Site-Specific Ion Pairing of Monosubstituted Vanadium Carbonylates, $LV(CO)_5^-$

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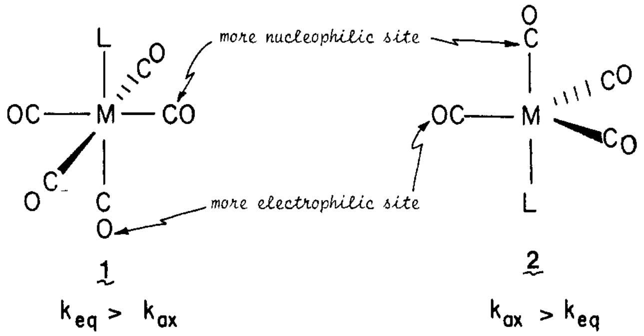
Analysis of ν(CO) infrared spectra has shown that Na^+ cation interacts specifically with the CO group trans to substituent ligands of $LV(CO)_5^-$ (L = PPh_3, $P(OPh)_3$, $P(n\text{-}Bu)_3$ and CNMe). Such site selectivity was predicted on the basis of asymmetric electron distribution in such anions as reflected in calculated Cotton–Kraihanzel CO stretching force constants. The Et_4N^+ cation was also found to form a close interaction with $LV(CO)_5^-$; however, the specific geometrical form could not be discerned. P-donor ligand substitution reactions of $PV(CO)_5^-$ were found to follow a dissociative mechanism. Vanadium–phosphorus bond cleavage was counterion dependent, with the tightly interacting Na^+ promoting faster dissociation rates.

Introduction

By arguing that CO stretching force constants in metal carbonyl complexes were an accurate reflection of the partial positive charge on carbon in such compounds, we were able to correlate the stereoselectivity of nucleophilic addition reactions in phosphine- and phosphite-substituted metal carbonyl complexes.[1] The equatorial CO stretching force constants of C_{4v} $LM(CO)_5$ complexes (M = Cr, Mo, W) are larger than axial force constants whereas for C_{3v} $LFe(CO)_4$ molecules the opposite order holds. In the former R^-, derived from RLi or RMgX, added to the equatorial carbonyl group producing *cis*-$LM(CO)_4C(O)R^-$, but for the latter, addition was axial producing *trans*-$LFe(CO)_3C(O)R^-$. Kinetic studies of the latter reaction showed that relative rates of addition varied inversely with the overall electron-releasing capacity of L as manifested by the force constant of the trans CO group.[2]

With the assumption that electronic asymmetry in such molecules, or, more importantly in anionic analogues of such molecules, is similarly felt by the carbonyl oxygen, the interaction of electrophiles with CO oxygens should likewise show site selectivity. The expected site selectivity could, however, be rationalized in other, and probably related, terms. Extended Hückel calculations of Hoffmann and Rossi indicated that for d^8 metal complexes the better σ-donor ligands prefer the axial position of a trigonal-bipyramidal complex whereas better π acceptors prefer the equatorial position.[3] For derivatives of the octahedral hexacarbonyls of 6B metals there are several empirical observations that would suggest that better π-accepting ligands prefer to be trans to a substituent phosphine or phosphite ligand as opposed to CO. The $CO\cdots Na^+$ groupage is a better π-accepting ligand than is CO or PR_3.

It has been determined that the contact ion pairs of $LMn(CO)_4^-\cdots Na^+$ (L = CO, PPh_3, $P(OPh)_3$) and of $HFe(CO)_4^-\cdots Na^+$ are of the form suggested by structure **2**; i.e., the sodium ion contact interaction is specific for the equatorial carbonyl oxygen.[4,5] Whether site selectivity exists for ion-pair interactions in structures of type **1**, however, had not been established and is the subject of a communication[6] for which full details are reported herein.



1
$k_{eq} > k_{ax}$

2
$k_{ax} > k_{eq}$

(for L = better e^--releasing ligand than CO)

Experimental Section

Materials. The solvents tetrahydrofuran, diethyl ether, and hexane were distilled under N_2 from sodium benzophenone ketyl. Hexamethylphosphorictriamide was dried over sodium and vacuum distilled. Benzene was vacuum transferred after standing over sodium and further degassed by freeze–thaw cycles. Ethanol, water, and petroleum ether were purged with argon prior to use. The $Na(diglyme)_2^+$ salt of $V(CO)_6^-$ was obtained from Strem Chemicals and used without further purification. Triphenyl phosphite and tri-*n*-butylphosphine were purified by fractional distillation from sodium wire under vacuum. Triphenylphosphine was used as received from Aldrich.

Preparations. All syntheses and transfers of compounds were performed with rigorous exclusion of air by using Schlenk or drybox techniques and N_2 or Ar as inert gas. The tetraethylammonium salt of $V(CO)_5PPh_3^-$ was prepared by the method of Ellis et al.[7] Sodium salts of $V(CO)_5P(n\text{-}Bu)_3^-$ and $V(CO)_5PPh_3^-$ were prepared according to Hieber.[8] Recrystallization of $Na^+[V(CO)_5PPh_3^-]$ from THF/hexane yielded a yellow powder which was dried in vacuo overnight. The proton NMR spectrum showed that ca. three molecules of THF per Na^+ remained in the powder. Isolated yields for all ligand-exchange and ion-exchange preparations were 70% or better. The $Na^+[V(CO)_5P(n\text{-}Bu)_3^-]$ was obtained as a red oil which was purified by column chromatography (silica gel, 1 × 12 cm, slight Ar pressure) using THF as eluant. The triphenyl phosphite derivative, $Na^+[V(CO)_5P(OPh)_3^-]$, was prepared by addition of a 20-fold excess of $P(OPh)_3$ to a THF solution of $Na^+[V(CO)_5PPh_3^-]$ (0.76 mmol of $P(OPh)_3$ to 4.3×10^{-2} mmol of the sodium salt). Upon completion of the substitution (ca. 1.5 h as confirmed by the IR spectrum) the product was driven out of solution upon the addition of hexane. The yellow powder was washed with hexane and recrystallized

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[1] Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691.

