that calculated by Many.[8] It appears prudent, therefore, not to attempt definite assignment of the transitions to doublet states until more information is available.

With $Dq = 800$ cm^{-1} and $B = 755$ cm^{-1} the electronic energy of the $^4T_{1g}(^4P)$ level is 22.24×10^3 cm^{-1}. The observed highly structured spectrum in this region becomes more intense at higher temperatures and is probably mainly vibronically allowed transitions to the $^4T_{1g}(^4P)$ level. The absorption observed above 24×10^3 cm^{-1} is very strong for transitions from the ground state to excited doublet states and does not become weaker at low temperatures. It is probable that this strong intensity derives from admixture of the doublet states with the nearby charge-transfer states of the crystal responsible for the very strong absorbance above 32×10^3 cm^{-1}.

Addendum.—Axial spectra of VCl$_2$ at room temperature, liquid nitrogen temperature, and liquid helium temperature have recently been reported by Smith,[9] who gave a graph of optical density *vs.* wave number but did not report quantitative intensities of absorption. There is qualitative agreement between our spectra and those reported by Smith.

(8) A. Many, *Phys. Rev.*, **70**, 511 (1946).
(9) W. E. Smith, *J. Chem. Soc., A*, 2677 (1969).

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Kinetic Studies of the Reactions of Cyclopentadienylvanadium Tetracarbonyl with Lewis Base Ligands

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It has been reported that the carbonyl substitution reaction of C$_5$H$_5$V(CO)$_4$ with triphenylphosphine, C$_5$H$_5$V(CO)$_4$ + P(C$_6$H$_5$)$_3$ → C$_5$H$_5$V(CO)$_3$P(C$_6$H$_5$)$_3$ + CO, proceeds according to a second-order rate law, first order in C$_5$H$_5$V(CO)$_4$ and first order in P(C$_6$H$_5$)$_3$.[1] The absence of a term first order in C$_5$H$_5$V(CO)$_4$ only suggested that this complex did not react according to a mechanism in which unimolecular dissociation of a carbonyl group was rate determining. This was unusual in view of the fact that essentially all carbonyl substitution reactions of octahedral metal carbonyl complexes have been found to proceed, at least in part, according to a path governed by the unimolecular

dissociation of CO.[2] The pseudo-seven-coordinated nature of C$_5$H$_5$V(CO)$_4$ would suggest that it would be even less likely to react by an associative (SN2) mechanism for steric reasons. Thus, it was believed a reinvestigation of the reaction of C$_5$H$_5$V(CO)$_4$ with Lewis base ligands was warranted. Herein are reported the results of the investigation.

Experimental Section

Preparation and Purification of Materials.—C$_5$H$_5$V(CO)$_4$ was prepared according to a standard procedure.[3] The complex was sublimed twice and stored under nitrogen at $-80°$ in a foil-wrapped vial. Triphenylphosphine, P(C$_6$H$_5$)$_3$ (Aldrich Chemical Co.), was recrystallized from ethanol, washed with pentane, and dried at 85°, as the melt, under high vacuum for 1 hr. Tri-*n*-butylphosphine, P(C$_4$H$_9$)$_3$ (Aldrich Chemical Co.), was fractionally distilled under high vacuum and was stored under nitrogen. Tri-*n*-butyl phosphite, P(OC$_4$H$_9$)$_3$ (Matheson Coleman and Bell Chemical Co.), was used as obtained. Pure samples of the bicyclic phosphite, 4-*n*-propyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$, were kindly supplied by G. K. McEwen. The solvent, decalin (Baker Chemical Co.), was stirred over sodium for 6 hr at 130° and was carefully distilled under reduced pressure. Chlorobenzene (Mallinckrodt Analytical reagent) was used as obtained.

