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## Correlations between Taft $E_s$ Parameters and $^{13}C$ Chemical Shifts in $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ (R = Alkyl) Complexes. A New Method for the Measurement of Taft $E_s$ Parameters

*Sir:*

Complexes of the type $Mo(CO)_4((Ph_2PO)_2Y(R')R)$ (Y(R′) = P(O), Si(Me); R = alkyl, haloalkyl, aryl) exhibit a number of unusual properties that make them useful for the study of the relationships between the steric and electron $\sigma$-donor/$\pi$-acceptor properties of phosphorus-donor ligands and the multinuclear NMR spectra of their complexes.[1-4] When R $\neq$ R′, two $^{13}C$ NMR resonances are observed for the two carbonyl ligands cis to both of the diphenylphosphino groups and for the phenyl C(1)'s of the two phenyl groups on the phosphorus.[2,3] Good correlations between the chemical shifts of the trans-carbonyl $^{13}C$, cis and trans-carbonyl $^{17}O$ and $^{31}P$ resonances, and the averaged chemical shifts of the two cis-carbonyl and phenyl C(1) $^{13}C$ resonances are observed.[4] These good correlations suggest that changes in the steric effects of the Y(R)R′ groups do not affect the averaged chemical shift values of these resonances since good correlations between the chemical shifts in question are not observed in similar $Mo(CO)_{6-n}(Ph_2PXR)_n$ (X = NH, O, S; *R* = alkyl, aryl, silyl; *n* = 1, 2 (cis)) complexes when changes in the steric properties of the XR groups do occur.[1,5,7] We now wish to report that the differences in the $^{13}C$ chemical shifts of the two cis-carbonyl, phenyl C(1), phenyl C(2,6), phenyl C(3,5), and phenyl C(4) resonances of complexes of the type $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ (R = alkyl, haloalkyl) are linearly related to the Taft steric parameters ($E_s$) of the alkyl groups. This is one of the first cases in which NMR spectroscopy can be used to measure variations in both the steric and electron $\sigma$-donor/$\pi$-acceptor properties of a phosphorus-donor ligand. More importantly, this provides a relatively simple method for the measurement of the Taft steric parameters in an organometallic system.

The $^{13}C\{^1H\}$ NMR data for the carbonyl and phenyl groups of the $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ complexes are summarized in Table I. The $^{13}C$ resonances of the trans- and cis-carbonyl carbons, the phenyl C(1)'s, and the remaining phenyl carbons of $Mo(CO)_4((Ph_2PO)Si(Me)c\text{-}Hx)$ are shown in Figures 1–3, respectively. As can be seen in these figures, two resonances are observed for the cis-carbonyl and phenyl carbons when R $\neq$ Me. The trans carbonyls are symmetry related by a mirror plane that contains the methyl and R groups and thus remains equivalent regardless of the R group used. The trans-carbonyl and phenyl C(1), C(2,6), and C(3,5) $^{13}C$ resonances are apparent triplets or apparent pentets (the A portion of an AXX′ spin system) due to coupling to magnetically inequivalent phosphorus nuclei.[8,9] The cis-carbonyl $^{13}C$ resonance is a 1:2:1 triplet (the A portion of an $AX_2$ spin system) since the phosphorus nuclei are symmetry related by a mirror plane that contains the cis carbonyls. The C(4)'s of