[2] Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919.

[3] Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

[4] Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

[5] Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297.

[6] Darensbourg, M. Y.; Hanckel, J. M. *J. Organomet. Chem.* **1981**, *217*, C9.

[7] Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1971**, *31*, 239.

[8] Hieber, W.; Peterhaus, J.; Winter, E. *Chem. Ber.* **1961**, *94*, 2572.

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from THF/hexane. A proton NMR spectrum in CD_3CN indicated that three molecules of THF per Na^+ remained in the powder; and C, H, and P elemental analysis supported this formulation.

The tetraethylammonium salts of $V(CO)_5P(n\text{-}Bu)_3^-$ and $V(CO)_5P(OPh)_3^-$ were prepared by the addition of a 20-fold excess of Et_4NBr to THF solutions of the purified sodium salts. The solutions were shaken vigorously and then allowed to stand for 1 h. The solutions were filtered, and the solvent was evaporated. The resulting oils were solidified by repeated trituration with petroleum ether or hexane. The solids were filtered and washed with hydrocarbon solvent. Acceptable elemental analyses were obtained.

The isocyanide complexes $Ph_4As^+V(CO)_5CNMe^-$ and $Et_4N^+V(CO)_5CNMe^-$ were generously provided by Professor J. E. Ellis.[9] The sodium salt of this anion was prepared by ion exchange using $Na^+BPh_4^-$ (in 20-fold excess to a 0.01 M THF solution of $Et_4N^+V(CO)_5CNMe^-$) as the Na^+ source. $Et_4N^+BPh_4^-$ precipitated out, and IR measurements were made on the supernatant.

Carbon-13 enriched $[Na(diglyme)_2^+][V(CO)_6^-]$ was prepared by photolysis in THF under an atmosphere of ^{13}CO (93.3% ^{13}CO, Prochem, B.O.C., Ltd., London). This salt was used to prepare carbon-13 enriched $Et_4N^+V(CO)_5PPh_3^-$ according to the method of Ellis et al.,[7] and the analogous Na^+ derivative was prepared by ion exchange as described above.

Each of the phosphine or phosphite derivatives were found to contain small amounts of $V(CO)_6^-$ which could be reduced by photolysis in THF in the presence of excess phosphine ligand.

Kinetics Measurements. Ligand substitution reactions were carried out in oven dried, 25-mL tubes whose single entry was fitted with a stopcock and a wired-on septum cap. Solutions of known concentrations of $[Et_4N^+][V(CO)_5PPh_3^-]$ and $Na^+[V(CO)_5PPh_3^-]$ were prepared and placed in the kinetics tubes inside a drybox. The tubes were then removed and placed in a constant temperature bath maintained at 68.0 °C. After temperature equilibration an appropriate amount of $P(OPh)_3$ was added with a microsyringe and the reactants were mixed. (Pseudo-first-order conditions using at least a 20-fold excess of $P(OPh)_3$ were employed.) Samples for IR measurements were periodically removed by syringe and placed in a sealed 0.1-mm NaCl IR cell which had been flushed with Ar. Reaction rates were followed by observing the decrease in absorption of the reactants' high frequency ν(CO) $A_1{}^2$ band. The linear relationship between concentration of $V(CO)_5PPh_3^-$ and absorption was established by a Beer's law plot which was linear in the range over which spectral measurements for kinetics data were made, 0.010 to 1.57×10^{-3} M.

Spectral Measurements. All IR spectra were taken on a Perkin-Elmer 283B spectrophotometer calibrated in the region below 2000 cm^{-1} with water vapor. All spectra were recorded with an expanded abscissa scale of 2.5 cm^{-1}/mm at a slow scan rate (50 cm^{-1}/min). Data for the spectral calculations were taken every 0.1 cm^{-1} from the original spectra. Band fit calculations were performed with a modified Cauchy–Gauss product function computer program developed by Pitha and Jones.[10] Force constants were calculated according to a modified Cotton–Kraihanzel approach.[11]

In addition, infrared spectra of ^{13}CO-enriched $Na^+[V(CO)_5PPh_3]^-$ enabled a more accurate calculation of the force constants. Observation of six bands for the enriched $Na^+[V(CO)_5PPh_3]^-$ permitted calculation of the two CO stretching force constants and three interaction constants making no assumptions regarding the relative magnitudes of k_t, k_c, and $k_{c'}$. These computations were performed with an iterative program based on the work of Schachtschneider and Snyder.[12] All computations were performed on the DEC-20 at the Tulane University Computing Center.

