+4 oxidation states, only forms an anhydrous sulfate with a +3 state, while Hf and Zr both form anhydrous sulfates with a +4 state. Except for Ta (+5), Tc (+7), and Au (+1 or +3), all of the metals for which anhydrous sulfates are not known commonly are present as +4 in other compounds. In the structure $Zr(SO_4)_2$, each Zr atom is in sevenfold coordination with bonds to one oxygen of each of seven sulfate tetrahedra.[9] Each Mo in both $K_4Mo_2(SO_4)_4\cdot 2H_2O$[3] and $K_3Mo_2(SO_4)_4\cdot 3.5H_2O$[2] is bonded to oxygen atoms of each of five sulfate tetrahedra and to one Mo atom, resulting in a $Mo_2(SO_4)_4^{4-}$ ion in the former structure and a $Mo_2(SO_4)_4^{3-}$ ion in the latter. Thus, the coordination of the Mo and Zr in these compounds is very different. In the structure of $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$, the Nb occurs as $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$.[4] The Nb atoms form a triangular cluster, where each Nb is bonded to two other Nb atoms rather than to just one metal atom as occurs in the Mo structure mentioned above. Like the Mo in the above two Mo-containing compounds, the Re in $Na_2Re_2(SO_4)_4\cdot 8H_2O$ is coordinated by five oxygens and another Re atom.[10]

In all the known simple anhydrous sulfates, the metals are bonded only to oxygens from the sulfate groups, and no metal-to-metal bonding is present. For Mo, Re, and Nb, only complex binary sulfate hydrates in which the Mo, Re, and Nb are bonded to other Mo, Re, and Nb atoms as well as to oxygen atoms have been described. Cotton suggested that in compounds other than carbonyls, Nb, Mo, Tc, Ta, W, and Re formed metal–metal bonds much easier than did the other metals in the second and third transition series.[11] If his idea is correct, then sulfates of these metals may not be known because earlier attempts at syntheses may have used starting materials such as MoO_2, which contains a metal–metal bond[12] or the bond may have formed during synthesis and prevented anhydrous sulfate formation. Use of the proper starting materials and avoidance of metal–metal bond formation during synthesis may be necessary for the crystallization of these anhydrous sulfates that have never been crystallized.

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(13) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Observation of a Novel ^{31}P NMR Cis-Influence Series: Implications for the Relative Basicity of PPh_3 and PMe_3 in Tungsten Carbonyl Complexes

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The correlation of ligand donor strength with trends in spectroscopic data has been sought repeatedly.[1-6] The attraction of such an approach is that widely divergent ligand types can be examined fairly readily and more importantly be compared to each other. Conventionally, infrared[1] and NMR[2,3] data have been used and are directly applicable if one assumes a direct correlation of ligand donor strength with ligand trans influence.[4,5] More recently, spectra that probe electronic energy levels have also been used to compare ligand donor strength:[4,6] in a study of $PtCl_3L^-$ complexes,[6] PEt_3 was found to be a better donor than PPh_3, while in a study of tungsten carbonyl phosphine complexes, the provocative conclusion was reached that PPh_3 is a better donor than PMe_3,[4] a direct challenge to the common wisdom.[7] In fact, the infrared and NMR data brought to bear on the question of phosphine basicity toward tungsten carbonyl fragments are undeniably equivocal,[3,4] even though broader trends are often in accord with expectation. For instance, Schenk has reported two trans-influence series based on $^1J(^{183}W\text{–}X)$ ($X = {}^{31}P, {}^{13}C$) in *trans*-$LW(CO)_4X$ ($X = PR_3$, CO).[3] When strictly applied to the narrow region of L = P-donor ligands, however, his results suggest the basicity order $P(OPh)_3 > P(i\text{-}Pr)_3 > PPh_3$ based on *trans*-$LW(CO)_4(P\text{-}i\text{-}Pr_3)$ but $P(OPh)_3 > PPh_3 > PMe_3$ based on $LW(CO)_5$. The differences in the coupling constants are not large however—Schenk grouped the three ligands together—and of course, the common wisdom would hold that $P(OPh)_3$ is also misplaced in these series.[7] The question we wish to address here, then, is whether a simple NMR-derived ligand series can be found that is reliable both for a broad series of ligands and for the narrower range of phosphines. We report here a novel ^{31}P NMR *cis*-influence series based on both chemical shifts and phosphorus–metal coupling constants

