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Origin of the Exceptional Reactivity of Vanadium Pentacarbonyl Nitrosyl

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The complex $V(CO)_5(NO)$ undergoes substitution of CO at or below 0 °C by L = PMe_3, PPh_3, $P(O\text{-}i\text{-}Pr)_3$, $P(OMe)_3$, and NEt_3 to yield $V(CO)_4L(NO)$. Substitution proceeds according to a two-term rate law: $-d[V(CO)_5(NO)]/dt = k_1[V(CO)_5(NO)] + k_2[V(CO)_5(NO)][L]$. For the extremely weak NEt_3 nucleophile, the substitution reaction occurs only via the k_1 path. Substitution of a second CO ligand to afford $V(CO)_3(PMe_3)_2(NO)$ proceeds solely by a dissociative pathway and is 10^6 times slower than loss of CO from $V(CO)_5(NO)$ at 25 °C. The thermal instability of $V(CO)_5(NO)$ results from facile CO dissociation at room temperature, which occurs faster than in any other first-row-metal carbonyl or carbonyl nitrosyl. This remarkable reactivity of $V(CO)_5(NO)$ may be attributed to a trans effect from the NO ligand. Ground-state SCF–Xα–DV calculations have been performed for $V(CO)_5(NO)$ and compared with those for $V(CO)_6$. In $V(CO)_5(NO)$, the fully occupied π-bonding t_{2g} orbitals split into $b_2(d_{xy})$ and $e(d_{xz,yz})$ orbitals. The e level, which can π-bond to NO, is preferentially stabilized, and the NO π-orbital contribution is 4–5 times that of the axial CO ligand. This superior π-acceptor character of NO also leads to the purple color of $V(CO)_5(NO)$. One-electron transitions from the $b_2(d_{xy})$ and $e(d_{xz,yz})$ levels into a low-lying empty NO π^* orbital are calculated at 2.29 and 2.52 eV and observed experimentally at 2.23 and 3.14 eV, respectively.

Introduction

Although $V(CO)_5(NO)$ was first prepared over 20 years ago by Hieber and co-workers,[1] only recently has this molecule been fully characterized by Fjare and Ellis.[2] Synthetic studies show[2] that $V(CO)_5(NO)$ is much more reactive than the isoelectronic molecule $Cr(CO)_6$; however, the mechanistic basis for this high reactivity is not known. Our recent studies in vanadium carbonyl chemistry[3] and interest[4] in the reaction mechanisms of metal nitrosyls prompted us to investigate the carbon monoxide substitution reactions of vanadium pentacarbonyl nitrosyl. Herein we report kinetic measurements of the carbon monoxide substitution reactions of $V(CO)_5(NO)$ and its phosphine-substituted derivatives. The facile substitution of $V(CO)_5(NO)$ by both dissociative and associative mechanisms may be attributed to the great π-acceptor ability of the nitrosyl ligand,[5] and this interpretation is supported by SCF–Xα–DV calculations.

Experimental Section

All operations were carried out under an atmosphere of prepurified nitrogen. Hexane was distilled from sodium benzophenone ketyl and CH_2Cl_2 from P_2O_5. Trimethylphosphine was distilled and transferred on a high-vacuum line; $P(OMe)_3$, $P(O\text{-}i\text{-}Pr)_3$, and $P(n\text{-}Bu)_3$ were distilled from Na (Me = CH_3, Pr = C_3H_7, Bu = C_4H_9). Triethylamine was dried with molecular sieves, and PPh_3 (Ph = C_6H_5) was recrystallized from absolute ethanol and dried under vacuum. Vanadium pentacarbonyl nitrosyl and $V(CO)_4(PMe_3)(NO)$ were prepared by the procedure of Fjare and Ellis.[2] A hexane solution of $V(CO)_5(NO)$ was stored at −78 °C and was stable for at least 1 month at this temperature. Substitution products were characterized by their IR and visible spectra, which were in agreement with literature reports.[2,6]