Results and Discussion

Infrared Measurements. Ion-pairing phenomena have generally been a complicating factor in the deciphering of ν(CO) IR spectra of metal carbonyl anions.[13] We have recently shown that for $Na^+R_3PV(CO)_5^-$ the specific contact ion pair formed actually clarified assignments of the ν(CO) vibrational modes.[6] The following is a more complete presentation of the site and extent of alkali cation as well as Et_4N^+ interactions with $LV(CO)_5^-$ (L = phosphines, phosphites, and isocyanide ligands) in the very

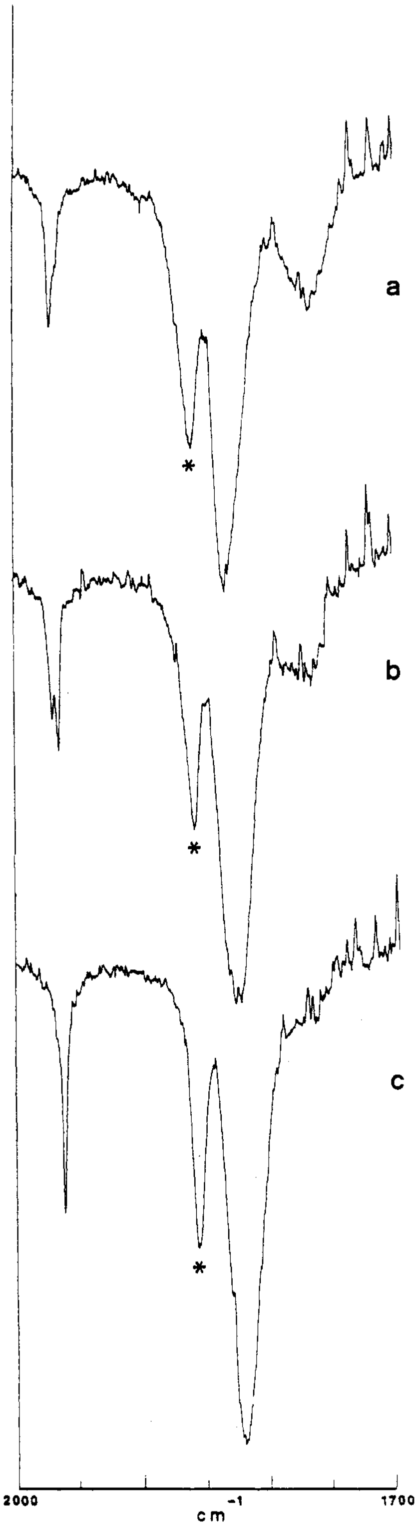

Figure 1. ν(CO) spectra of 0.01 M THF solutions of $Na^+V(CO)_5PPh_3^-$: (a) pure THF; (b) THF with 2 equiv of HMPA/Na^+; (c) THF with 6 equiv of HMPA/Na^+. The absorption marked with an asterisk is predominantly due to $V(CO)_6^-$.

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[9] Ellis, J. E.; Fjare, K. L., submitted for publication.

[10] Pitha, J.; Jones, R. N. *N.R.C.C. Bull.* **1968**, *No. 12.*

[11] Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

[12] Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 85, 117.

[13] Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 147.

Table I. ν(CO) IR Data and Cotton–Kraihanzel Force Constants for Salts of $LV(CO)_5^-$ in THF Solution

		ν(CO) vibrational modes[a,b]				force constants,[c] mdyn/A		
cation	L	A_1^2	E	A_1^1	B_1	k_1	k_2	k_i
Na^+	$P(n\text{-}Bu)_3$	1964	1820	1749	~1858	12.51	14.07	0.34
$Na(HMPA)_x^+$	$P(n\text{-}Bu)_3$	1957	1809	1809[d]	~1850	13.45	13.90	0.34
Na^+	PPh_3	1970	1832	1764	~1860	12.72	14.22	0.33
$Na(HMPA)_x^+$	PPh_3	1965	1823	1823[d]	~1860	13.65	14.08	0.33
Na^+	$P(OPh)_3$	1987	1850	1801	1890	13.27	14.48	0.33
$Na(HMPA)_x^+$	$P(OPh)_3$	1984	1843	1843[d]	1880	13.94	14.38	0.33
Na^+	CNMe[e]	1964	1835	1769	~1860	12.78	14.22	0.31
Ph_4As^+	CNMe[e]	1957	1823	1823[d]	~1860	13.63	14.04	0.31

[a] The A_1^2, E, and A_1^1 are IR-allowed bands under C_{4v} symmetry whose relative intensities are medium (sharp), strong (broad), and medium (broad), respectively. Band positions are ±1–2 cm^{-1}. [b] The B_1 band is formally forbidden and appears as a very weak band often not resolvable due to the presence of contaminant $V(CO)_6^-$ whose absorption is at 1860 cm^{-1}. [c] Cotton–Kraihanzel force constants.[11] k_1 and k_2 refer to the axial and equatorial stretching force constants, respectively. k_i represents the cis interaction constants, k_c and k_c'. The Cotton–Kraihanzel method assumes $k_c = k_c' = k_i$ and $2k_i = k_t$. [d] The position of the A_1^1 underneath the broad E band could be ±5 cm^{-1} without disturbing the observed symmetry of the E band. [e] The ν(CN) for the Na$^+$ salt is at 2112 cm^{-1} and for the Ph_4As^+ salt at 2100 cm^{-1}.

common, low-polarity solvent tetrahydrofuran (D = 7.4 at 25 °C).[14]

