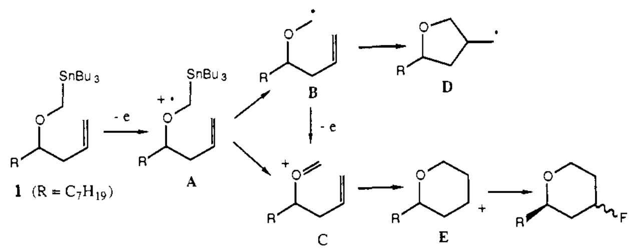
Scheme III



less positive than those of α-silyl ethers. The oxidation potentials of α-stannyl ethers, however, are 0.5–0.7 V less positive than those of the corresponding α-silyl ethers.[9] Therefore, we reasoned that in the anodic oxidation of α-stannyl ethers the radical intermediate **B** might have a chance to cyclize before oxidation to the carbocation (radical cyclization). Other possibilities to be considered were that anodic oxidation of **B** might still be faster than cyclization or that the carbon–tin bond in **A** would be cleaved homolytically to give cation **C** directly. Thus generated, cation **C** would also have a chance to cyclize to give cation **E** (cation cyclization).[10] If the radical cyclization took place, then the five-membered-ring product would be formed (**B** → **D**), and if the cation cyclization took place, then the six-membered-ring product would be formed (**C** → **E**). Therefore, compound **1** seemed to be a suitable substrate for distinguishing between the radical and the cation cyclization pathways.

Although anodic oxidation of **1** in methanol gave the noncyclized acetal **2**, we found that switching the solvent to dichloromethane resulted in the facile formation of the six-membered-ring compound **3** (Table I).[11] The absence of the corresponding five-membered ring suggested that the cyclizations involved carbocation rather than radical intermediates.[12] To our surprise, the cyclized product contained a fluorine atom at one of the original olefinic carbons, indicating that fluoride ion from Bu_4NBF_4 attacked the cyclized cation **E** as a nucleophile.[13] Bu_4NPF_6 was also found to be effective as the fluoride source. Anodic oxidation of the corresponding α-silyl ether **4** also gave the cyclized product **3** under similar conditions, but the yield was lower and significant amounts of unidentified byproducts were formed.

The present method is generally applicable to endo cyclization to form six- and seven-membered rings (**1** → **3**, **5** → **6**, **8** → **9** + **10**). Endo cyclization to form a five-membered ring was not successful (**7**→). It is worth noting that α-stannyl carbamates also cyclized under similar conditions to give the corresponding fluorine-containing piperidine derivatives (**11** → **12**, **13** → **14**).

In summary, effective intramolecular carbon–carbon bond formation has been achieved by the anodic oxidation of unsaturated α-stannyl ethers and α-stannyl carbamates. The reactions also provide an efficient route to fluorine-containing compounds.[7,8] Studies concerning the reaction mechanism and synthetic applications are underway.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for Scientific Research as financial support.

Supplementary Material Available: Listing of spectral data for the cyclized products (4 pages). Ordering information is given on any current masthead page.

---

(9) Introduction of a silyl or stannyl group on the α-carbon of ethers results in a dramatic decrease in the oxidation potential. The effect of tin is larger than that of silicon. (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962–1970. (b) Yoshida, J.; Ishichi, Y.; Nishiwaki, K.; Shiozawa, S.; Isoe, S. *Tetrahedron Lett.* **1992**, *33*, 2599–2602.

(10) Perron-Sierra, F.; Promo, M. A.; Martin, V. A.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 6188–6199.

(11) In an undivided cell equipped with a carbon rod anode, a platinum plate cathode, a Teflon stir bar, and an argon balloon were placed compound **1** (119 mg, 0.25 mmol), dichloromethane (2.5 mL), Bu_4NBF_4 (201 mg, 0.61 mmol), and 4A molecular sieves (ca. 500 mg). A constant electric current of 5 mA was applied. After 3.1 faradays/mol of electricity was consumed, the aqueous workup followed by preparative TLC yielded compound **3** (83%, cis:trans = 2.8:1).

(12) Sometimes a heteroatom in the chain may also favor six-membered-ring formation in radical cyclization. See: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986; p 147.

(13) For the formation of fluorine-containing compounds by nucleophilic reaction of BF_4^- or BF_3: (a) Faller, J. W.; Linebarrier, D. L. *Organometallics* **1990**, *9*, 3182–3184. (b) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 5768–5774.

