have a transient existence as discussed above. The loss of a carbonyl group (CO) by either of these species would give a gas-phase precursor for $Fe_4(CO)_{13}^-$. Were these precursor ions to react to solution with the same rate constants as they do in the gas phase, they would have lifetimes of less than a 1 ms and not be observable by ESR. If the energy required for $Fe(CO)_4^-$ and $Fe_2(CO)_{11}^-$ to lose a CO is not too large,[22] then it is possible that $Fe_4(CO)_{13}^-$ is formed in solution by the same mechanism as in the gas phase.

The other ions observed in condensed phase are $Fe_3(CO)_{11}^-$ and $Fe_3(CO)_{12}^-$. These ions could also result from reaction sequences beginning with $Fe(CO)_4^-$ or $Fe(CO)_3^-$. In the condensed phase the loss of CO ligands in the individual steps of the clustering reaction could be moderated by the solvent medium. In the gas phase the collision complex of $Fe_2(CO)_6^-$ with $Fe(CO)_5$ can only dissipate reaction exothermicity by losing some fragment such as CO. In the condensed-phase reaction exothermicity can be dissipated to the medium without loss of CO. Thus, in the condensed phase $Fe_2(CO)_6^-$ might associate directly with $Fe(CO)_5$ to form $Fe_3(CO)_{11}^-$. $Fe_3(CO)_{12}^-$ might similarly result from direct association of $Fe(CO)_5$ and $Fe_2(CO)_7^-$ formed by loss of CO from $Fe_2(CO)_8^-$ or from reaction of $Fe_2(CO)_8^-$. Although not observed to react in the gas phase, $Fe_2(CO)_8^-$ could react as a rate fast enought to produce observable product in the condensed-phase studies, but too slow to be observed in the present gas-phase studies.

Acknowledgment. Paul Krusic and Gary Weddle are acknowledged for helpful discussions. The NSF is acknowledged for partial support of this work under Grant No. CHE-8110516.

Registry No. $Fe(CO)_5$, 13463-40-6; $Fe(CO_3)^-$, 53221-56-0; $Fe(CO)_4^-$, 51222-96-9.

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[22] If $D(Fe(CO)_3^-{-}CO)$ F 0.25 eV, then $Fe(CO)_3^-$ might form by dissociation of $Fe(CO)_4^-$ at a sufficiently rapid rate to produce observable products in condensed phase. Appearance potential measurements (ref 17) do not give a definitive value for $D(Fe(CO)_3^-{-}CO)$, but do suggest that it is substantially less than 1 eV.

Mechanism of Carbon Monoxide Substitution in Metal Carbonyl Radicals: Vanadium Hexacarbonyl and Its Phosphine-Substituted Derivatives

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Abstract: Carbon monoxide substitution in the metal radical $V(CO)_6$ proceeds at or below room temperature to form monosubstitution products $V(CO)_5L$ (L = phosphine or phosphite). The substitution occurs solely by a second-order process according to a rate law that is first order in both $V(CO)_6$ and phosphorus nucleophile. The rate of reaction is strongly dependent on the basicity and size of the ligand. Activation parameters further support the associative nature of the reaction: $P(n\text{-}Bu)_3$, $\Delta H^\ddagger = 7.6 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -25.2 \pm 1.7$ cal/mol·deg; $P(OMe)_3$, $\Delta H^\ddagger = 10.9 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -22.6 \pm 0.8$ cal/mol·deg; PPh_3, $\Delta H^\ddagger = 10.0 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -27.8 \pm 1.6$ cal/mol·deg. The rate of substitution of $V(CO)_6$ by PPh_3 is unchanged under 1 atm of carbon monoxide or in the presence of $[V(CO)_6]^-$. The carbon monoxide substitution reactions of $V(CO)_5L$ with additional L also proceed by an associative mechanism with the rate of substitution approximately three orders of magnitude slower than for $V(CO)_6$. The disubstituted product adopts the cis stereochemistry with small phosphorus donor ligands or with chelating phosphines. For L = $P(OMe)_3$, activation parameters were determined: $\Delta H^\ddagger = 13.2 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -27.6 \pm 1.8$ cal/mol·deg. Phosphine exchange reactions of $V(CO)_5L$ were also observed indicating that, in addition to carbon monoxide, phosphine ligands on vanadium are substitution labile. Nucleophilic attack of $P(n\text{-}Bu)_3$ at $V(CO)_5[P(n\text{-}Bu)_3]$ is 10^5 times slower than that at $V(CO)_6$, presumably because the increased electron density on the metal hinders nucleophilic attack. Quantitative comparisons between the 17-electron complex $V(CO)_6$ and its 18-electron analogue $Cr(CO)_6$ indicate that associative carbon monoxide substitution takes place 10^{10} times faster in the vanadium system.