Table I. ^{31}P NMR Data for **1**

		*P*Me$_3$		L		
entry	L	δ^a	$^1J(P\text{–}W)^b$	δ	$^1J(P\text{–}W)$	$J(P\text{–}P)$
1	SbF_6^-	−16.25[c]	282.9			
2	PF_6^-	−16.64[d]	283.2	−139.30[e]	0	0
3	BF_4^-	−17.46[f]	282.0			
4	acetone	−20.40	275.5			
5	C_6H_9CHO[g]	−20.42	277.1			
6	acrolein	−20.45	276.6			
7	Me_2SO_2	−21.07	275.9			
8	camphor	−21.07	274.7			
9	Me_2NCHO	−21.10	276.5			
10	$PF_2O_2^-$	−21.48	274.4	−17.35[h]	0	4.7
11	EtOH	−21.49	272.8			
12	CD_3OD	−21.61	272.8			
13	D_2O	−21.85	273.6			
14	THF	−21.92	274.4			
15	MeCN	−27.03	263.8			
16	Et_3N	−28.34	264.9			
17	Ph_3P	−35.96	252.4	9.29	178.2	23.2
18	$MePh_2P$	−36.55	251.0	−14.56	172.3	23.6
19	Me_2PhP	−36.92	251.5	−31.26	165.4	23.6
20	Me_3P	−37.45	250.1	−42.57	163.4	24.6
21	Cl^-	−28.34	263.8			
22	Br^-	−34.43	263.7			
23	I^-	−44.83	261.9			
24	CO[i]	−33.23	244.1			
25	$(MeO)_3P$	−34.76	247.6	109.73	286.0	38.4
26	Cy_3P[j]	−38.92	252.8	25.64	219.1	21.9

[a] ppm; negative values upfield of H_3PO_4. [b] Hz. [c] Septet, $J_{PF} = 39.8$ Hz. [d] Broad singlet. [e] Septet, $J_{PF} = 731.7$ Hz. [f] Quintet, $J_{PF} = 39.7$ Hz. [g] Diels–Alder adduct of butadiene and acrolein. [h] Triplet, $J_{PF} = 966.2$ Hz. [i] Structure in question; see text. [j] Cy = cyclohexyl.

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0020-1669/87/1326-1826$01.50/0

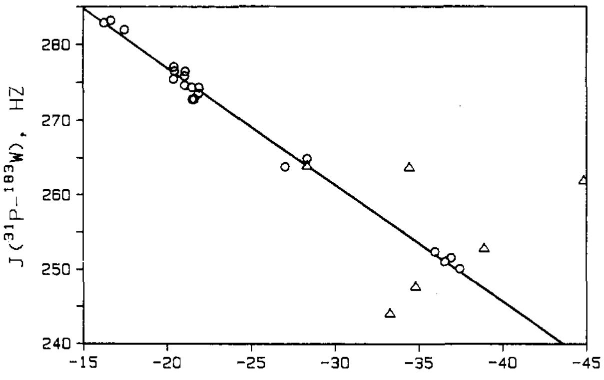


Figure 1. Plot of $^1J(^{31}P-^{183}W)$ vs. $\delta(^{31}P)$ for the PMe_3 ligand cis to L and NO in **1**. The circles, entries 1–20 in Table I, are the data fit to the least-squares line. $^1J = (1.55 \pm 0.03)\delta + (308.0 \pm 0.9)$; correlation coefficient = 0.9958; standard deviation (Hz) = 1.03.

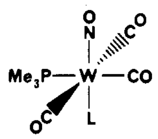
in tungsten carbonyl *nitrosyl* compounds, in which these two quantities are linearly correlated for 20 ligands. A hypothesis for the origin of this correlation is presented, and implications for ligand donor strength are discussed. The key feature that distinguishes our approach from all others is that only ligands that fit the *correlation* are compared with respect to ligand donor strength. Those ligands that do not fit the correlation cannot be compared objectively with those that do, so while our method will not allow *all* ligands to be compared with each other, those that *can* be compared will be ordered with some confidence.