NMR Evidence for the Existence of a π-Accepting PMe_3 Ligand. Estimates of the Magnitude of π Effects in $WL(CO)_5$ Complexes

S. P. Wang,[1a] M. G. Richmond,*,[1b,c] and M. Schwartz*,[1b]

Department of Chemistry and Center for
Organometallic Research and Education
University of North Texas, Denton, Texas 76203

Received May 14, 1992

While it is well established that alkylphosphite ligands function as relatively strong π electron acceptors in transition metal carbonyls,[2] the π bonding properties of the alkylphosphines remain poorly understood. The traditional view that they are moderate π acceptors[2] has been challenged by recent experiments inferring that these ligands can be π neutral or even, in some cases, net π electron donors.[3,4]

Unfortunately, Cotton–Kraihanzel (C–K) force constants,[5] classically used to monitor π bonding, are now known to depend upon both the σ and π components of the M–CO bond.[6] In contrast, it has been demonstrated that variations in the oxygen-17 quadrupole coupling constants (QCCs), $\chi(^{17}O)$, in multiply bonded systems[7,8] including metal carbonyls[9–11] reflect almost entirely changes in the π bond strength and are relatively insensitive to the σ bond component.

In order to assess the relative π acceptor capabilities of a typical alkylphosphine, we have performed a comparative NMR (^{17}O and

---

(1) (a) Robert A. Welch Predoctoral Fellow. (b) Department of Chemistry, University of North Texas. (c) Center for Organometallic Research and Education, University of North Texas.

(2) (a) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Co.: Monterey, CA, 1985. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(4) (a) Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, Md. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Ibid.* **1987**, *6*, 650. (c) Rahman, Md. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Ibid.* **1989**, *8*, 1. (d) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Ibid.* **1990**, *9*, 1758.

(5) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(6) (a) Dobson, G. R. *Inorg. Chem.* **1965**, *4*, 1673. (b) Brown, T. L.; Darensbourg, D. J. *Ibid.* **1967**, *6*, 971. (c) Darensbourg, D. J.; Brown, T. L. *Ibid.* **1968**, *7*, 959. (d) Brown, D. A.; Rawlinson, R. M. *J. Chem. Soc. A* **1969**, 1530. (e) Fenske, R. F.; DeKock, R. L. *Inorg. Chem.* **1970**, *9*, 1053. (f) Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61.

(7) (a) Das, T. P.; Hahn, E. L. *Nuclear Quadrupole Resonance Spectroscopy*; Academic Press: New York, 1958. (b) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: New York, 1969.

(8) (a) Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2327. (b) Cheng, C. P.; Brown, T. L. *Ibid.* **1980**, *102*, 6418. (c) Bronsen, S. G. P.; Edmonds, D. T.; Poplett, J. J. *J. Magn. Reson.* **1981**, *45*, 451.

(9) (a) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Chem. Commun.* **1983**, 794. (b) Hawkes, G. E.; Randall, E. W.; Aime, S.; Osella, D.; Elliot, J. E. *J. Chem. Soc., Dalton Trans.* **1984**, 279. (c) Aime, S.; Gobetto, R.; Osella, D.; Hawkes, G. E.; Randall, E. W. *Ibid.* **1984**, 1863. (d) Hawkes, G. E.; Randall, E. W.; Aime, S.; Gobetto, R. *J. Magn. Reson.* **1986**, *68*, 597. (e) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *J. Chem. Soc., Dalton Trans.* **1988**, 791.

(10) (a) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *61*, 22. (b) Brownlee, R. T. C.; Shehan, B. P. *Ibid.* **1986**, *66*, 503. (c) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 931.

(11) Wang, S. P.; Yuan, P.; Schwartz, M. *Inorg. Chem.* **1990**, *29*, 484.