Metal carbonyl radicals have become increasingly prevalent in organometallic chemistry.[1] In addition to their postulated role as intermediates in a variety of catalytic and stoichiometric chemical transformations, several stable, paramagnetic organometallic complexes have been isolated recently.[2] Typically these are stabilized by phosphine or cyclopentadienyl ligands. Vanadium hexacarbonyl is unique as the only stable homoleptic metal carbonyl radical.[3] This has prompted a number of investigations of the physical properties of $V(CO)_6$ by X-ray crystallography,[4] EPR,[5] electrochemical techniques,[6] electronic spectra, and theoretical calculations.[7] In addition, synthetic studies resulting in phosphine substitution,[8] disproportionation,[3,9] or reduction of $V(CO)_6$ have been reported.[10] Indeed, substitution and electron-transfer processes are often competitive reactions in the

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Table I. Second-Order Rate Constants and Activation Parameters for Substitution of $V(CO)_6$ by Ligand L according to Eq 1 at 25 °C in Hexane

ligand[a]	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol·deg
PMe_3	132	7.6 ± 0.7[b]	−23.4 ± 3.4
$P(n\text{-}Bu)_3$	50.2	7.6 ± 0.4	−25.2 ± 1.7
$PMePh_2$	3.99	8.9 ± 0.3	−25.9 ± 1.1
$P(O\text{-}i\text{-}Pr)_3$	0.94		
$P(OMe)_3$	0.70	10.9 ± 0.2	−22.6 ± 0.8
PPh_3	0.25	10.0 ± 0.4	−27.8 ± 1.6
$P(i\text{-}Pr)_3$	0.11		
$AsPh_3$	0.018[c]		

[a] Abbreviations: Me = methyl; *n*-Bu = *n*-butyl; *i*-Pr = isopropyl; Ph = phenyl. [b] Uncertainties are three standard deviations from a linear least-squares analysis. [c] Rate constant at 17 °C.

chemistry of $V(CO)_6$. In this and in the following paper[11] we describe kinetic and mechanistic studies of the ligand substitution and of the Lewis base induced disproportionation reactions of $V(CO)_6$.

Although the lability of many 17-electron organometallic radicals has been recognized,[1] the precise mechanisms available are not well defined. In part this is a consequence of the transient nature of most metal carbonyl radicals as exemplified by $M(CO)_5$ (M = Mn, Re), which have been extensively studied.[12] Carbon monoxide substitution in $Mn(CO)_5$ apparently proceeds by a dissociative mechanism,[12a–c] but $Re(CO)_5$ reacts by an associative process.[12e] Phosphine substituted $Mn(CO)_xL_{5-x}$ (x = 3, 4) complexes are more stable to dimerization than $Mn(CO)_5$ and exhibit associative substitution behavior.[12a,13] It should be noted that not all 17-electron radicals are substitution labile, as shown by recent work on $Co(P(OMe)_3)_4$[14] and $Mn(\eta^4\text{-butadiene})_2L$ (L = CO, PMe_3).[15] As a consequence of its relative stability, $V(CO)_6$ provides an attractive model system for elucidating reaction pathways for metal radicals. Herein, we report the kinetics and mechanism of substitution of $V(CO)_6$ by phosphines and phosphites to afford $V(CO)_5L$. These monosubstituted derivatives are also substitution labile, and the kinetics of the second CO replacement step and phosphine exchange reactions are also reported. A portion of this work has been the subject of a preliminary communication.[16]