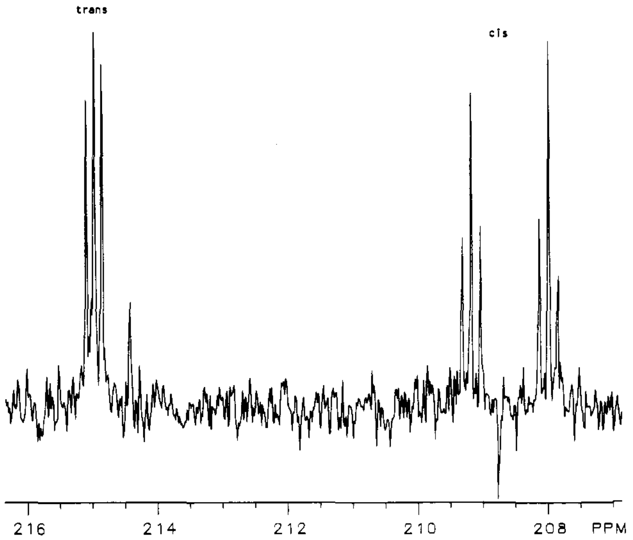

**Figure 1.** $^{13}C\{^1H\}$ NMR spectrum of the cis- and trans-CO ligands of $Mo(CO)_4((Ph_2PO)_2Si(Me)c\text{-}Hx)$.

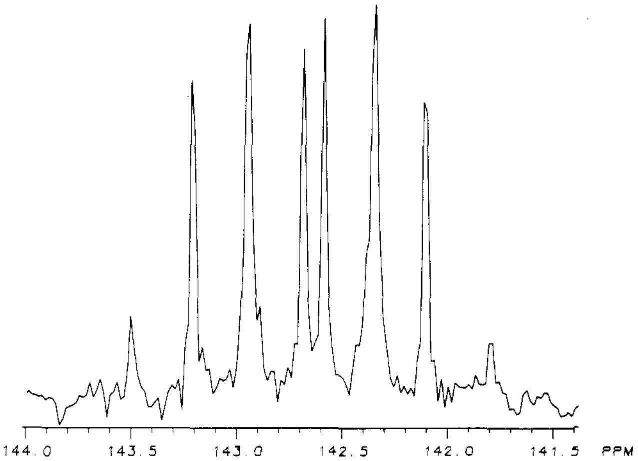

**Figure 2.** $^{13}C\{^1H\}$ NMR spectrum of the phenyl C(1) carbons of $Mo(CO)_4((Ph_2O)_2Si(Me)c\text{-}Hx)$.

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[1] Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1978**, *146*, 23.
[2] Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1982**, *238*, 209.
[3] Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1983**, *241*, 201.
[4] Gray, G. M.; Redmill, K. A. *J. Organomet. Chem.* **1985**, *280*, 105.
[5] Gray, G. M.; Kraihanzel, C. S. *Inorg. Chem.* **1983**, *22*, 2959.
[6] Gray, G. M. *Inorg. Chim. Acta* **1984**, *81*, 157.
[7] Gray, G. M.; Gray, R. J.; Berndt, D. C. *J. Magn. Reson.* **1984**, *57*, 347.
[8] Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.
[9] Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50.

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Table I. $^{13}C$ NMR Data for the $Mo(CO)_4((PPh_2O)_2Si(Me)R)$ Compounds[a]