Kinetic Methods. All reactions were conducted under pseudo-first-order conditions with a large excess of nucleophile relative to $V(CO)_5(NO)$ (ca. 5×10^{-5} M). Reactions were carried out in a 4-cm path length Pyrex cell with an integral Dewar for temperature regulation. The cell was cooled with solvent slush baths frozen with liquid nitrogen. Temperatures were measured with a thermocouple and are believed to be an accurate measure of the reaction solution to ±1 °C. A solution of the ligand in hexane (20 mL) was cooled to the appropriate temperature in the cell and the reaction initiated by injecting a cold (ca. −20 °C) solution of $V(CO)_5(NO)$ in hexane (0.5 mL). Mixing was facilitated by a small magnetic stir bar in the cell. Visible spectra were recorded as a function of time on a Cary 17D spectrometer. An isosbestic point was maintained throughout the course of the reaction (Figure 1). The observed pseudo-first-order rate constants were obtained from the slope of plots of ln $(A_t - A_\infty)$ vs. time, which were linear for at least 3 half-lives. Observed rate constants were reproducible within ±5%.

The rate of CO substitution of $V(CO)_4L(NO)$ (L = PMe_3 or $P(n\text{-}Bu)_3$) by additional L was followed by absorbance-mode IR measurements on a Perkin-Elmer 283 spectrometer in 0.1-mm CaF_2 cells. Aliquots of the thermostated (±0.2 °C) reaction mixture were sampled as a function of time, and the disappearance of the 1957-cm^{-1} band was monitored. The rate of thermal decomposition of $V(CO)_5(NO)$ was measured by observing the decrease in the absorbance at 1989 cm^{-1} on a Nicolet 7199 FT-IR instrument.

Electronic spectra were recorded on a Perkin-Elmer 330 spectrometer in 0.1-cm quartz cells equipped with a solution reservoir and Teflon in glass valve. The solution spectrum of $V(CO)_5(NO)$ was measured in hexane with the cell under a CO atmosphere to retard decomposition of the complex. Extinction coefficients of this complex were calculated from those obtained[2] for $V(CO)_4(PMe_3)(NO)$ with the assumption that the conversion of $V(CO)_5(NO)$ to $V(CO)_4(PMe_3)(NO)$ was quantitative.

Theoretical Methods. Electronic structure calculations of $V(CO)_5(NO)$ were performed on a Harris 800 minicomputer and employed the discrete variational (DV)[7] Xα method. Numerical atomic orbitals were used as basis functions. For vanadium, all orbitals through 4d were included; for C, N, and O, orbitals through 2p were used. Orbitals 1s, 2s, and 2p on vanadium and 1s on carbon, nitrogen, and oxygen were treated as part of a frozen core in the molecular calculations. Atomic orbital populations were computed by using the Mulliken scheme.[8] The molecular Coulomb potential was calculated by utilizing a least-squares fit of the model electron density to the true density,[9] as described previously[3b] for $V(CO)_6$. The structure

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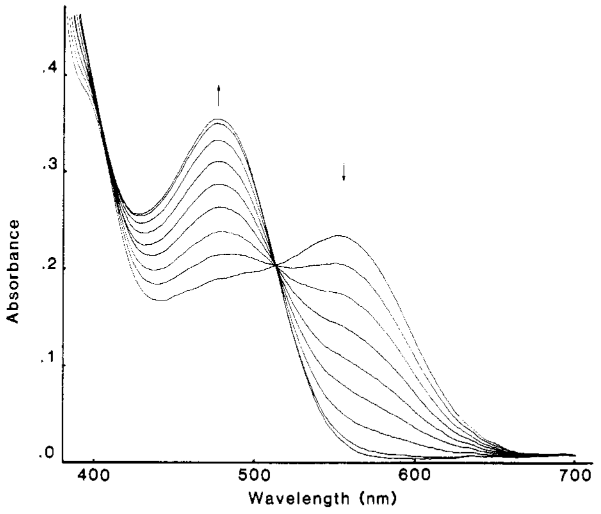

Figure 1. Electronic absorption spectral changes during the reaction between $V(CO)_5(NO)$ and $P(OMe)_3$ in hexane solution at −6 °C.