Experimental Section

All manipulations and NMR sample preparations were carried out in a Vacuum Atmospheres inert-atmosphere glovebox under recirculating nitrogen. The compounds in Table I were prepared as described elsewhere.[8a,b] Briefly, entries 1–3 were prepared by nitrosylation of $Me_3PW(CO)_5$ with the appropriate NO^+ salt, entries 4–9 and 11–26 were prepared by ligand exchange with entry 1, and entry 10 was prepared by hydrolysis of entry 2 with 2 equiv of D_2O. Entries 1–3, 6, 8, 15, 17, 20, and 24 were fully characterized, while the rest were characterized by ^1H and ^{31}P NMR; these latter compounds were prepared in situ by addition of 1 equiv of the neutral ligand or of the Et_4N^+ or $(Ph_3P)_2N^+$ salt of the anion to a CD_2Cl_2 solution of entry 1. NMR spectra were recorded on JEOL FX90Q and Bruker WP-200 spectrometers, the latter with the probe thermostated at 298 K. Chemical shifts reported are with reference to external 8.5% H_3PO_4.

Results and Discussion

The ^{31}P chemical shifts and one-bond phosphorus–tungsten coupling constants for **1** are collected in Table I and plotted in Figure 1, together with the best-fit (to the circle data points) least-squares line. The fit is remarkably good for a wide range of ligands cis to the reporter PMe_3 ligand. We propose to use this correlation as the criterion for inclusion of any ligand in this cis-influence series. Of the ligands examined, only CO, Br^-, and I^- are markedly anomalous and therefore not included; while Cl^- does fit, this could be fortuitous (given that the three halides have similar coupling constants), and so to be conservative, it too is not included. The last two entries not included in the least-squares fit, $P(OMe)_3$ and PCy_3, are not quite as anomalous but are still greater than five standard deviations away from the line.



1

Before discussing the observed cis-influence series, a few comments on the compounds themselves, and in particular on the anomalies, are in order. The complexes of the noncoordinating ligands SbF_6^-, PF_6^-, and BF_4^- each have the $W(\mu\text{-}F)MF_n$ (MF_n = SbF_5, PF_5, BF_3) linkage, as established by X-ray crystallography and ^{31}P and ^{19}F NMR.[8a,b] Addition of each of the ligands in Table I results in immediate displacement of SbF_6^- from **1** (L = SbF_6^-), as judged by the loss of the characteristic phosphorus–fluorine coupling seen in the ^{31}P NMR. We believe that the aldehyde, ketone, amide, and sulfone ligands each bind via an η^1 tungsten–oxygen linkage, on the basis of an X-ray diffraction study of **1** for L = acrolein.[8c] Similarly, the $PF_2O_2^-$ ligand[9] apparently binds via oxygen, since no phosphine P–F coupling is seen. Of the anomalous compounds, entry 24 (L = CO) has provided the most difficulty: an X-ray diffraction study shows that rearrangement to *trans*-$(PMe_3)(NO)W(CO)_4{}^+SbF_6^-$ has occurred,[8b] but the ^{13}C NMR spectrum of this extremely insoluble compound is presently interpreted[8e] as suggesting that the solution structure is **1**. There is no evidence to suggest that the structures of the halide, $P(OMe_3)$, or PCy_3 adducts are incorrect, however. For instance, we have noticed that whenever a phosphorus ligand is trans to NO,[8d] substantial line broadening is seen in the ^{31}P NMR spectra. This allows assignment of the signals in entry 20 (L = PMe_3) in particular but is also seen for each of entries 17–19 and 25–26 as well. Since no such broadening is seen for the halides, the placement of phosphorus ligands in the halide, $P(OMe)_3$, and PCy_3 adducts with respect to NO is unambiguous. In combination with IR data for entry 22 (X = Br^-),[8b,10] the structures of these compounds do not account for the fact that they do not fit our observed correlation. These anomalies will be reconsidered below.