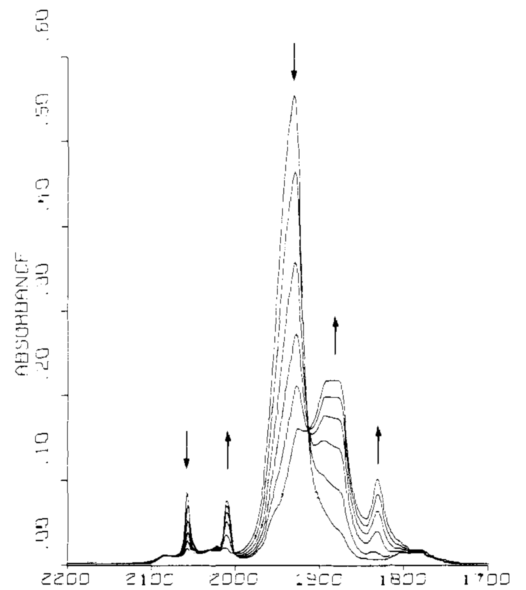

Figure 1. Infrared spectral changes as a function of time during the reaction between $V(CO)_5[P(OMe)_3]$ and $P(OMe)_3$ (eq 3) in hexane at 25 °C.

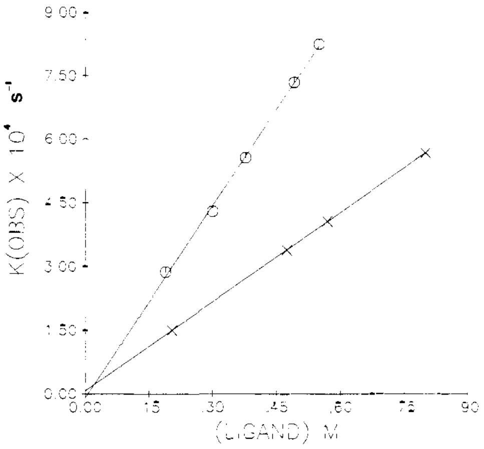

Figure 2. Plot of k_{obsd} (s^{-1}) vs. nucleophile concentration (M) for the following reactions: ○, $V(CO)_5[P(OMe)_3]$ + $P(OMe)_3$; ×, $V(CO)_5[P(n\text{-}Bu)_3]$ + $P(OMe)_3$ in hexane at 25 °C.

Results

Carbon monoxide replacement in $V(CO)_6$ by phosphines and phosphites proceeds readily at or below room temperature in hexane solution according to eq 1. These reactions can be

$$V(CO)_6 + L \rightarrow V(CO)_5L + CO \qquad (1)$$

monitored conveniently by observing changes in the visible absorption spectra as a function of time. Isosbestic points were observed in a number of these reactions. For all nucleophiles examined (Table I), substitution obeys the second-order rate law given in eq 2. No ligand-independent (i.e., dissociative) reaction

$$-d[V(CO)_6]/dt = k[V(CO)_6][L] \qquad (2)$$

pathway exists under these conditions. Second-order rate constants and activation parameters for eq 1 are listed in Table I. A complete listing of pseudo-first-order rate constants as a function of ligand concentration and temperature for all reactions reported is available as supplementary material.

Monosubstitution products were identified by their IR spectra (supplementary material). The triphenylphosphine monosubstitution product is identical with that prepared by Ellis and co-workers.[8a] We were unable to isolate other $V(CO)_5L$ derivatives because of their thermal instability under vacuum and their high solubility in nonreactive solvents. The compounds $V(CO)_5[P(OMe)_3]$, $V(CO)_5[P(n\text{-}Bu)_3]$, and $V(CO)_5[AsPh_3]$ were further characterized by reduction with Na/Hg and the resulting anions isolated as tetraethylammonium salts following cation exchange.

The rate of CO substitution was found to be unchanged under 1 atm of carbon monoxide ([CO] ~ 8 × 10^{-3} M; [PPh_3] = 1.24

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Table II. Second-Order Rate Constants for the Reaction of $V(CO)_5L$ with Nucleophile L′ according to Eq 3 in Hexane at 25 °C

L	L′	10^4k, M^{-1} s^{-1}	ratio[b]
$P(n\text{-}Bu)_3$	$P(n\text{-}Bu)_3$	5.42[a]	92600
$PMePh_2$	$PMePh_2$	22.8[a]	470
$P(O\text{-}i\text{-}Pr)_3$	$P(O\text{-}i\text{-}Pr)_3$	7.38[a]	1750
$P(OMe)_3$	$P(OMe)_3$ [c]	14.9 ± 0.6[a]	1270
PPh_3	PPh_3	2.81[a]	880
$P(OMe)_3$	$P(n\text{-}Bu)_3$	5.83[d]	
$P(n\text{-}Bu)_3$	$P(OMe)_3$	7.00 ± 0.04[e]	