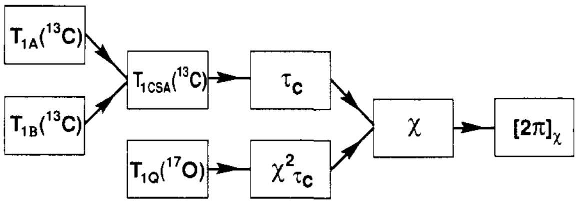
0002-7863/92/1514-7595$03.00/0

Table I. Relaxation Times and Quadrupole Coupling Constants[a,b]

complex	T (°C)	site	$T_{1Q}(^{17}O)$ (ms)	$T_{1A}(^{13}C)$ (s)	$T_{1B}(^{13}C)$ (s)	$T_{1CSA}(^{13}C)$ (s)	$\Delta\sigma(^{13}C)$ (ppm)	τ_c (ps)	X (MHz)
W[P(OMe)$_3$](CO)$_5$	11	axial	12.3 (0.1)	4.03 (0.06)	8.26 (0.51)	4.37	413.7	44.6	1.39
	21	axial	18.3 (0.7)	5.27 (0.08)	10.9 (0.8)	5.69		34.3	1.30
	11	radial	10.1 (0.1)	5.00 (0.06)	9.65 (0.08)	5.76	409.7	34.5	1.74
	21	radial	14.4 (0.3)	6.50 (0.07)	12.4 (0.2)	7.62		26.1	1.67
W[PMe$_3$](CO)$_5$	21	axial	52.3 (1.8)	10.6 (0.1)	24.4 (0.2)	10.4	417.3	18.4	1.05
	38	axial	71.8 (4.0)	12.0 (0.5)	28.5 (1.0)	11.5		16.7	0.94
	21	radial	27.9 (0.5)	11.7 (0.1)	26.3 (0.1)	11.6	412.7	16.9	1.50
	38	radial	34.8 (0.8)	12.5 (0.4)	30.0 (0.3)	11.9		16.5	1.36
W[NMe$_3$](CO)$_5$	21	axial	502 (47)	11.5 (0.4)	32.7 (0.7)	9.80	419.7	19.3	0.330
	38	axial	541 (54)	11.8 (0.4)	30.8 (3.8)	10.6		17.9	0.330
	21	radial	27.6 (0.4)	12.2 (0.6)	30.6 (0.6)	11.3	416.0	17.1	1.50
	38	radial	34.1 (2.3)	12.4 (0.3)	28.2 (3.8)	12.4		15.6	1.41

[a] Relaxation times are the average of three measurements at each temperature. [b] Quantities in parentheses represent the mean deviation between measurements.

Scheme I



^{13}C) relaxation time analysis to obtain $\chi(^{17}O)$ and antibonding π orbital populations of both axial and radial carbonyls in the complexes W[P(OMe)$_3$](CO)$_5$, W[PMe$_3$](CO)$_5$, and W[NMe$_3$](CO)$_5$. A comparison of the results has permitted a determination of the π acceptor properties of trimethylphosphine relative to the phosphite and amine ligands. This investigation represents the first quantitative determination of the site dependence of ^{17}O QCCs and π bond strengths in a metal carbonyl complex.[12-14]

Chemical shift anisotropies ($\Delta\sigma$) were estimated by using methods described elsewhere.[15] Details of the calculation of $\chi(^{17}O)$ (last column of Table I) have been presented in an earlier investigation.[11]

Recently,[11] we developed a semiquantitative relationship between $\chi(^{17}O)$ and the quantity $[2\pi]$, the population of the carbonyl's 2π (or π^*) antibonding molecular orbital, whose magnitude provides a direct measure of the strength of the M–CO π bond. We have used this expression,[11] together with the experimental QCCs, to calculate the total antibonding orbital occupancies of both axial and radial carbonyls in the three tungsten complexes ($[2\pi]_\chi$ in Table II). Scheme I illustrates the relationship between the T_1, QCC, and orbital population data.

To quantify the effect of CO replacement by L upon π bond strengths in the remaining carbonyls, it is informative to consider the *increase* in $[2\pi]_\chi$ relative to the parent hexacarbonyl, $\Delta[2\pi]_\chi = [2\pi]_\chi - [2\pi]_\chi\{W(CO)_6\}$; the results are displayed in square brackets in Table II.

One observes that antibonding π orbital occupancies are enhanced comparatively slightly (by 0.04–0.08 electron) in the radial carbonyls, compared to the axial carbonyls, in which $[2\pi]_\chi$ is increased by as much as 0.25 electron in the amine complex.