Identification of Products.—The products of the reactions, C$_5$H$_5$V(CO)$_3$L (where L = P(C$_6$H$_5$)$_3$, P(C$_4$H$_9$)$_3$, P(OC$_4$H$_9$)$_3$, and P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$), were not isolated. However, the products were identified by comparison of their infrared carbonyl stretching spectra with those of the already reported C$_5$H$_5$V-(CO)$_3$P(C$_6$H$_5$)$_3$[4] and C$_5$H$_5$V(CO)$_3$P[N(CH$_3$)$_2$]$_3$.[5] The infrared spectra of the products were recorded with a Beckman IR-12 infrared spectrophotometer, and the carbonyl stretching frequencies are given in Table I. The infrared spectra of the reac-

TABLE I

CARBONYL STRETCHING FREQUENCIES FOR

C$_5$H$_5$V(CO)$_3$L PRODUCTS

L	Medium	Carbonyl str freq, cm^{-1}
P(C$_4$H$_9$)$_3$	*n*-Heptane	1957, 1878, 1855
P[N(CH$_3$)$_2$]$_3$[6]	Mull	1953, 1853, 1839
P(C$_6$H$_5$)$_3$[5]	Mull	1950, 1855, 1840
P(OC$_4$H$_9$)$_3$	Decalin	1970, 1893, 1868
P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$	Decalin	1983, 1907, 1892

tion solutions after 3 or 4 half-lives indicated the presence of another product of the type C$_5$H$_5$V(CO)$_2$L$_2$ (only when L = P(C$_4$H$_9$)$_3$ and P(OC$_4$H$_9$)$_3$). The lowest carbonyl stretching frequencies of the phosphine and phosphite products occurred at 1766 and 1817 cm^{-1}, respectively. These frequencies correspond to the lowest CO stretching frequency (1787 cm^{-1})[6] of C$_5$H$_5$V(CO)$_2$diphos.[7] Since the other CO absorption of C$_5$H$_5$V-(CO)$_2$diphos occurs at 1864 cm^{-1}, it is probable that this absorption of the phosphine and phosphite product, C$_5$H$_5$V(CO)$_2$L$_2$, is masked by the bands of the predominant product, C$_5$H$_5$V-(CO)$_3$L.

In reactions where the ligand concentrations were less than 0.1 M, decomposition was observed. When triphenylphosphine was employed, decomposition was even observed at higher concentrations. Hence, ligand concentrations employed were, for the most part, greater than 0.1 M and reactions with triphenylphosphine were not studied in detail.

Determination of Rates.—Reaction rates were determined by monitoring the decrease of the high-frequency infrared carbonyl stretching absorption of C$_5$H$_5$V(CO)$_4$ at 2019 cm^{-1}. In a typical

(1) W. Strohmeier and H. Blumental, *Z. Naturforsch.*, **22b**, 1351 (1967).

(2) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).
(3) R. B. King, *Organometal. Syn.*, **1**, 107 (1965).
(4) R. Tsumra and N. Hagihara, *Bull. Soc. Chem. Japan*, **38**, 1901 (1965).
(5) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).
(6) H. Behrens and H. Brandle, *Z. Naturforsch.*, **22b**, 1353 (1967).
(7) diphos = 1,2-bis(diphenylphosphino)ethane.

experiment, 10 mg of $C_5H_5V(CO)_4$ was dissolved in 10 ml of ligand solution in a foil-wrapped vessel equipped with a rubber septum. Air was rigorously excluded from the reaction by carefully purging the solution and vessel with nitrogen. Samples were withdrawn from the reaction solution with a syringe, preceded by the injection of a small volume of nitrogen; the absorbances of the samples were immediately measured on a Perkin-Elmer 237b infrared spectrophotometer. The initial experiments with the various ligands were also monitored by scanning the carbonyl stretching region on a Beckman IR-8 equipped with an external recorder or a Beckman IR-12 infrared spectrophotometer. The concomitant increase in product bands was observed with the disappearance of the $C_5H_5V(CO)_4$ bands. Pseudo-first-order reaction conditions were maintained by using ligand concentrations of greater than 10-fold excess. Plots of $\ln (A_t - A\infty)$ *vs.* t (where A_t is absorbance at time t and $A\infty$ is absorbance after completion of reaction; in most cases, $A\infty$ was taken to be the absorbance of the solvent–ligand blank since the values were essentially identical with those at the completion of the reaction) were linear to at least 75% of reaction. The pseudo-first-order rate constants, k_{obsd}, were determined graphically and are reproducible to within 6% or better (Table II).
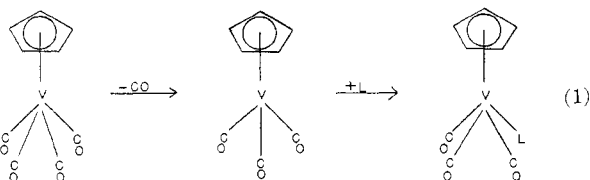
TABLE II
RATES OF REACTION OF $C_5H_5V(CO)_4$
WITH VARIOUS LIGANDS IN DECALIN^a