The ν(CO) IR spectra of $Na^+V(CO)_5PPh_3^-$ in pure THF solution and in THF to which small stoichiometric amounts of the good alkali cation complexing agent, HMPA, have been added are shown in Figure 1. In all three spectra of Figure 1 as well as the spectra of all other $LV(CO)_5^-$ investigated there is a band at 1860 cm^{-1} due to contaminant $V(CO)_6^-$. The intensity of the band at 1860 cm^{-1} varies with the purity of the compound and can be diminished upon photolysis with excess ligand. However its position is invariant with counterion, as is the case with isolated salts of $V(CO)_6^-$.[15]

The overall effect of the addition of 6 equiv of HMPA/Na$^+$ is to change the three-band spectrum of $Na^+V(CO)_5PPh_3^-$ into an apparent two-band spectrum. The 1970- and 1832-cm^{-1} bands of the former are shifted to 1965 and 1823 cm^{-1}, respectively, and the 1764-cm^{-1} band of the former shifted directly underneath the 1823-cm^{-1} band. Figure 1b shows the intermediate situation, realized on addition of 2 equiv of HMPA, in which it is clear than the low frequency band is "moving" to higher frequencies as the competition for the cation by solvating molecules becomes significant.

Our interpretation of these events is that the ν(CO) IR spectrum of $Ph_3PV(CO)_5^-$ is a three-band spectrum, as is to be expected for C_{4v} symmetry, in both a symmetrical solvent environment as in $Na(HMPA)_x^+Ph_3PV(CO)_5^-$ as well as in an environment where contact ion pairing is highly likely.[4] In the former there is an accidental degeneracy of the E and A_1^1 vibrations, as has been observed for neutral isoelectronic $Ph_3PCr(CO)_5$,[11] and that degeneracy is lifted in the presence of an interacting Na$^+$ cation. The fact that the major spectral perturbation occurs on the vibrational mode which is primarily comprised of the stretch of the CO group trans to PPh_3, i.e., the A_1^1 mode (Figure 2), suggests that it is this specific group which interacts with Na$^+$. [Were the $Na^+\cdots OC$ interaction to be through a CO group cis to the P ligand, C_s symmetry should result with the corresponding expectation of five ν(CO) IR active bands: 4A′ + A″.]

The positions of the ν(CO) bands and the corresponding force constants (vide infra) in the different solution environments are also consistent with this interpretation. When compared to the symmetrically solvated $V(CO)_5PPh_3^-$, the displacement to lower frequency for the A_1^1 band in $Ph_3PV(CO)_4CO^-\cdots Na^+$ is indicative of the better π-withdrawing ability of the $CO\cdots Na^+$ ligand, which concomitantly induces a slight shift to higher frequencies for those CO groups which do not interact with the couterion. The form of the contact ion pair is thus suggested to be **3**.

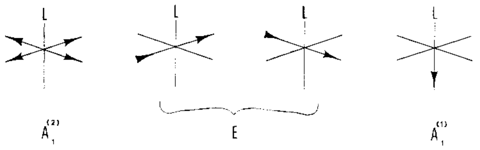
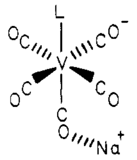


Figure 2. Stretching motions of the allowed ν(CO) vibrations in symmetrically solvated, C_{4v} $PV(CO)_5^-$.



3

On the basis of previous work which included solution conductivity measurements,[4] the structure of $Na(HMPA)_x^+V(CO)_5PPh_3^-$ will be described as a solvent-separated ion pair. As will be seen later, solvent-separated ion pairs containing the solvated cations $Na(HMPA)_x^+$ or $Na(THF)_y^+$ cannot be differentiated on the basis of the ν(CO) spectra of carbonylates. Under such conditions the carbonylate is in a symmetrical solvent environment comprised mainly of the hydrocarbon side of the donor molecules THF or HMPA. The existence of a cation one or one hundred solvent molecules removed from the anion cannot be determined by infrared spectroscopy. Conductivity studies indicated that a predominance of associated ion pairs existed in THF solutions of $Na^+Mn(CO)_4P(OPh)_3^-$ to which 10 equiv of HMPA had been added and which at higher salt concentrations displayed IR spectra typical of symmetrically solvated $Mn(CO)_4P(OPh)_3^-$.[4] Hence solvent-separated ion-pair status was bestowed on those salts, and by analogy, the salts under investigation in the current study.

Similar observations were made for other $LV(CO)_5^-$ salts for which ν(CO) spectral data and assignments may be found in Table I.[16,17] The Cotton–Kraihanzel approach

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(14) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 318.

(15) Hanckel, J. M., unpublished results.

(16) There exists in the literature a report[17] of the spectral properties of a series of $LV(CO)_5^-$ which includes ν(CO) assignments and C–K force constant values which are substantially different from those of Table I. Those workers incorrectly assumed the 1860-cm^{-1} band to be the E vibrational mode for all anions studied.