Table I. Rate Constants for CO Substitution of $V(CO)_4L(NO)$ by L′ in Hexane Solution

L	L′	T, °C	k_1, s^{-1}	k_2, M^{-1} s^{-1}
CO	PMe_3	0		1.09×10^{-1} [a]
		−16		1.61×10^{-2}
		−16		2.59×10^{-2} [b]
	PPh_3	0	4.18×10^{-4}	2.27×10^{-2}
	$P(O\text{-}i\text{-}Pr)_3$	0	5.06×10^{-4}	1.43×10^{-2}
	$P(OMe)_3$	0	5.71×10^{-4}	9.24×10^{-3}
	NEt_3	0	4.95×10^{-4}	
PMe_3	PMe_3	45	6.36×10^{-5}	
$P(n\text{-}Bu)_3$	$P(n\text{-}Bu)_3$	45	1.39×10^{-4}	

[a] Extrapolated value from low-temperature data. [b] In CH_2Cl_2 solution.

of $V(CO)_5(NO)$ was idealized to C_{4v} symmetry with V–N–O and V–C–O distances assumed to be the same as in the $V(CO)_3(PMe_3)_2(NO)$ structure.[6b] Calculations were also performed with the axial V–C bond lengthened by 0.1 Å. Although the orbital energies changed slightly, there was no significant change (±2%) of the character of the frontier orbitals. About 23 cycles (SCF mixing parameter of 0.18) and 23 min of CPU time were required to achieve a converged ground state. Thereafter about 10 cycles were sufficient to converge transition-state calculations.

Results

Carbon monoxide substitution in $V(CO)_5(NO)$ occurs readily at low temperatures in hexane solvent to afford the monosubstituted products *trans*-$V(CO)_4L(NO)$ (eq 1).[2] The

$$V(CO)_5(NO) + L \rightarrow \textit{trans}\text{-}V(CO)_4L(NO) + CO \quad (1)$$

substitution reaction was monitored by observing changes in the visible spectra as a function of time as illustrated in Figure 1 for L = $P(OMe)_3$. The purple color of the starting material is replaced by the yellow color of the substituted derivatives, and an isosbestic point is maintained throughout the course of the transformation. As can be seen from Figure 2, the reaction obeys a two-term rate law corresponding to ligand-independent and ligand-dependent pathways (eq 2). The

$$\frac{-d[V(CO)_5(NO)]}{dt} = k_1[V(CO)_5(NO)] + k_2[L][V(CO)_5(NO)] \quad (2)$$

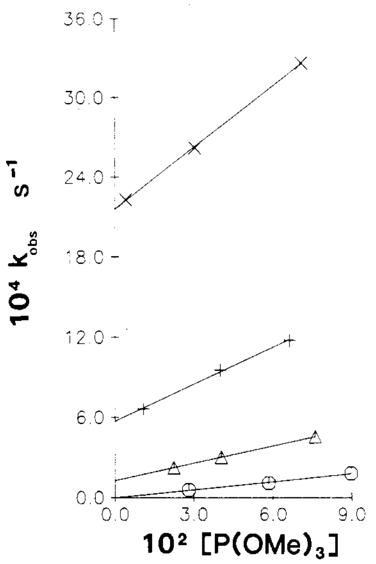

Figure 2. Dependence of the observed rate of disappearance of $V(CO)_5(NO)$ upon the $P(OMe)_3$ concentration in hexane solvent at the following temperatures: ×, 6 °C; +, 0 °C; △, −6 °C; ○, −16 °C.

Table II. Activation Parameters for CO Substitution of $V(CO)_4L(NO)$ by L′ in Hexane Solution[a]

L	L′	$\Delta H_1^{\ddagger}$ [b]	$\Delta S_1^{\ddagger}$ [b]	$\Delta H_2^{\ddagger}$ [c]	$\Delta S_2^{\ddagger}$ [c]
CO	PMe_3			16 ± 2	−3 ± 0.4
CO	$P(OMe)_3$			13 ± 2	−20 ± 6
CO	NEt_3	25 ± 1	14 ± 3		
PMe_3	PMe_3	27 ± 2	6 ± 1		

[a] Units: $\Delta H^{\ddagger}$, kcal/mol; $\Delta S^{\ddagger}$ cal/(mol deg). [b] Ligand-independent pathway. [c] Ligand-dependent pathway.

values of k_1 and k_2 for the ligands studied are collected in Table I. A complete listing of observed rate constants as a function of temperature and ligand concentration is available as supplementary material. Activation parameters are provided in Table II; however, these values should be used with caution since rate constants could only be measured over a relatively narrow temperature range (ca. 20 °C with an estimated uncertainty of ±1 °C) because of the thermal instability of $V(CO)_5(NO)$.