| | carbonyl | | | | phenyl | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | trans | | cis | | C(1) | | C(2,6) | | C(3,5) | | |
| R | δ | $\lvert ^2J(PC) + {}^2J(P'C)\rvert$ | δ | $\lvert ^2J(PC)\rvert$ | δ | $\lvert ^1J(PC) + {}^3J(P'C)\rvert$ | δ | $\lvert ^2J(PC) + {}^4J(P'C)\rvert$ | δ | $\lvert ^3J(PC) + {}^5J(PC) +$ | C(4) δ |
| Me (**1**) | 214.94 | 18.2 | 208.57 | 10.6 | 142.42 | 19.0 | 129.24 | 15.0 | 128.20 | 9.7 | 129.92 |
| Et (**2**) | 214.94 | 17.9 | 208.41 | 10.8 | 142.48 | 18.5 | 129.23 | 14.9 | 128.19 | 7.1 | 129.91 |
| | | | 208.72 | 10.9 | 142.60 | 19.1 | 129.33 | 14.9 | | | 129.94 |
| $CH_2Cl$ (**3**) | 214.43 | 18.6 | 208.30 | 10.8 | 141.86 | 19.2 | 129.24 | 15.6 | 128.30 | 9.5 | 130.17 |
| | | | 208.43 | 10.9 | 142.01 | 19.0 | 129.29 | 15.2 | | | 130.20 |
| *n*-Pr (**4**) | 214.95 | 18.3 | 208.34 | 10.7 | 142.41 | 18.2 | 129.24 | 14.9 | 128.17 | 8.5 | 129.88 |
| | | | 208.84 | 10.6 | 142.69 | 18.9 | 129.43 | 14.9 | 128.21 | 8.9 | 129.98 |
| c-Hx (**5**) | 214.97 | 18.2 | 207.98 | 10.6 | 142.34 | 18.1 | 129.14 | 14.9 | 128.15 | 11.2 | 129.80 |
| | | | 209.17 | 10.6 | 142.94 | 19.7 | 129.61 | 15.2 | 128.22 | 9.8 | 130.05 |
| *t*-Bu (**6**) | 214.88 | 18.1 | 207.56 | 10.6 | 142.31 | 17.6 | 128.96 | 14.7 | 128.17 | 9.8 | 129.75 |
| | | | 209.43 | 10.5 | 143.09 | 20.0 | 129.66 | 15.2 | 128.26 | 9.6 | 130.13 |
| Ph (**7**) | 214.83 | 18.8 | 207.55 | 10.3 | 142.16 | 18.4 | 129.21 | 14.5 | 128.22 | 11.6 | 129.81 |
| | | | 209.28 | 10.7 | 142.58 | 19.5 | 129.71 | 15.0 | 128.29 | 9.9 | 130.18 |

[a] *J* values are in Hz.

Table II. Coefficients (*r*) Calculated for the Linear Correlations between the $E_s$ Parameters of the R Groups and the Differences in the $^{13}C$ Chemical Shifts of the Cis-Carbonyl and Phenyl Resonances of the $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ Complexes

| | cis CO | Ph C(1) | Ph C(2,6) | Ph C(3,5) | Ph C(4) |
|---|---|---|---|---|---|
| *r* | −0.978 | --0.981 | −0.982 | −0.936 | −0.984 |
| level of signif | 99.9 | 99.9 | 99.9 | 99.0 | 99.9 |

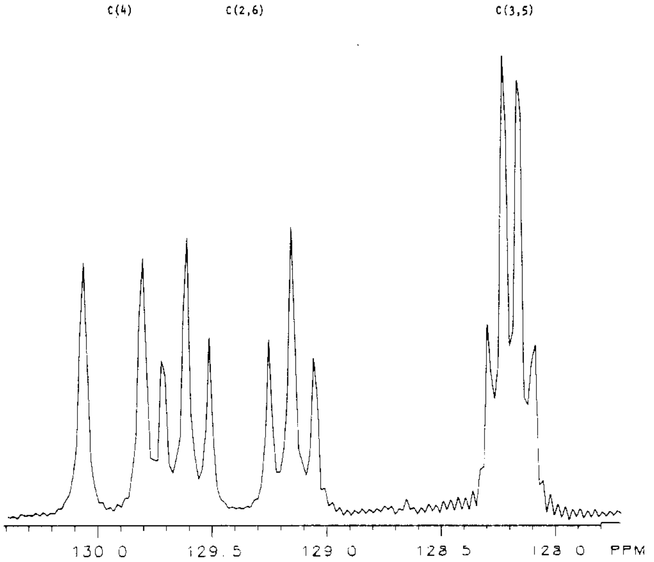

**Figure 3.** $^{13}C\{^1H\}$ NMR spectrum of the phenyl C(2,6), C(3,5), and C(4) carbons of $Mo(CO)_4((Ph_2O)_2Si(Me)c\text{-}Hx)$.