[a] Rate of carbon monoxide substitution according to eq 3. [b] Ratio of the rate of carbon monoxide substitution in $V(CO)_6$ by L (eq 1) to that of carbon monoxide substitution in $V(CO)_5L$ by L′ (eq 3) when L = L′. [c] Activation parameters: $\Delta H^{\ddagger} = 13.2 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -27.6 \pm 1.8$ cal/mol·deg. [d] Replacement of $P(OMe)_3$ by $P(n\text{-}Bu)_3$ is very rapid; the measured rate is the further substitution of $V(CO)_5P(n\text{-}Bu)_3$ by $P(n\text{-}Bu)_3$ to afford $V(CO)_4(P(n\text{-}Bu)_3)_2$ (eq 5). [e] Rate of substitution of $V(CO)_5\text{-}P(n\text{-}Bu)_3$ by $P(OMe)_3$ to yield $V(CO)_5P(OMe)_3$ according to eq 6.

$\times 10^{-2}$ M). More importantly, added $[Et_4N][V(CO)_6]$ also did not affect the rate of CO substitution. In CH_2Cl_2 at 10 °C the rate of substitution in the absence of $[Et_4N][V(CO)_6]$ is 7.47×10^{-2} M^{-1} s^{-1}. Addition of the anion, such that $[V(CO)_6^-] = [V(CO)_6] = 3.6 \times 10^{-4}$ M, did not influence the rate (7.14×10^{-2} M^{-1} s^{-1}) within experimental error. No phosphine substitution of $[V(CO)_6]^-$ was observed in this experiment.

Replacement of a second carbon monoxide ligand by a phosphorus donor ligand affords $V(CO)_4L_2$ (eq 3). For the smaller

$$V(CO)_5L + L \rightarrow V(CO)_4L_2 + CO \quad (3)$$

ligands L = $P(OMe)_3$, $P(O\text{-}i\text{-}Pr)_3$, and $PMePh_2$ or when L_2 = diphos, cis products are observed, while $P(n\text{-}Bu)_3$, $P(i\text{-}Pr)_3$, and PPh_3 yield products with a trans stereochemistry.[8c] In the case where L = $P(O\text{-}i\text{-}Pr)_3$, *cis*-$V(CO)_4L_2$ is a kinetic product which was isomerized to the trans isomer by heating the reaction solution to 80 °C. The rate of the second substitution step is at least three orders of magnitude slower than that of the first. Thus with proper adjustment of nucleophile concentration, each substitution step could be observed without interference from the other. Most of these reactions (eq 3) were monitored by IR (absorbance mode) measurements; excellent agreement was obtained with other rates determined by visible spectroscopy. The IR spectral changes as a function of time for eq 3 with L = $P(OMe)_3$ are illustrated in Figure 1. Isosbestic points are maintained at 2030, 2002, and 1915 cm^{-1}. The rate law is first order in incoming nucleophile, as illustrated in Figure 2, and second-order rate constants are collected in Table II. Substitution products were identified by a comparison of their IR spectra (supplementary material) with literature reports.[8] The previously unreported complex *cis*-$V(CO)_4[P(OMe)_3]_2$ was isolated from hexane as a thermally unstable yellow powder. On standing overnight under nitrogen the powder acquires a drab green color, and its mass spectrum indicated the presence of some $V(CO)_3(P(OMe)_3)_3$. This complex also forms slowly when $V(CO)_4[P(OMe)_3]_2$ is treated with excess $P(OMe)_3$, and its IR spectrum (toluene solution) has absorbances at 1953 (m) cm^{-1} and 1824 (s) cm^{-1}. The reaction of $V(CO)_6$ with diphos (1,2-bis(diphenylphosphinoethane)) in hexane proceeded directly to $V(CO)_4$(diphos),[17] and no intermediates were observed in the IR spectrum.