Kinetics of further CO substitution of the thermally robust $V(CO)_4L(NO)$ (L = PMe_3 or $P(n\text{-}Bu)_3$) derivatives were also examined (eq 3). Under the experimental conditions $V(CO)_3L_2(NO)$ reacts with additional L to afford $V(CO)_2L_3(NO)$,[10] but the kinetics of this process were not investigated. The

$$\textit{trans}\text{-}V(CO)_4L(NO) + L \rightarrow \textit{mer}\text{-}V(CO)_3L_2(NO) + CO \quad (3)$$

rate of reaction (eq 3) was found to be independent of nucleophile concentration and thus obeys the simple first-order rate law given in eq 4. Rate constants and activation parameters for L = PMe_3 are included in Tables I and II, respectively.

$$\frac{-d[V(CO)_4L(NO)]}{dt} = k[V(CO)_4L(NO)] \quad (4)$$

The thermal decomposition of $V(CO)_5(NO)$ was monitored by FT-IR spectroscopy. No CO- or NO-containing products are formed as decomposition products.[2] In a CO-saturated solution, the half-life for $V(CO)_5(NO)$ decomposition is 1000 s. However, in a solution purged with nitrogen to remove CO generated by the decomposition reaction, the half-life is less than 400 s.

Discussion

Vanadium pentacarbonyl nitrosyl reacts readily with nucleophiles by both ligand-dependent and ligand-independent pathways to afford *trans*-$V(CO)_4L(NO)$. The ligand-de-

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Table III. Rate Constants for Dissociative and Associative CO Substitution of First-Row-Transition-Metal Carbonyl and Carbonyl Nitrosyl Complexes at 25 °C[a]

	k_1, s^{-1}	k_2, M^{-1} s^{-1} [b]
$V(CO)_5(NO)$	4×10^{-2}	7×10^{-2} [c]
$V(CO)_4(PMe_3)(NO)$	5×10^{-8}	
$Mn(CO)_4(NO)$	$<10^{-7}$	3×10^{-4}
$Mn(CO)(NO)_3$	4×10^{-3}	54
$Fe(CO)_2(NO)_2$	$\sim 10^{-7}$	10^{-3}
$Co(CO)_3(NO)$	$\sim 10^{-7}$	10^{-3}
$V(CO)_6$		3×10^{-1}
$Cr(CO)_6$	10^{-12}	10^{-10} [d]
$Fe(CO)_5$	$<10^{-8}$	
$Ni(CO)_4$	1.5×10^{-2}	

[a] Data taken from ref 3, 4, 11a, and 13. [b] For PPh_3 except as noted. [c] For $P(OMe)_3$. [d] For $P(n\text{-}Bu)_3$.

pendent pathway is qualitatively similar to that observed[4] for other metal carbonyl nitrosyl complexes. The relatively small enthalpy of activation (13 kcal/mol) and the large negative entropy of activation (−20 cal/(mol deg)) for L = $P(OMe)_3$ are typical for metal carbonyl complexes that substitute CO by an associative mechanism.[4,11]

As expected for the associative term, the rate of reaction depends on the nature of the nucleophile. The rate of nucleophilic attack at vanadium increases in the series $P(OMe)_3 < P(O\text{-}i\text{-}Pr)_3 < PPh_3 < PMe_3$, but the rate of substitution of the first and last members of this group only spans one order of magnitude at 0 °C. Thus, the high reactivity of $V(CO)_5(NO)$ is coupled with reduced selectivity. The reduced selectivity could be interpreted as V–N–O bending preceding V–nucleophile bonding by a significant amount. The extreme limiting case would involve a preequilibrium between the linear form and small amounts of a bent $V(CO)_5(NO)$ species. Dissociation of CO would occur from the linear $V(CO)_5(NO)$ isomer, and associative attack could occur on a bent intermediate. Within the temperature range available, it would be difficult to exclude the latter mechanism as it too predicts a two-term rate law.