the phenyl rings do not couple to either of the phosphorus nuclei and give rise to singlets. All $^{13}C$ NMR spectra were obtained on a Nicolet 300-MHz NMR spectrometer under experimental conditions that have previously been reported.[4]

A plot of the differences between the chemical shifts of the two resonances of the cis-carbonyl and phenyl carbons vs. the Taft $E_s$ parameters[10] of the alkyl and haloalkyl groups of the $Mo(CO)_4(PPh_2O)_2Si(Me)R)$ complexes is given in Figure 4. As is evident from this figure, all the chemical shift differences increase with increasing $|E_s|$. The coefficients (*r*) calculated for these correlations and the levels of significance of the correlations are given in Table II. The lower correlation coefficient and level of significance of the correlation between the chemical shift differences of the phenyl C(3,5)'s and the $E_s$ parameters are a result of the small size of the chemical shift differences being measured (0.09 ppm maximum) relative to the data point resolution of the experiment (±0.016 ppm).

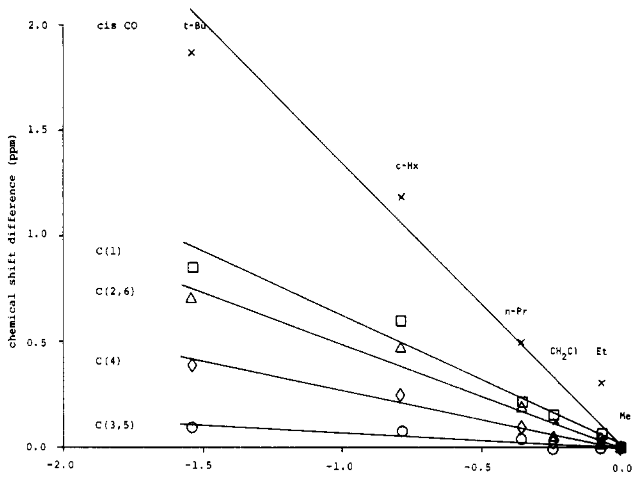

**Figure 4.** Plot of the differences in the $^{13}C$ chemical shifts of the cis-carbonyl and phenyl carbons vs. the $E_s$ parameters of the alkyl groups in the $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ (R = alkyl) complexes.

The correlations are significant for two reasons. The first is that these complexes are among the first reported in which it is possible to use NMR spectroscopy to measure simultaneous changes in both steric and electronic effects. This suggests that $(Ph_2PO)_2Y(R')R$ ligands could be useful in multinuclear NMR studies of the relationship between the steric and electron σ-donor/π-acceptor properties of these phosphorus-donor ligands and the catalytic activity and selectivity of their transition-metal complexes.

Secondly, the correlations allow the Taft $E_s$ parameters to be easily measured as these complexes are readily synthesized from $[Et_3NH][Mo(CO)_4((Ph_2PO)_2H)]$ and the appropriate dichlorosilane.[1,4] Since a variety of dichlorosilanes are commercially available, a number of $E_s$ parameters can be measured and compared with those obtained from other sources.[11] More importantly, this method allows the $E_s$ parameter to be measured at several different sites within the complex. If a constant value is obtained, the effect can be safely assumed to be a steric effect as is the case for the alkyl and haloalkyl complexes. However, if the value varies when measured at the different sites, this indicates that through-space diamagnetic anisotropic shielding or deshielding may be occurring since this should not be constant at all five sites. This is illustrated by the $^{13}C$ NMR data for $Mo(CO)_4((Ph_2PO)_2Si(Me)Ph)$, which are included in Table I. The $E_s$ parameters for the Ph group calculated with the corre-

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(10) Taft, R. W., Jr. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 598.