The reactions between the monosubstituted derivatives $V(CO)_5L$ and attacking nucleophiles, L′, were examined. Reactions of $V(CO)_5L$ (L = $P(OMe)_3$ and $P(n\text{-}Bu)_3$ with L′ = $P(n\text{-}Bu)_3$ and $P(OMe)_3$, respectively, were investigated, since the IR spectra of these complexes can be resolved. In these systems, replacement of L by the large excess of incoming ligand L′ occurs *prior* to loss of carbon monoxide. The ultimate product is $V(CO)_4(L')_2$, and

Table III. Variation of the Rate of Carbon Monoxide Substitution of $V(CO)_6$ with Some Properties of the Phosphine Nucleophile

L	cone angle,[a] deg	ΔHNP[b]	log *k*[c]
1, PMe_3	118	114	2.12
2, $P(n\text{-}Bu)_3$	132	131	1.70
3, $PMePh_2$	136	424	0.60
4, $P(O\text{-}i\text{-}Pr)_3$	135	520[d]	−0.03
5, $P(OMe)_3$	107	580	−0.16
6, PPh_3	145	573	−0.61
7, $P(i\text{-}Pr)_3$	160	33[e]	−0.98

[a] Reference 18. [b] Reference 19. [c] Temperature = 25 °C. [d] Value for $P(O\text{-}n\text{-}Bu)_3$. [e] Value for tricyclohexylphosphine.

no mixed $V(CO)_4LL'$ species are observed. Initial replacement of $P(OMe)_3$ by $P(n\text{-}Bu)_3$ is very rapid (eq 4): the subsequent

$$V(CO)_5[P(OMe)_3] + P(n\text{-}Bu)_3 \xrightarrow{\text{fast}} V(CO)_5[P(n\text{-}Bu)_3] + P(OMe)_3 \quad (4)$$

$$V(CO)_5[P(n\text{-}Bu)_3] + P(n\text{-}Bu)_3 \xrightarrow{\text{slow}} V(CO)_4[P(n\text{-}Bu)_3]_2 + CO \quad (5)$$

substitution of carbon monoxide (eq 5) proceeds at the same rate as the independently measured second substitution step for L = $P(n\text{-}Bu)_3$ (eq 3). The rate of replacement of $P(n\text{-}Bu)_3$ by $P(OMe)_3$ can also be measured (eq 6), and the second substitution step (eq

$$V(CO)_5P[n\text{-}Bu)_3] + P(OMe)_3 \xrightarrow{\text{slow}} V(CO)_5[P(OMe)_3] + P(n\text{-}Bu)_3 \quad (6)$$

$$V(CO)_5[P(OMe)_3] + P(OMe)_3 \xrightarrow{\text{fast}} V(CO)_4[P(OMe)_3]_2 + CO \quad (7)$$

7) is fast compared to eq 6. Consequently, no $V(CO)_5[P(OMe)_3]$ is observed during the course of this reaction. Replacement of $P(n\text{-}Bu)_3$ by $P(OMe)_3$ shows a first-order dependence on nucleophile concentration, as seen in Figure 2.

Phosphite exchange also occurs in the reaction between $V(CO)_5[P(OMe)_3]$ and a tenfold excess of $P(OEt)_3$. When the reaction is monitored by ^{31}P NMR spectroscopy (only the free ligands can be observed since the complexes are paramagnetic), a peak attributable to free $P(OMe)_3$ grows in as the bis-substituted phosphite complex forms.

Discussion

Substitution of $V(CO)_6$. Thermal ligand substitution in $V(CO)_6$ is facile for a wide variety of phosphine and phosphite bases. Carbon monoxide substitution depends directly on the concentration of the incoming nucleophile, and no dissociative pathway is evident under these conditions. Thus an associative ligand substitution mechanism is indicated by the data. This is corroborated by the variation of the rate (Table I) with the nature of the nucleophile. Although both size[18] and basicity influence the rate of substitution, examination of the data in Table III reveals that the basicity of the incoming ligand dominates. The relative protonic base strength of the phosphorus ligands may be quantified by the difference in half-neutralization potentials, ΔHNP, from that of *N,N*-diphenylguanidine taken as standard, measured in nitromethane.[19] Indeed, a good correlation can be drawn between the basicity of the nucleophile and the rate of substitution, as illustrated in Figure 3. Only the very bulky triisopropylphosphine ligand reacts significantly slower than would be expected according to the correlation in Figure 3. Other metal carbonyl systems which react with phosphines by associative mechanisms show similar behavior,[20] although steric effects usually are evident at consid-