Comparison of the associative rates of substitution of $V(CO)_5(NO)$ with other first-row-transition-metal carbonyl nitrosyl compounds (Table III) shows that, despite its high coordination number, $V(CO)_5(NO)$ is more reactive than the other complexes except for $Mn(CO)(NO)_3$. Apparently, vanadium can readily expand its coordination sphere to allow for nucleophilic attack. Similar behavior has been observed[3] for the 17-electron complex $V(CO)_6$. The occurrence of associative substitution for the 18-electron $V(CO)_5(NO)$ may be a consequence of the ability of the NO ligand to accept a pair of electrons and thus avoid a 20-electron transition state.

ground state transition state

This behavior appears to be general[4] for transition-metal carbonyl nitrosyl compounds and is supported by structural studies[13] of intermediates previously suggested on the basis of kinetic behavior.

Table IV. Frontier Orbitals, Eigenvalues, and Atomic Orbital Character[a] $V(CO)_5(NO)$

orbital	energy, eV	orbital type derived from atomic compositions
$2a_2$	−1.791	pure CO π^*
12e	−2.393	7% V $d_{xz,yz}$; 34% CO_{eq} π^*; 10% NO π^*; 45% CO_{ax} π^*
$5b_1$	−2.627	pure CO π^*
11e	−2.821	90% CO_{eq} π^*
$13a_1$	−3.230	91% CO_{eq} π^*
10e	−4.183	6% V $d_{xz,yz}$; 44% NO π^*; 36% CO_{ax} π^*
$2b_2$	−6.000[b]	V–CO π-bond: 55% V d_{xy}; 45% CO_{eq} π^*
9e	−6.560	V–CO and V–NO bond: 45% V $d_{xz,yz}$; 13% CO_{eq} π^*; 34% NO π^*; 7% CO_{ax} π^*
8e	−10.499	3% V 3p; 89% CO_{eq} 5σ; 6% CO_{ax} 5σ
$4b_1$	−11.253	23% V $d_{x^2-y^2}$ σ-bonded to 76% CO_{eq} donor lone pair
$12a_1$	−11.290	58% CO_{ax}; 17% NO; 28% CO_{eq}
$11a_1$	−12.065	similar to $12a_1$: 11% V d_{z^2}; 69% CO_{eq}; 18% NO
7e	−12.257	45% $C\text{–}O_{eq}$ π-bond; 53% N–O π-bond
$3b_1$	−12.388	99% C–O π-bond
$1a_2$	−12.436	pure C–O π-bonding

[a] The orientation of the coordinate system was such that z points along the V–N bond and x and y lie along orthogonal $V\text{–}C_{eq}$ bonds. [b] The highest occupied molecular orbital.

Although the reactivity of $V(CO)_5(NO)$ at low temperatures (<−15 °C) is dominated by associative substitution behavior, at higher temperatures a ligand-independent process becomes important. Poor nucleophiles such as NEt_3 react exclusively by this mechanism. The first-order rate constants do not depend on the nature or concentration of the nucleophile (Table I), and the rate of dissociation at 0 °C is about 5×10^{-4} s^{-1}. At 0 °C with $[P(OMe)_3] = 0.05$ M, the associative and dissociative pathways contribute equally to the overall rate of substitution. The activation parameters for L = NEt_3 are consistent with rate-determining CO dissociation.[11-13a] The decomposition of $V(CO)_5(NO)$ also appears to proceed by CO dissociation since the rate of decay can be reduced by a factor of 3 in the presence of 1 atm of CO. As can be seen from the data in Table III, CO dissociation from $V(CO)_5(NO)$ proceeds markedly faster than in other first-row-transition-metal carbonyl and carbonyl nitrosyl complexes. This unusual behavior appears to be a consequence of the great π-acceptor ability of the nitrosyl ligand. In particular, the NO group should labilize the trans CO for dissociation. The very high stretching frequency of the CO group ($\nu_{CO} = 2105$ cm^{-1}) trans to NO as well as the low nitrosyl stretching frequency ($\nu_{NO} = 1695$ cm^{-1}) suggests that this is a reasonable explanation. It should be noted that the carbonyl stretching frequency in the next most reactive carbonyl nitrosyl, $Mn(CO)(NO)_3$, is also quite high (2095 cm^{-1}).[4]