Ligand, L	Concn, M	Temp, °C	$10^4 k_{obsd}$, sec^{-1}
$P(C_4H_9)_3$	0.062^b	109.5	0.810
	0.062		0.840
	0.178		0.722
	0.407		0.770
	0.454		0.789
	0.103	119.3	2.48
	0.190		2.68
	0.491		2.62
	0.176^c		2.45
	0.405^c		2.45
$P(OC_4H_9)_3$	0.129		2.62
$P(OCH_2)_3C(CH_2)_2CH_3$	0.386		2.51
$P(C_4H_9)_3$	0.198	129.5	8.25
	0.429		8.25
	0.653		8.43

^{a} $\Delta H^* = 55.1 \pm 1.2$ kcal/mol; $\Delta S^* = 36.0 \pm 2.8$ eu. ^{b} Rate determined in the presence of room light. ^{c} Chlorobenzene solvent.

Results and Conclusions

Kinetic data in Table II indicate that the reaction $C_5H_5V(CO)_4 + L \rightarrow C_5H_5V(CO)_3L + CO$ proceeds according to the first-order rate law: rate $= k[C_5H_5V(CO)_4]$. The rate is thus independent of the ligand L concentration and ligand identity. As indicated in Table II some rate determinations were performed with and without the exclusion of light and in solvents of varying dielectric constant; the rates were very little affected by these alterations. The first-order rate law obtained for the reaction is consistent with a mechanism involving rate-determining dissociation of a carbonyl group (eq 1). The positive entropy of acti-

$$(1)$$

vation (+36 eu) also supports a dissociative mechanism.

The enthalpy of activation of 55.1 kcal/mol is, to our knowledge, the largest value known for substitution reactions of metal carbonyl complexes. Other $\Delta H^{\neq}$ values of approximately 40 kcal/mol have been reported for carbonyl dissociation reactions of $M(CO)_6$[8] (where M = Cr, W) and diphosM(CO)$_4$[9] (where M = Cr, Mo). The fact that the reaction of $C_5H_5V(CO)_4$ proceeds under milder conditions than those of the Cr, Mo, and W complexes previously mentioned is attributable to the large favorable entropy effect accompanying the reaction.

Although second-order kinetics have been reported for the carbonyl substitution and CO-exchange reactions of $C_5H_5Co(CO)_2$[10] and $(C_5H_5)_2Ni_2(CO)_2$,[11] the absence of a second-order term for the $C_5H_5V(CO)_4$ reactions is apparently due to steric influences which inhibit expansion of the metal coordination sphere and/or prevent nucleophilic attack at the carbonyl carbon.

Since the work of Strohmeier and Blumental[1] indicated that the reaction of $C_5H_5V(CO)_4$ with $P(C_6H_5)_3$ was first order in each of the reactants, contrary to our results with other Lewis bases, we attempted to study the reaction under conditions very close to those employed by those investigators. Thus at 102.5° using $0.2 M$ $P(C_6H_5)_3$ in decalin solvent, $C_5H_5V(CO)_4$ was observed to disappear but at a rate which was much slower than reported. Also very little product, $C_5H_5V(CO)_3L$, formed during the reaction; a great deal of decomposition accompanied the small amount of product formation. While the discrepancy between our results and those of Strohmeier and Blumental cannot be accounted for in detail, it is apparently related to the fact that the other authors measured the rates of reaction by following the increase in product absorptions in the visible spectrum; we have found that in fact very little product is formed under their conditions.

(8) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).
(9) G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, **2**, 479 (1968).
(10) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).
(11) A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

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Base Adducts of Nickel Ethylxanthate

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We reported several years ago[1] that planar, diamagnetic bis(ethylxanthato)nickel(II), $Ni[S_2CO(C_2H_5)_2]_2$,

(1) R. L. Carlin, J. S. Dubnoff, and W. T. Huntress, *Proc. Chem. Soc.*, 228 (1964).