(17) Rehder, D.; Schmidt, J. *J. Inorg. Nucl. Chem.* **1974**, *36*, 333.

was used to calculate trans (axial) and cis (equatorial) CO force constants which are also found in Table I for both the contact and solvent-separated ion pairs. The position of the formally forbidden B_1 modes listed in Table I are in close agreement with values calculated by the Cotton–Kraihanzel method[6] and vary with the ion-paired form as do the allowed bands. The synthesis of $Na^+V(CO)_5PPh_3^-$ enriched in ^{13}CO afforded more CO frequency data which permitted calculation of the two CO stretching force constants and the three interaction constants, making no assumptions regarding their relative magnitudes. This approach of Schachtschneider and Snyder[12] yielded k_1 and k_2 values of 12.72 and 14.21 mdyn/Å respectively, which is in excellent agreement with the Cotton–Kraihanzel force constants for $Na^+V(CO)_5PPh_3^-$ found in Table I. Values of the interaction constants were k_t (interaction of equatorial CO groups trans to each other) = 0.66_5, k_c (interaction of equatorial CO groups cis to each other) = 0.31_8, and k_c' (interaction of axial and equatorial CO groups) = 0.33_9.

Notable about the data represented in Table I are the following points. (1) The average CO stretching force constant decreases as the overall electron-donating ability of the P-donor ligands increases ($P(OPh)_3 < PPh_3 < P(n\text{-}Bu)_3$). The CNMe ligands appears to have electronic effects very similar to PPh_3. (2) The axial CO force constant (k_1) is smaller than the equatorial (k_2) for $LV(CO)_5^-$ in a symmetrical solvent environment. (3) On contact with Na^+ the value of k_1 becomes substantially less than its value in the symmetrical solvent field and the value of k_2 increases somewhat. (4) The difference between k_1(solvent-separated ion pair) and k_1(contact ion pair) is about the same for L = $P(n\text{-}Bu)_3$ and PPh_3 but significantly less for L = $P(OPh)_3$ (i.e., $\Delta(k_1(\text{ssip}) - k_1(\text{contact}))$ = 0.94, 0.93, and 0.67 mdyn/Å, respectively). (5) The A_1^1 vibration is consistently buried underneath the E in the symmetrically solvated anion regardless of the nature of L. In all cases of ssip's this band appears to be symmetrical. However it is a fairly broad band and its width could mask positional shifts of the A_1^1 of possibly 10 cm^{-1} underneath the band envelope without inducing major asymmetry of the band.

The larger value of the k_2 in the contact ion pair forms as compared to ssip forms is consistent with the argument presented earlier. The CO groups which are not interacting with the cation compete for metal d electrons with less efficiency than does the $Na^+\cdots OC$ group. There is a corresponding shift in the ν(CN) position of the CNMe ligand which is at 2112 cm^{-1} for the Na^+ salt and at 2100 cm^{-1} for the Ph_4As^+ salt. In the latter the anion appears to be nonperturbed or in a symmetrical solvent environment.

Close inspection of the IR spectra of all salts of $LV(CO)_5^-$ listed in Table I revealed that some solvent-separated ion pairing existed for $Na^+LV(CO)_5^-$ in pure THF. (For example, the band at 1965 cm^{-1} in Figure 1a is ascribed to ssip's of the form $Na(THF)_x^+V(CO)_5PPh_3^-$.) Precise quantitative data was difficult to obtain, however, estimates for the extent of contact ion pairing in pure THF, based on the best fit possible through band shape analysis of the A_1^2 bands, were greater than 70% for P = PPh_3 and $P(n\text{-}Bu)_3$ and less than 50% for P = $P(OPh)_3$. It was also noted that the intensity of the A_1^2 band was reduced in the contact ion pairs when compared to analogous ssip's. The most obvious reason for this is due to the decrease in coupling of the two A modes as they become energetically further apart in the the contact ion pair.

Earlier it was pointed out that the Ph_4As^+ salt of $MeNCV(CO)_5^-$ yielded the anion in an unperturbed state much like that expected in a symmetrical solvent environment. Solution conductivity measurements of $Ph_3P–N–PPh_3^+$ (PPN^+) salt of $Co(CO)_4^-$, $HFe(CO)_4^-$, and other such carbonylates showed that these salts existed in solution as associated ion pairs; however, no perturbation of the carbonylate by such large counterions was evident in their ν(CO) IR spectra even at much higher concentrations.[18] The Et_4N^+ cation is considerably smaller and presents the possibility of an observable interaction with a carbonylate.