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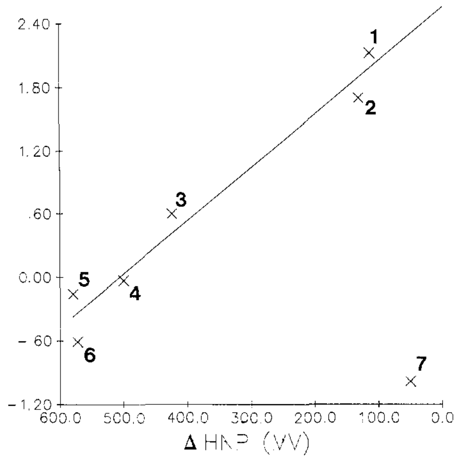

Figure 3. Plot of log k vs. ΔHNP (mV) for carbon monoxide substitution in $V(CO)_6$ by various phosphorus ligands. The numbers refer to the ligands listed in Table III.

erably smaller ligand cone angles.

Apparently $V(CO)_6$ can easily expand its coordination sphere to accommodate the incoming ligand. The notion of a seven-coordinate transition state is not common,[21] but for this system, it seems reasonable, since vanadium forms a number of derivatives (albeit 18-electron systems) of the form $EV(CO)_6$, where E represents a bulky, polarizable electrophile such as $SnPh_3$ or $AuPPh_3$.[22] Activation parameters provide further support for an associative process. The relatively small energies of activation (7.6 to 10.9 kcal/mol) and the large, negative entropies of activation (−22.6 to −27.8 cal/mol·deg) are typical[20,23] for reactions with a transition state of higher coordination number than that of the ground state.

Several experiments were performed to test for alternative substitution mechanisms. The rate of PPh_3 substitution is unchanged, within experimental error, when the reaction is carried out under an atmosphere of carbon monoxide. If CO dissociation from vanadium were an important (i.e., rate determining) step in the substitution process, then added CO would be expected to suppress the rate. A mechanism involving electron transfer and rapid reaction of a 16-electron $[V(CO)_6]^+$ species also appears unlikely. Although $[V(CO)_6]^+$ has been generated electrochemically, it is exceedingly unstable and decomposes irreversibly with loss of CO at −78 °C on the cyclic voltammetry time scale.[6] Additionally, $[V(CO)_6]^-$ cannot be involved in the mechanism because it is inert to thermal substitution. Definitive experimental evidence against such a process arises from the observation that added $[V(CO)_6]^-$ does not suppress the rate of PPh_3 substitution even when $[V(CO)_6]^- \simeq [V(CO)_6]$. Furthermore, although electron transfer has recently been invoked to explain the black color of solid $V(CO)_6$, the ion pair $[V(CO)_6]^+[V(CO)_6]^-$ could not be detected in the ground state.[7] The energy change calculated for the disproportionation of $V(CO)_6$ to form $[V(CO)_6]^+[V(CO)_6]^-$ is unfavorable by approximately 50 kcal/mol.[7] Also the highly reproducible kinetics observed suggest that catalysis by trace oxidants is unlikely. Thus, all evidence is in accord with a substitution mechanism involving rate-determining nucleophilic (I_A) attack at the metal center to form a seven-coordinate transition state or intermediate.

The kinetic data reveal a puzzling trend. The reactions of $V(CO)_6$ show slight sensitivity to the steric properties of an attacking nucleophile. Only with L = $P(i\text{-}Pr)_3$ is there a marked decrease in rate from that expected on the grounds of proton basicity (Figure 3). One might have anticipated that a mechanism which involves a seven-coordinate transition state (or intermediate) would exhibit far greater steric preferences. This observation suggests to us that the transition state occurs at a relatively long vanadium–nucleophile distance. When a filled nucleophile orbital attacks a half-filled $d(t_{2g})$ orbital of $V(CO)_6$ then the formal vanadium–nucleophile bond order will be 1/2. The net V–L bonding interaction expected for a $V(CO)_6L$ transition state (or intermediate) allows facile associative substitution.