Since a wide range of ligands in **1** do in fact give rise to a good correlation of coupling constant with chemical shift, the first question to be addressed involves the origin of this effect. As noted above, trans-influence series have been observed on the basis of $^1J(M-X)$ where X is a reporter nucleus (^{13}C or ^{31}P) trans to the ligand that is being varied.[2,3] This is typically understood in terms of the Fermi contact term, which dominates the magnitude of one-bond spin–spin coupling.[3] For a series of closely related compounds, change in this term is associated with the degree of s character in the bonding orbitals. When the trans ligand is strongly bound, it will demand more s and d character from the metal hybrid orbitals and thus lower the s character available to the reporter nucleus; hence, high-trans-influence ligands result in low $^1J(M-X)$. A similar result might be expected for the cis ligand,[11] but in tungsten carbonyl complexes previously examined, little correlation was observed.[3] Presumably, the effect is mitigated in the cis reporter ligand, since three other cis ligands share the same orbitals, unlike the trans ligand. Nonetheless, a correlation between donor strength and cis-coupling constant *is* apparent in **1**: the weakly donating "noncoordinating" anions SbF_6^-, PF_6^-, and BF_4^- give rise to the largest tungsten–phosphorus coupling constants of ~283 Hz, the strongly donating PMe_3 ligand gives rise to a significantly smaller coupling constant of 250 Hz, and all the other ligands that fit the coupling constant/chemical shift correlation—and most of which are obviously intermediate in donor ability—give rise to tungsten–phosphorus coupling constants that fall between these two extremes.

Ligand effects on chemical shift are much more complicated, since for atoms other than hydrogen, chemical shift is thought to be dominated by the paramagnetic term.[3,12] This is particularly unfortunate in the case at hand, since diamagnetic shielding of the reporter PMe_3 ligand would provide a sound rationalization for the observed correlation. That is, the PMe_3 ligand in **1** is most

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(8) (a) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599–4601. (b) Honeychuck, R. V.; Hersh, W. H., manuscript in preparation. (c) Honeychuck, R. V., unpublished results. (d) Hersh, W. H., manuscript in preparation. (e) Doubly labeled compound 1-*di*(*carbonyl*-^{13}C) (L = ^{13}CO) should clarify this point.

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(10) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 1487–1492.

(11) This expectation is contradicted by square-planar platinum complexes, however, in which the opposite effect on cis-coupling constants was seen.[2c]

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deshielded for the weakly donating SbF_6^-, PF_6^-, and BF_4^- ligands (−16.25 to −17.46 ppm) but much more strongly *shielded* for the strong donor PMe_3 ligand (−37.45 ppm). Nonetheless, since the Me_3P–W linkage itself is unchanged, it would be unwarranted to ascribe this 20 ppm change to diamagnetic shielding. The paramagnetic term will be affected by (1) steric interactions, (2) electronegativity of substituents on the magnetically active nucleus, and (3) most generally the orbital populations and energy levels.[12] Obviously, steric interactions can present a problem in comparing cis ligands, since calculations indicate that large ^{31}P NMR shifts occur upon bond angle changes of only 1–2°.[12b] Of the ligands we have examined, PCy_3 is obviously the most bulky, so it is perhaps not surprising that it does not fit our correlation. Interestingly, a small upfield shift is apparent, in accord with Schenk's observations on bulky cis phosphines.[3a] Nonetheless, with this one exception steric interactions do not appear to be a factor here. We therefore further suggest that steric interactions play no role in the lack of a correlation of the type reported here when the sterically innocent carbonyl ligand is the cis reporter group.[3b] The second factor in the paramagnetic term will also likely have little effect, since no change occurs in the atoms attached to phosphorus, although one could argue that the electronegativity of the tungsten fragment changes. Thus, the more abstract changes in orbital populations and energy levels most likely account for the observed chemical shift changes. High-field shifts will arise due to an increase in the mean excitation energy (the energy difference between filled and empty molecular orbitals)[12] and due to increases in d-electron density on phosphorus.[12d] This latter mechanism is attractive, since it can directly account for why increasing ligand donor ability correlates with the chemical shift of the reporter ligand increasing to higher field.