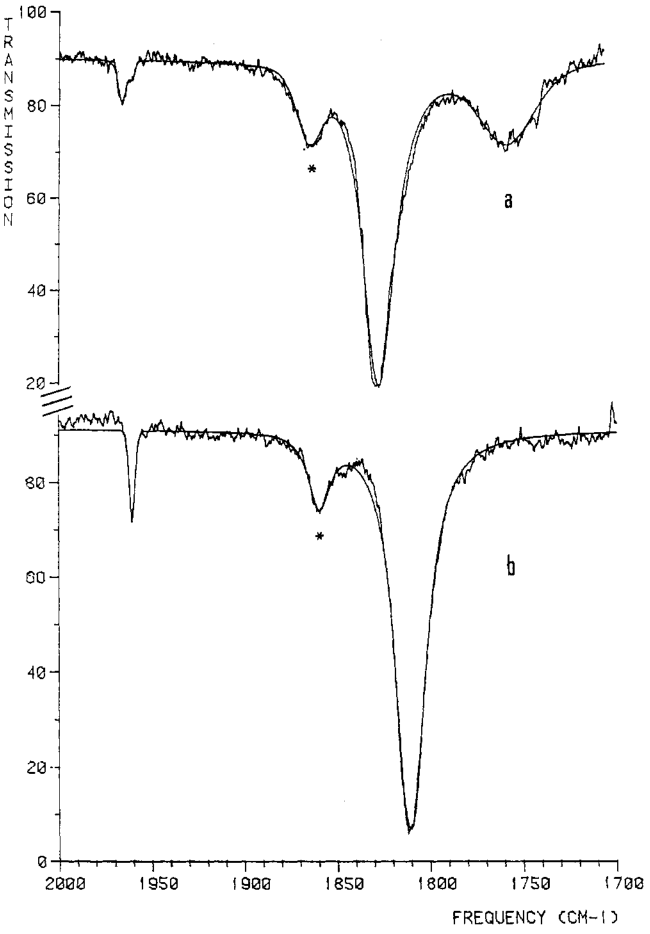

Figure 3. ν(CO) spectra of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$, 0.01 M in THF solution: (a) pure THF; (b) THF with 10 equiv of $HMPA/Na^+$. The solid line represents the calculated spectrum based on a spectral band fit optimization in both cases.

For comparison the spectra of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$ and $Na(HMPA)_x^+V(CO)_5P(n\text{-}Bu)_3^-$ in THF are shown in Figure 3. The spectrum of the Et_4N^+ analogue, as shown in Figure 4a, is not straightforwardly analyzed. The most intense adsorption is markedly asymmetric. Band-shape analysis achieved a best fit of this envelope on assuming the presence of a minimum of three composite bands (Figure 4b). (Attempts to fit the band envelope with only two composite bands were much less successful.) The initial interpretation was that the carbonylate remained in C_{4v} symmetry and that the lowest frequency band was for the A_1^1 vibrational mode of a contact, perturbed ion-pair form similar to that of the Na^+ salt. The two higher frequency components were the E mode of the contact ion pair form and the degenerate (A_1^1 + E) due to a symmetrically solvated species. (The latter would be the middle band of the three-band composite shown in Figure 4b.) Despite the reasonableness of these assumptions, problems due to intensity ratios are apparent. For C_{4v} symmetry

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[18] Darensbourg, M. Y.; Barros, H. L. C.; Borman, C. *J. Am. Chem. Soc.* **1977**, *99*, 1647.

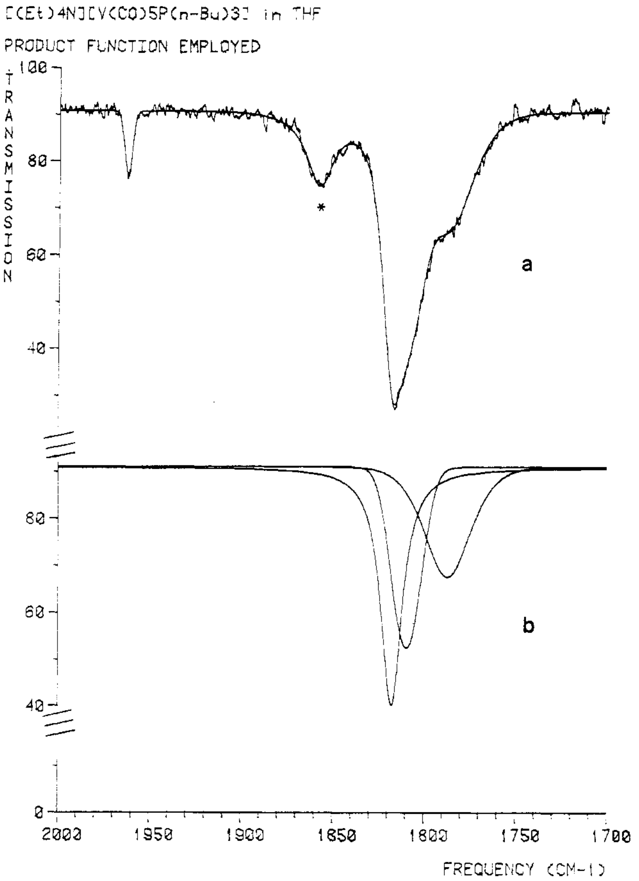


Figure 4. (a) ν(CO) spectrum of $Et_4N^+V(CO)_5P(n\text{-}Bu)_3^-$ in THF (the absorption marked with an asterisk is predominantly due to $V(CO)_6^-$). (b) Three components of the major absorption in a as determined by band-shape analysis. The fit or composite is represented by the solid line drawn through the real spectrum of a.

the intensity ratio of $(A_1^2 + A_1^1)/E$ is expected to be on the order of 0.25.[19] Indeed the $(A_1^2 + A_1^1)/E$ ratio for the band-resolved spectrum of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$ (Figure 3a) was approximately 0.30. For the Et_4N^+ salt, however, the ratio was found to be 0.72. The ratio can be expected to vary somewhat from the prediction due to deviation of the P–M–CO_{eq} angle from 90° and/or π-bonding effects of the substituent P-donor ligand.[19] However, a ratio of 0.72 seems unreasonably large. Thus it seems likely that interaction of the carbonylate with Et_4N^+ causes a departure from C_{4v} symmetry which results in splitting the degeneracy of the E mode. It should be noted that addition of HMPA (ca. 20% by volume) resulted in a spectrum similar to that of $Na(HMPA)_x^+V(CO)_5P(n\text{-}Bu)_3^-$ (Figure 3b) and furthermore that addition of $NaBPh_4$ converted the $Et_4N^+V(CO)_5P(n\text{-}Bu)_3^-$ to the contact ion paired form of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$ (Figure 3a). That is, the complexity of the spectrum of the Et_4N^+ salt is induced due to a different ion-paired form.