(11) Gallo, R. "Progress in Physical Organic Chemistry"; Taft, R. W., Jr., Ed.; Interscience: New York, 1983; Vol. 14, pp 115-163.

lations with the cis-carbonyl, phenyl C(1), phenyl C(2,6), phenyl C(3,5), and phenyl C(4) data are respectively −1.33, −0.70, −1.01, −1.00, and −1.53. The variation in these numbers is considerably greater than the error of the calculations, and these values are also considerably different from the $E_s$ parameter of −0.90, which has been reported for the phenyl group.[10] Thus, this method allows for the separation of steric from electronic effects by multiple measurement of the $E_s$ parameter.

Since this method appears to be extremely useful for the measurement of $E_s$ parameters, this study is currently being extended to determine the limits of the method. Included in this study are complexes in which the R group is a long-chain alkyl group or a polyhaloalkyl group and complexes in which the diphenylphosphino group is replaced by a 1,3,2-dioxaphosphorinane group. The results of this research will be reported in a subsequent communication.

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## A Polymeric Peroxo Heteroligand Vanadate(V). Synthesis, Spectra, and Structure of $M^I[VO(O_2)(C_4H_5O_4N)]$

*Sir:*

Vanadium peroxo complexes are known to act as catalysts[1,2] and have been proposed as one of the model systems for the biochemistry of vanadium.[3,4] Although recently recognized as an essential element for mammals,[5] the vanadium function remains unknown.[6,7] Some of the peroxo heteroligand vanadates(V) have shown antitumor activity against L1210 murine leukemia, and the biological activity of these complexes[4] strongly depends upon the heteroligands. We have been interested in the peroxovanadates(V) before[8] and have now decided to investigate such complexes containing amino carboxylato or polycarboxylato ligands, to find out some general trends regarding the influence of the heteroligand on the mode of coordination, the bond distances and the bond angles, the charge-transfer bands, the stability, and the reactivity of coordinated peroxides.

We report now our work with the iminodiacetic acid, $C_4H_7NO_4$, which reacts with V(V) in the presence of hydrogen peroxide to form crystalline compounds[9] of the formula $M^I[VO(O_2)IDA]$ $M^I$ = K, $NH_4$; IDA = $[C_4H_5NO_4]^{2-}$). Unlike other analogous oxo peroxo heteroligand vanadates[8,10] these complexes crystallize anhydrous from the aqueous solutions and are remarkably stable toward decomposition. Aqueous solutions of the compounds show a band centered at 420 nm, as observed for some other monoperoxovanadates.[11] This absorption remains constant over a wide pH range of 2–8 but shifts at pH ≤1 to 450–460 nm, and a new band appears at 280 nm. In such acid solutions the complexes obviously rearrange, but the peroxo group remains coordinated to the metal.[11-13] In aqueous solutions the potassium and the ammonium complexes show identical cyclic voltammograms with characteristic irreversible cathodic and anodic peaks. Study of the electrochemical behavior of these complexes is in progress. The ammonium complex has shown marginal antitumor activity against L1210 murine leukemia.[4]

The significant features in the IR spectra of the potassium and the ammonium compounds involve bands of coordinated IDA, peroxo frequencies, and V═O stretchings. The NH stretchings of the three-coordinated ligand shift to higher energy, and a sharp strong band occurs at 3215 $cm^{-1}$ as compared to strong absorption found at 3100 $cm^{-1}$ in the acid. The coordinated carboxylato groups cause a distinct shift of antisymmetric CO stretchings,[14] which occur as strong bands at 1680 to 1660 and 1560 $cm^{-1}$. Very strong absorption in addition to the organic ligand bands is observed in the region of 980 and 920 $cm^{-1}$ and assigned to the V═O and O—O stretchings, respectively.[8,15]