Although *trans*-$V(CO)_4(PMe_3)(NO)$ substitutes CO solely by a dissociative mechanism, further substitution of $Co(CO)_2L(NO)$ and $Mn(CO)_3L(NO)$ proceeds[4] by an associative mechanism. Apparently, the electron-rich PMe_3 ligand trans to NO greatly reduces the ability of the NO group to accept electron density in the transition state for an associative pathway. Dissociation of CO (trans to CO) from *trans*-$V(CO)_4(PMe_3)(NO)$ is 10^6 times slower at 25 °C than in the parent complex, where CO is trans to NO. In contrast, the rate of CO dissociation from octahedral complexes such as $Cr(CO)_5L$ and $Mn(CO)_4L(X)$ (L = phosphine ligand; X = halide) is usually faster than from the parent compound (L = CO) because of the cis-labilizing influence of L.[11a,13] Thus, from a comparison of the lability of $V(CO)_5(NO)$ and $Cr(CO)_6$ toward CO dissociation with their respective phosphine-substituted derivatives $V(CO)_4L(NO)$ and $Cr(CO)_5L$, the ground-state trans effect of the NO ligand overrides any cis influence[13d] from L that is present in the transition state.

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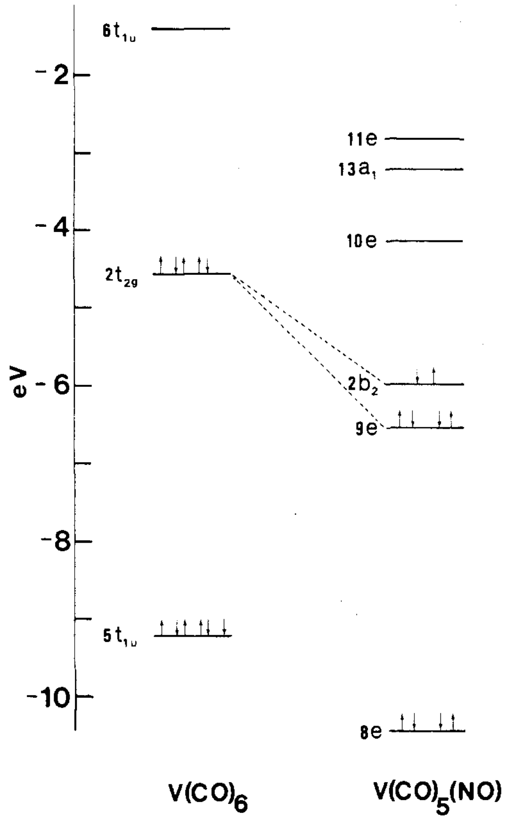

Figure 3. Comparative orbital-energy diagrams from SCF-Xα-DV calculations of $V(CO)_6$ and $V(CO)_5(NO)$. The occupied d orbitals are correlated with dashed lines.

There have been no theoretical studies of complexes where CO and NO ligands are trans to each other, although there has been considerable interest[14] in the electronic structures of metal nitrosyls. Therefore, we undertook SCF-Xα-DV calculations of $V(CO)_5(NO)$. An orbital-energy diagram of the frontier orbitals may be found in Figure 3 along with those reported[3b] previously for $V(CO)_6$. A listing of valence-level eigenvalues and the orbital-population analyses are available in Table IV. The π-acceptor ability of the NO ligand is superior to that of CO as judged by several criteria.