The Et_4N^+ salts of the PPh_3 and $P(OPh)_3$ derivatives produced similar spectra; however, resolution of the low-frequency shoulder became more difficult. Due to uncertainty in the locations of all components of the most intense band, only the approximate positions of the two most obvious constituents are reported in Table II.

The observations of contact, perturbing interactions of Et_4N^+ with $V(CO)_5P^-$ anions were consistent with recent results on THF solution spectra of $Me_4N^+CpMo(CO)_3^-$.[20]

Table II. Observed ν(CO) IR Bands of $Et_4N^+LV(CO)_5^-$ in THF Solution

L	ν(CO) [a]
$P(n\text{-}Bu)_3$	1959 m, 1856 vw, 1814 s, 1791 sh
PPh_3	1965 m, 1860 vw, 1826 s, 1800 sh
$P(OPh)_3$	1984 m, 1881 vw, 1846 s, 1832 sh
CNMe [b]	1960 m, 1858 vw, 1826 s, 1800 sh

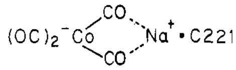
[a] The second band listed for each anion is a very weak band which is frequently partially obscured by some contaminant $V(CO)_6^-$. [b] The ν(CN) is at 2104 cm^{-1}.

Table III. Counterion Effects on First-Order Rate Constants for P-donor Ligand/$P(OPh)_3$ Substitution Reactions

compd	$V(CO)_5P^-$/ $P(OPh)_3$ [a]	k_1
$Et_4NV(CO)_5PPh_3$	1:50	$4.80\ (\pm 0.39) \times 10^{-4}$ [b]
$Et_4NV(CO)_5PPh_3$	1:20	$5.07\ (\pm 0.48) \times 10^{-4}$ [b]
$NaV(CO)_5PPh_3$	1:20	$1.15\ (\pm 0.13) \times 10^{-3}$ [b]
$NaV(CO)_5P(n\text{-}Bu)_3$	1:20	$8.86\ (\pm 0.94) \times 10^{-6}$ [c]
$Et_4NV(CO)_5P(n\text{-}Bu)_3$	1:20	$6.72\ (\pm 1.27) \times 10^{-6}$ [c]

[a] The concentration of $V(CO)_5P^-$ was 0.01 M in THF for P = PPh_3 and 0.02 M for P = $P(n\text{-}Bu)_3$. [b] These k_1 values were averaged over two runs. This error is the average of the errors of individual runs, calculated at 95% confidence levels. Replication was well within 10%. [c] These k_1 values were obtained from one run; error is calculated at 95% confidence level.

Similarly the precise form of the strong contact interaction could not be inferred from spectral analysis. It was clear, however, that a straightforward H-bonding interaction with one CO group, viz., $CpMo(CO)_2CO^- \cdots HCH_2N(CH_3)_4^+$, similar to that found in the crystal structure of $Me_4N^+CpCr(CO)_3^-$[21] and analogous to that found in the solution spectrum of $CpMo(CO)_2CO^- \cdots Na^+$, was *not* an appropriate conclusion. It is likely that the low electrostatic potential of these medium-sized cations will allow for close interaction involving more than one CO group as Edgell and Chanjamsri have proposed for the interaction of a cryptand-enclosed Na^+ with $Co(CO)_4^-$.[13]



Reactivity: Ligand Substitution Reactions. As a chemical probe of the effect of ion pairing on these carbonylates, we elected to study ligand substitution reactions of $PV(CO)_5^-$. By comparison with neutral analogues,[22] it was expected that the reaction would proceed via a dissociative path. We were interested in (1) whether tightly interacting cations would enhance the kinetic lability of the vanadium–phosphorus bond as has definitely been shown for the iron–carbon bond in $HFe(CO)_4^-$[5] and (2) whether the *anionic* coordinatively unsaturated metal carbonyl fragment could be scavenged by Lewis bases with efficiencies similar to neutral counterparts.[23] Both

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(19) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959. Brown, T. L.; Darensbourg, D. J. *Ibid.* **1967**, *6*, 971.

(20) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.*, in press.

(21) Feld, R.; Hellner, E.; Klopsch, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1978**, *442*, 173.

(22) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1979**, *184*, 77.

(23) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286. Covey, W. D.; Brown, T. L. *Ibid.* **1973**, *12*, 2820. Dobson, G. R.; Rousche, J. C. *J. Organomet. Chem.* **1979**, *179*, C42. Dobson, G. R. *Inorg. Chem.* **1980**, *19*, 1413.

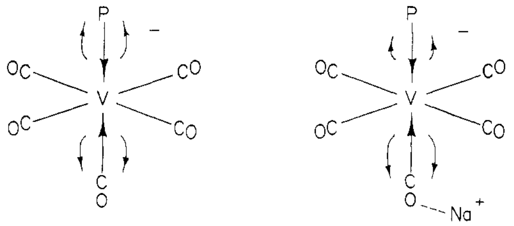

Figure 5. Competition for π density along the z axis in the symmetrical va. sodium ion perturbed $PV(CO)_5^-$.

problems are complex and the salient features only are reported here.