Table II. Experimental 2π Orbital Populations and C–K Force Constants[a-c]

complex	$[2\pi]_\chi$ $[[2\pi]_\chi - [2\pi]_\chi\{W(CO)_6\}]$ axial	radial	k_{CO}[d] $[k_{CO} - k_{CO}\{W(CO)_6\}]$ axial	radial
W(CO)$_6$	0.38	0.38	16.35	16.35
W[P(OMe)$_3$](CO)$_5$	0.47	0.42	15.82	15.99
	(0.007)	(0.005)	[0.53]	[0.36]
	[0.09]	[0.04]		
W[PMe$_3$](CO)$_5$	0.53	0.46	15.53	15.79
	(0.009)	(0.01)	[0.82]	[0.56]
	[0.15]	[0.08]		
W[NMe$_3$](CO)$_5$	0.63	0.46	15.05	15.72
	(0.001)	(0.007)	[1.30]	[0.63]
	[0.25]	[0.08]		

[a] Values of $[2\pi]_\chi$ are the average obtained from $\chi(^{17}O)$ at the two temperatures. [b] Quantities in parentheses represent the deviation between the two calculated values of $[2\pi]_\chi$. [c] Quantities in square brackets constitute the variation in the values from those in W(CO)$_6$. [d] k_{CO} for W(CO)$_6$ is taken from Jones et al.: Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349. Other force constants were calculated from frequencies measured in these laboratories.

Most significantly, one sees that $\Delta[2\pi]_\chi$(ax) in W[PMe$_3$](CO)$_5$ (0.15 electron) actually lies closer to the result in W[P(OMe)$_3$](CO)$_5$ (0.09 electron) than to the value in the amine complex (0.25 electron). One cannot attribute the smaller antibonding orbital population in the phosphine complex to a difference in σ basicities since the lower pK_a of PMe$_3$ compared to NMe$_3$ (8.65[16a] and 9.81,[16b] respectively) indicates that it is a slightly stronger σ base [which would enhance $[2\pi]_\chi$(ax)]. Hence, these results reveal quite clearly that trimethylphosphine is, indeed, a substantially stronger π electron acceptor than the π neutral amine ligand.

Finally, it is informative to compare the ligand dependence of 2π orbital populations with variations in the C–K force constants[5] (last two columns in Table II). One observes that, in all three pentacarbonyls, the ratio $[-\Delta k_{CO}(\text{rad})]/[-\Delta k_{CO}(\text{ax})]$ is greater than the equivalent ratio of antibonding orbital populations, $\Delta[2\pi]_\chi(\text{rad})/\Delta[2\pi]_\chi(\text{ax})$, obtained from the NMR experiments. Hence, use of the force constants as a predictor tends to overestimate variations in π bond strengths of the radial carbonyls.

The NMR technique described here will be employed in the analysis of other ligands whose π accepting properties have not been conclusively demonstrated. The results of these studies will be presented in due course.

Acknowledgment. We thank the Robert A. Welch Foundation [Grants B-1039 (M.G.R.) and B-657 (M.S.)] and the UNT Faculty Research Fund for financial support.

---

(12) There have been two *approximate* determinations of the site dependence of $\chi(^{17}O)$ in polynuclear metal carbonyls (refs 9a and 9c). These studies, however, assume that the molecular reorientation is isotropic (i.e., equal rotational rates about the various molecular axes).

(13) The complexes used in this study were prepared from W(THF)(CO)$_5$ and the appropriate ligand. The isolated complexes displayed IR spectra identical with the reported IR data.

(14) $T_{1A}(^{13}C)$ and $T_1(^{17}O)$ were determined (at natural abundance) using the standard inversion recovery technique on a Varian VXR-300 FT-NMR spectrometer (75.4 MHz for ^{13}C and 40.7 MHz for ^{17}O). $T_{1B}(^{13}C)$ was also measured at 50.3 MHz on a Varian Gemini-200 spectrometer. The results, with standard deviations, are displayed in Table I. All measurements were repeated three times at each of two temperatures [in order to obtain two independent determinations of $\chi(^{17}O)$].

(15) (a) Spiess, H. W.; Mahnke, H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 990. (b) Mahnke, H.; Sheline, R. K.; Spiess, H. W. *J. Chem. Phys.* **1974**, *61*, 55. (c) Gleeson, J. W.; Vaughan, R. W. *J. Chem. Phys.* **1983**, *78*, 5384.

(16) (a) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (b) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 56th ed.; CRC Press, Inc.: Boca Raton, FL, 1975; p D149.