First, the LUMO orbital 10e consists of NO π^* and CO π^* character and lies at a relatively low energy above the HOMO $2b_2$ level. We calculate the dipole-allowed $2b_2 \rightarrow 10e$ and $9e \rightarrow 10e$ electronic transitions (spin-restricted transition state) to occur at 2.20 and 2.52 eV, respectively. In the low-energy region of the optical spectrum (hexane solvent), we find absorptions at 2.23 and 3.14 eV with molar extinction coefficients of 420 and 600 M^{-1} cm^{-1}, respectively. These absorptions are responsible for the characteristic purple color of $V(CO)_5(NO)$. By contrast, the isoelectronic molecule $Cr(CO)_6$ and the closely related complex $V(CO)_6$ (in dilute conditions)[3b] do not absorb at low energies. In this context the absorption spectrum of $V(CO)_5(NO)$ resembles the situation in transition-metal pentacyano nitrosyl complexes. Manoharan and Gray[15] found the lowest energy electronic excitations in these systems could be attributed to charge-transfer transitions to the low-lying NO π^* orbital.

For $V(CO)_5(NO)$ the LUMO also contains significant CO π^* character from the axial carbon monoxide ligand (Table IV). Consequently, when the axial CO is replaced, as in *trans*-$V(CO)_4(PMe_3)(NO)$, the LUMO becomes more localized on NO and is raised in energy. Thus, the "metal to π^* NO" charge-transfer transitions shift to 2.69 eV (450 M^{-1} cm^{-1}) and 3.54 eV (2360 M^{-1} cm^{-1}), respectively (CH_2Cl_2 solvent). Compared to the case of $V(CO)_6$, the predominantly vanadium d orbitals $2b_2$ and 9e of $V(CO)_5(NO)$ are stabilized and split in energy (Figure 3). The 9e level ($d_{xz,yz}$), which can π-bond to the axial NO group, is preferentially stabilized. The character (Table IV) of the 9e dπ orbital of $V(CO)_5(NO)$ also illustrates effective π-bonding between vanadium and the linear NO ligand. Nitrosyl-localized π^* orbitals contribute a factor of 4–5 times more to the metal–ligand π-bonding 9e molecular orbital than does the axial CO ligand. Similar behavior had been previously observed by Fenske and DeKock[16] in MO calculations of pentacyano nitrosyl systems. Metal–ligand covalent σ-bonding orbital character is found in the $4b_1$ and $11a_1$ orbitals. It is interesting that the NO ligand contributes in preference to the axial CO group in the $11a_1$ σ-bonding level. Therefore, NO predominates over the axial CO group in both the σ- and π-bonding molecular orbitals.

The facile dissociation of CO from $V(CO)_5(NO)$ explains the high reactivity of this complex with even poor nucleophiles such as THF and NEt_3. This dissociative lability leads to facile decomposition, and thus the rarity[17] of metal carbonyl complexes with mutually trans NO and CO ligands can be understood. Of the first-row-transition-metal nitrosyls and carbonyl nitrosyls, only $Ni(CO)_4$ (Table III) dissociates CO as rapidly as $V(CO)_5(NO)$. Modi and Atwood[18] have attributed the high reactivity of $Ni(CO)_4$ to the low crystal field activation energy (CFAE) expected for a d^{10} complex. Our data for the d^6 complex $V(CO)_5(NO)$, where the CFAE will be a maximum, indicate that the trans effect of certain ligands can be as important as CFAE considerations. We are aware of only one other complex with trans NO and CO groups: $[Fe(CO)_5(NO)][Cl]$,[17] which was prepared in liquid HCl and presumably contains a bent nitrosyl ligand.

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Registry No. $V(CO)_5(NO)$, 14883-03-5; $V(CO)_4PMe_3(NO)$, 84911-07-9; $V(CO)_4P(n\text{-}Bu)_3(NO)$, 88548-51-0; PMe_3, 594-09-2; PPh_3, 603-35-0; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; $P(OMe)_3$, 121-45-9; NEt_3, 121-44-8; $P(n\text{-}Bu)_3$, 998-40-3.

Supplementary Material Available: Tables of observed rate constants for reactions of $V(CO)_5(NO)$ and $V(CO)_4L(NO)$ where L = PMe_3 or $P(n\text{-}Bu)_3$ (2 pages). Ordering information is given on any current masthead page.

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