The displacement of PPh_3 from $V(CO)_5PPh_3^-$ was determined to be independent of entering ligand concentration (Table III) and showed a first-order dependence on the vanadium complex (eq 1 and 2). Carbon monoxide

$$PV(CO)_5^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V(CO)_5^- + P \xrightarrow{\text{excess L}} LV(CO)_5^- \quad (1)$$

$$\text{rate} = k_1[PV(CO)_5^-] \quad (2)$$

or $P(OPh)_3$ completely scavenged the coordinatively unsaturated $V(CO)_5^-$ anion, yielding 100% of the ligand-substituted product, $LV(CO)_5^-$.

As Table III shows, the Na^+ salt of $Ph_3PV(CO)_5^-$ undergoes P-ligand exchange with greater facility than does the less tightly interacting Et_4N^+ salt. There is less difference (possibly no *significant* difference) between the rates of reaction for the Na^+ and Et_4N^+ salts of $(n\text{-}Bu)_3PV(CO)_5^-$. The ratio of k_1 values for the $P(OPh)_3$ substitution of PPh_3 with Na^+ vs. Et_4N^+ is 2.1:1 and for the $P(OPh)_3$ substitution of $P(n\text{-}Bu)_3$ is 1.3:1.

Since the counterion effect is greater for the poorer σ-donor, better π-accepting PPh_3 ligand, we suggest that the counterion effects acts primarily through a sodium cation polarization of π-electron density as given in Figure 5. The polarization of the carbonylate in the sodium ion contact ion pair is expected to actually strengthen the $P \rightarrow V$ σ-bond donation in the absence of a substantial π-back-bonding, σ-donating synergic effect. That the bond *is* weakened supports the contention that there is a loss of V–P π-back-bonding in the species containing the good π-accepting ligand, $CO\cdots Na^+$. The greater loss of π-back-bonding is suffered by PPh_3, a better π-accepting ligand than $P(n\text{-}Bu)_3$, and hence a significant counterion effect is observed in the case of $V(CO)_5PPh_3^-$.

In agreement with all known crystal structures of alkali salts of transition-metal carbonylates in which Na^+ is contacting a carbonyl oxygen, Figure 5 shows an angular $V\text{–}CO\cdots Na^+$ linkage. The Na^+ is presumably directed by the best electrostatic potential to a site where simultaneous interaction with σ lone pair and π density is possible.[24] It is reasonable that the polarization of π-bonding electrons toward the Na^+ is the most important aspect in the enhanced donation of metal d electrons into the π^* orbitals of $CO\cdots Na^+$.

Conclusion. Infrared analysis of the ν(CO) region has determined the specific site of Na^+ interaction with C_{4v} $PV(CO)_5^-$ and $MeNCV(CO)_5^-$ to be at the carbonyl oxygen *trans* to the substituent phosphine, phosphite, or isocyanide ligand. The extent of the interaction is directly dependent on the overall electron-releasing ability of the P-donor ligands. The effect of the $Na^+\cdots OC\text{–}V$ interaction on ligand substitution is significant and positive for π-accepting ligands. The faster rates are suggested to be due to a loss of $V \rightarrow P$ π-back-bonding in the presence of $CO\cdots Na^+$, a ligand group that competes better for metal d electrons than does CO.

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Registry No. $NaV(CO)_5P(n\text{-}Bu)_3$, 79152-71-9; $NaV(CO)_5PPh_3$, 79152-72-0; $NaV(CO)_5P(OPh)_3$, 79152-73-1; $NaV(CO)_5(CNMe)$, 79152-74-2; $Ph_4AsV(CO)_5(CNMe)$, 78954-00-4; $Et_4NV(CO)_5P(n\text{-}Bu)_3$, 34089-20-8; $Et_4NV(CO)_5PPh_3$, 10170-61-3; $Et_4NV(CO)_5P(OPh)_3$, 79152-75-3; $Et_4NV(CO)_5(CNMe)$, 78953-99-8.

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[24] Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, *18*, 3286.

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^{13}CO Exchange Reactions of Metal–Carbene Complexes

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The rate of ^{13}CO exchange with $(CO)_5Cr{=}C(OCH_3)C_6H_5$, $(CO)_5Mo{=}C(OCH_3)C_6H_5$, $(CO)_5W{=}C(OCH_3)C_6H_5$, $(CO)_5Cr{=}\overline{CO(CH_2)_2C}(CH_3)_2$, and $(CO)_5W{=}C(C_6H_5)_2$ have been measured by ^{13}C NMR spectroscopy. The rates of ^{13}CO exchange are compared with the rates of reaction of these carbene complexes with other substrates. Selective exchange of ^{13}CO into the cis position was observed for all of the metal–carbene complexes studied except $(CO)_5W{=}C(C_6H_5)_2$ which showed no stereoselectivity. The variation of the cis:trans ^{13}CO ratio was measured as a function of the extent of ^{13}CO incorporation and was used to assess whether the 5-coordinate intermediate was rigid or fluxional.

The generation of a reactive coordinatively unsaturated intermediate by the dissociation of CO from $(CO)_5M{=}CRR'$ has been suggested as a crucial step in many of the reactions of metal–carbene complexes, including thermal decomposition, phosphine substitution, hydrogenolysis, and reactions with alkenes.

The first step in the mechanism for thermal decomposition of metal–carbene complexes to carbene dimers[1] was

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