Only a few well-refined X-ray structure analyses of peroxovanadates were reported.[1,16-19] The vanadium is seven-coordinated in all but one,[17] which is described as a distorted pentagonal pyramid. The distorted pentagonal bipyramid used as model in the other four structures invariably shows V═O on an apical position and the peroxo group(s) in the equatorial planes. Such seven-coordination is also common in peroxo complexes of Mo(VI)[21] and Ti(IV),[22] while Nb(V) prefers eight-coordinated dodecahedral structures.[23] The complexes are usually monomeric, and a few dimeric ones exist.[16,24] The coordination of the peroxo group, the O—O distance, and the MOO bond angles depend upon the metal ion, the symmetry of the ligand field, and the heteroligand. With only little sufficiently precise structural data available, some common trends expected within the family of the peroxometal coplexes cannot be detected. More accurate structure determinations of these compounds are needed, and we therefore looked for conditions to prepare crystals of $M[VO(O_2)IDA]$ adequate for X-ray structure analysis. The potassium salt precipitated invariably in small irregular crystal clusters. Acceptable crystals were obtained of $NH_4[VO(O_2)IDA]$, and we now report the structure of this compound, which represents the first polymeric structure of a transition-metal peroxo heteroligand complex.

X-ray diffraction data were collected on a crystal grown from aqueous solutions,[25] and the structure was solved by standard

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(1) Mimoun, H.; Saussine, L.; Daire, E.; Postal, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.
(2) Patai, S. "The Chemistry of Peroxides"; Wiley: New York, 1983.
(3) Djordjevic, C.; Craig, S. A.; Lee, M. 186th National Meeting of the American Chemical Society, Washington, D.C., 1983.
(4) Djordjevic, C.; Wampler, G. L. *J. Inorg. Biochem.*, in press.
(5) Mertz, W. *Science (Washington, D.C.)* **1981**, *213*, 1332.
(6) Chasteen, N. D. *Struct. Bonding (Berlin)* **1983**, *53*, 105.
(7) Kustin, K.; Macara, I. G. *Comments Inorg. Chem.* **1982**, *2*, 1.
(8) Vuletic, N.; Djordjevic, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1137.
(9) Anal. Calcd for $NH_4[VO(O_2)IDA]$: C, 19.4; H, 3.7; N, 11.3; $O_2^{2-}$, 12.9; V, 20.5. Found: C, 19.6; H, 3.7; N, 11.3; $O_2^{2-}$, 12.2; V, 20.5. Calcd for $K[VO(O_2)IDA]$: C, 17.9; H, 1.9; N, 5.2; $O_2^{2-}$, 11.9; K, 14.5; V, 18.9. Found: C, 17.9; H, 1.9; N, 5.2; $O_2^{2-}$, 12.5; K, 14.9; V, 19.4.
(10) Djordjevic, C.; Lee, M.; Vuletic, N.; Craig, S. A. XXIII International Conference on Coordination Chemistry, Boulder, CO, 1984; p 31.
(11) Okazaki, K.; Saito, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 785.
(12) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.
(13) Djordjevic, C. *Chem. Br.* **1982**, *18*, 554.
(14) Nakamoto, K.; Morimoto, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1962**, *84*, 2081.
(15) Griffith, K. P.; Wickins, T. D. *J. Chem. Soc. A* 1968, 397.
(16) Svensson, I.-B.; Stomberg, R. *Acta Chem. Scand.* **1971**, *25*, 898.
(17) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1972**, *11*, 1079.
(18) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1973**, *12*, 829.
(19) Begin, D.; Einstein, F. W. B.; Field, Y. *Inorg. Chem.* **1975**, *14*, 1785.
(20) Campbell, N. J.; Capparelli, M. V.; Griffith, W. P.; Skapski, A. C. *Inorg. Chim. Acta* **1983**, *77*, L215.
(21) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(22) Mimoun, H.; Postel, M.; Casabianca, F.; Fischer, J.; Mitshler, A. *Inorg. Chem.* **1982**, *21*, 1301.
(23) Mathern, G.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1572, 1582.
(24) Djordjevic, C.; Sinn, E. XXIII International Conference on Coordination Chemistry, Boulder, CO, 1984; p 249.

0020-1669/85/1324-1281$01.50/0