W(CO)_5$ derivatives. Thus, these anions are weaker trans-influence ligands toward tungsten.

The low trans influence of the halides toward both tungsten and platinum at first sight seems to be in contradiction to the stability of the metal–halogen bond. Their donor orbitals, however, are appreciably higher in energy. Thus, the optimum hybridization within a linear L–M–X fragment will be one with a high degree of metal p character in the M–X bond and consequently a high s character in the M–L bond. The relative order of trans influence toward tungsten

$$Cl^- > Br^- > I^-$$

is analogous to the order found for ER_3 ligands. Interestingly, Appleton and Bennett found in their platinum series $Cl^- < I^-$.[8a] Possibly it is the higher polarizability of I^- that is responsible for the stronger bond to the positively charged platinum fragment.

Conclusions

The trans influence of a number of neutral and anionic ligands toward tungsten(0) has been derived from $^1J(^{183}W-^{13}C)$ of the axial CO group of monosubstituted derivatives of hexacarbonyltungsten. Several mechanisms that, of course, are not independent from each other contribute to the trans influence of a particular ligand. Changes in overlap population and orbital energy separation for the interaction between tungsten and the unique ligand lead to a change of the hybridization within the linear L–W–CO fragment. Those ligands L have a particularly low trans influence whose donor orbitals have a low spatial extension (hard ligands, e.g. amines, and ligands with high s character of their donor orbital, e.g. arsines and stibines), whose donor orbitals are so high in energy

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that they prefer to interact with the tungsten $6p_z$ orbital (e.g. halides), and whose σ interaction with tungsten is not reinforced by an accompanying π interaction (e.g. hydride, methyl, amines, acetate).

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Registry No. $W(CO)_5H^-$, 77227-36-2; $W(CO)_5CH_3^-$, 57574-50-2; $W(CO)_5CPh_2$, 50276-12-5; $W(CO)_6$, 14040-11-0; $W(CO)_5CN^-$, 14971-29-0; $W(CO)_5(dmf)$, 76096-25-8; $W(CO)_5C_6H_{11}NH_2$, 61779-22-4; $W(CO)_5C_5H_5N$, 14586-49-3; $W(CO)_5CH_3CN$, 15096-68-1; $W(CO)_5NCS^-$, 45113-96-0; $W(CO)_5PMe_3$, 26555-11-3; $W(CO)_5P(NMe_2)_3$, 19976-82-0; $W(CO)_5P(OMe)_3$, 23306-42-5; $W(CO)_5PPh_3$, 15444-65-2; $W(CO)_5P(OPh)_3$, 23306-41-4; $W(CO)_5AsPh_3$, 29743-02-0; $W(CO)_5SbPh_3$, 29743-03-1; $W(CO)_5OC(O)CH_3^-$, 45146-15-4; $W(CO)_5SH^-$, 65198-80-3; $W(CO)_5SC(S)H^-$, 77227-31-7; $W(CO)_5Cl^-$, 14911-74-1; $W(CO)_5Br^-$, 15131-04-1; $W(CO)_5I^-$, 14911-58-1.

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Formation of Palladium(II) and Palladium(I) Carbonyl Halo Complexes

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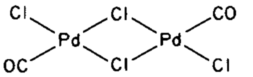
The preparation of the dimeric palladium(II) chloro carbonyl $Pd_2(CO)_2Cl_4$ from $PdCl_2$ and carbon monoxide in thionyl chloride as solvent was studied as a function of temperature and carbon monoxide partial pressure. The reaction, $2PdCl_{2(s)} + 2CO_{(SOCl_2)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)}$, was found to be exothermic with $\Delta H° = -13.6 \pm 0.2$ kcal/mol of dimer and with $\Delta S° = -30.8 \pm 0.8$ eu. The enthalpy change, together with the accepted mean Pd–Cl bond energies and other peripheral information, has been used to deduce a value of about 24 kcal for the Pd–CO bond energy in the palladium(II) carbonyl derivative. This is compared with the metal–CO bond energies of other metal carbonyl derivatives. A high-yield synthesis of the polymeric palladium(I) chloro carbonyl $[Pd(CO)Cl]_n$ is also reported, consisting of treating $PdCl_2$ or $Pd_2(CO)_2Cl_4$ with CO in acetic anhydride as solvent.