The obvious question raised by our data is whether such a linear correlation has been observed previously, given the possible theoretical justification described above. The answer is yes in square-planar platinum compounds, but only for limited series of cis- or trans-influence ligands, and furthermore chemical shift correlations have been in *both* the positive and negative sense relative to coupling constant.[2a,b,d,5d] The present work is the first report of such a correlation in octahedral complexes, and we suggest that the nitrosyl ligand is the critical factor. The NO ligand is one of the few considered to be a better π-acid than the CO ligand,[13] and hence, it ought to dominate any NMR observables affected by π-back-bonding. Thus, since a $d\pi$ orbital is shared by NO, PMe_3, and the cis-influence ligand L, any π-back-bonding effects *of L* on either $\delta(PMe_3)$ or $^1J(^{183}W-^{31}P)$ should be mitigated. For instance, any synergism that results in good π-back-bonding leading to apparent increases in σ-donor ability[5b,6,12c] will lead to concomitant changes in coupling constant and (presumably) chemical shift. Perhaps more directly, changes in d-orbital population, as noted above, will lead to changes in chemical shift. One must be careful in this interpretation of chemical shift mechanism, since here we are referring to changes in phosphorus d-orbital population via a $d\pi$ interaction, whereas above we were referring to changes due to the σ-donor strength of the cis-influence ligand L. Such a σ-framework effect could perhaps give rise to phosphorus d-orbital population changes via "direct donation", as described by Fenske.[14] Our suggestion then is that, in the *absence* of mitigation of π-effects by a nitrosyl ligand, the added complications must destroy the reasonable correlation of reporter coupling constant and chemical shift.[15] This still leaves the anomalous halide, carbonyl, and phosphite data to be explained. Phosphites as well as of course CO are considered to be stronger π-acids than phosphines[1,13] and any of the other ligands in our correlation, so we suggest that this degree of π-acidity is sufficient to disrupt the mitigation of π-effects by the nitrosyl ligand. At the other extreme, halides are *π-donors*,[16] which could similarly disrupt the NMR correlation. The fact that SbF_6^-, PF_6^-, and BF_4^- fit is still consistent with this, since π-donation here would be weak if existent.[17]

In conclusion, we have discovered a cis-influence series based not just on a list of chemical shifts or coupling constants, but on a remarkably strong *correlation* of these two quantities. We suggest this arises due to the presence of the strong π-acid nitrosyl ligand, which effectively decouples ligand σ- and π-effects. An *overall* correlation of this cis-influence series with ligand donor strength is obvious. *The strength of the present approach is that the coupling constant/chemical shift correlation itself will eliminate any ligands that cannot be confidently ordered on the basis of the NMR data.* Thus, ligands possessing π-acceptor ability equal to or greater than that of $P(OMe)_3$, or π-donor ability equal to or greater than that of Br^-, cannot be ordered with respect to σ-donor strength by using this NMR method, nor can ligands possessing steric bulk equal to or greater than that of PCy_3. Conversely, ligands that *do* fit the correlation, even within a narrow range of coupling constant/chemical shift, *can* be ordered on the basis of NMR data. The data are unambiguous with respect to PMe_3 and PPh_3, giving the ordering of ligand donor strength $PMe_3 > PMe_2Ph, PMePh_2 > PPh_3 > Et_3N, CH_3CN > THF, D_2O, ROH, PF_2O_2^- > Me_2NCHO, Me_2SO_2, R_2CO > BF_4^-, PF_6^-, SbF_6^-$. These data, combined with the weight of spectroscopic, thermodynamic, and kinetic data,[1,6,7] once again suggest that the traditional ordering of phosphine basicity[7] is correct.

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(15) A reviewer has suggested that ν(NO) in **1** should correlate with the chemical shifts and coupling constants, given these arguments. In fact, treatments of IR data suggest that trans-ligand stretching force constants will *not* be sensitive to σ-donor strength but will be sensitive to π-effects.[1] Thus, ν(NO) might be expected to be *independent* of L in **1**. In fact, ν(NO) for L = SbF_6^- (1690 cm^{-1}), acrolein (1698 cm^{-1}), acetonitrile (1703 cm^{-1}), and PMe_3 (1713 cm^{-1}) unexpectedly *increases* with donor strength. The calculated force constants[8b] follow this same order. This trend is not readily explained but could be a consequence of the required use of polar CH_2Cl_2 as the solvent.[1b]

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