In an earlier publication[1] we had established the existence of the elusive[2-5] dimeric chloro carbonyl complex $Pd_2(CO)_2Cl_4$ assumed to have the trans structure **1**. Its extremely high ν_{CO} value (2163 cm^{-1} in thionyl chloride) suggested a strongly reduced π-back-bonding contribution and a palladium–CO bond presumably weaker and/or more reactive than usually assumed for other metals of lower d^n configurations, i.e. toward the middle part of the transition series. Palladium thus appears to have unique behavior as far as its bonding to CO is concerned, a feature possibly typical of silver(I), for which no stable isolable carbonyl complexes are known.[6]



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A study of the formation of $Pd_2(CO)_2Cl_4$ from $PdCl_2$ and carbon monoxide and the measurement of some thermodynamic parameters, which are the subjects of this paper, was therefore in order. In addition a high-yield preparation of $[Pd(CO)Cl]_n$ is reported.

Experimental Section

The chloro carbonyl derivative $Pd_2(CO)_2Cl_4$ was prepared as previously described.[1] Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified carbon monoxide or nitrogen. Solvents were dried prior to use by the conventional methods. The IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with a grating monochromator, and each spectrum was calibrated with both CO and water vapor: the wavenumber values are believed to be accurate to ±1 cm^{-1}. The experiments were carried out in stainless-steel nickel–chrome (18/8) autoclaves, which were found to be unaffected by thionyl chloride up to 120 °C. Caution must be taken, however, to avoid contact of the autoclave with moisture prior to complete evaporation of the solvent in vacuo after each experiment.

Table I. Solubilities of Carbon Monoxide and $Pd_2(CO)_2Cl_4$ in Thionyl Chloride

CO				$Pd_2(CO)_2Cl_4$		
t, °C	p_{CO},[a] atm	$10^3[CO]$,[b] M	$-\ln X_2$[c]	t, °C	$[Pd_2(CO)_2Cl_4]$, M	$-\ln K$[d]
10.1	4.1	8.22	7.43	−10.00	0.139	1.97
23.2	0.85	6.30	7.68	0.0	0.195	1.64
31.5	0.75	6.27	7.67	14.0	0.349	1.05
42.5	5.1	6.73	7.60	16.5	0.363	1.01
51.7	5.0	7.33	7.50			
58.8	5.0	6.24	7.65			

[a] For experiments at superatmospheric pressure, this is the manometer reading plus 1 atm, corrected for the vapor pressure of the solvent. [b] This is the solubility normalized to 1 atm of pressure. [c] X_2 is the mole fraction of CO dissolved; see ref 8. [d] This is referring to the equilibrium $Pd_2(CO)_2Cl_{4(s)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)}$. From the $-\ln K$ vs. $1/T$ plot, the extrapolated concentrations of $Pd_2(CO)_2Cl_4$ were found to be 0.49 and 0.57 M, at 25 and 30 °C, respectively. From the slope of the same plot, an enthalpy change for the solubilization of $Pd_2(CO)_2Cl_4$ of +5.8 ± 0.2 kcal/mol was calculated.

Solubility of Carbon Monoxide in Thionyl Chloride. The solubility data are in Table I. For experiments at superatmospheric pressure, the autoclave (120.9-cm^3 capacity) was charged by suction with a known volume of thionyl chloride, which was then degassed by connecting the autoclave to a vacuum system and evaporating a small known amount of the liquid into a cold trap. The final volume of thionyl chloride in the autoclave was then determined exactly (the experiments were carried out with volumes of solvent between 85 and 95 cm^3). The autoclave was then introduced into an oil bath maintained at a constant temperature identical with that of a carbon monoxide pressure tank connected to the autoclave with a short stainless-steel high-pressure capillary tube. While the autoclave was maintained in a fixed position with the smallest possible surface area for the internal liquid, carbon monoxide from the tank was rapidly

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