Compare the behavior of the 17-electron $V(CO)_6$ complex with that of its 18-electron analogue $Cr(CO)_6$. For good nucleophiles, chromium hexacarbonyl substitutes CO according to a two-term rate law corresponding to associative (I_A) and dissociative pathways.[24] The latter route dominates at high temperatures, where an appreciable substitution rate is observed. The extrapolated value of the rate[24] for associative attack on $Cr(CO)_6$ by $P(n\text{-}Bu)_3$ at 25 °C is 10^{-9} M^{-1} s^{-1}. At room temperature the rate of dissociative loss of CO from $Cr(CO)_6$ is estimated to be even slower (10^{-12} s^{-1}). *Thus, associative substitution of* $V(CO)_6$ *by* $P(n\text{-}Bu)_3$ *is approximately* 10^{10} *times faster than that in* $Cr(CO)_6$! Similarly, the 18-electron anion $[V(CO)_6]^-$ is substitution inert, and only photochemical replacement of CO has been reported[25] for this species. These results afford the first quantitative comparison of rates of substitution between analogous 17- and 18-electron compounds.

In this context the electrocatalytic substitution of a number of group 6 metal carbonyl derivatives reported by Hershberger, Klinger, and Kochi[26a] should be mentioned. The same authors[26b] have also obtained more definitive evidence of associative ligand substitution in $[CpMn(CO)_2L]^+$ derivatives. A radical chain mechanism for ligand replacement was initiated by electrochemical oxidation of the inert complexes to form labile 17-electron cation radicals. Our results support the authors supposition of an associative mechanism for the substitution of the cation radical.

Substitution of $V(CO)_5L$. The rate of carbon monoxide displacement from $V(CO)_5L$ upon reaction with additional nucleophile, L, spans a deceptively narrow range (Table II). These data are not strictly comparable, since the reactivity of the metal complex $V(CO)_5L$ is of course dependent on the nature of L. As illustrated in Figure 2, only a ligand-dependent substitution pathway exists for eq 3. Activation parameters for L = $P(OMe)_3$ are consistent with an associative mechanism: $\Delta H^{\ddagger} = 13.2 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -27.6 \pm 1.8$ cal/mol·deg. Again a transition state of higher coordination number is implicated; the synthesis of seven-coordinate vanadium carbonyl derivatives containing two bulky ligands should be noted.[27] Disubstitution products with a cis stereochemistry are observed for phosphorus ligands with a small cone angle, but more sterically demanding phosphines afford the trans isomer. In the case of L = $P(O\text{-}i\text{-}Pr)_3$, the cis kinetic product can be thermally isomerized to afford *trans*-$V(CO)_4L_2$. Thus, attack cis to L in $V(CO)_5L$ seems feasible; however, our observations do not lead to unambiguous conclusions concerning the stereochemistry in the hypothetical seven-coordinate intermediate.

The rate of the second carbon monoxide substitution for $P(n\text{-}Bu)_3$ is nearly 10^5 times slower that that of the first step. For the other ligands studied (Table II), this ratio is approximately 10^3. We infer that attack of $P(n\text{-}Bu)_3$ on $V(CO)_5[P(n\text{-}Bu)_3]$ is inhibited because of electronic factors. Alternatively, $P(n\text{-}Bu)_3$ may readily attack to generate a seven-coordinate transition state or intermediate, but phosphine loss (a nonproductive reaction, see

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next section) may be favored over carbon monoxide loss (eq 8).

$$V(CO)_5L \underset{-L}{\overset{+L}{\rightleftharpoons}} V(CO)_5L_2 \xrightarrow{-CO} V(CO)_4L_2 \qquad (8)$$

Thus, the electron density at the metal center is important in governing the lability of $V(CO)_5L$ complexes. This is consistent with the importance of electronic factors in determining the rate of substitution of $V(CO)_6$.

Phosphine Exchange of $V(CO)_5L$. Phosphine ligand exchange, rather than simple CO substitution, is also a viable reaction pathway for $V(CO)_5L$ (eq 9 and 10). This was investigated by

$$V(CO)_5L + L' \rightarrow V(CO)_5L' + L \qquad (9)$$

$$V(CO)_5L' + L' \rightarrow V(CO)_4(L')_2 + CO \qquad (10)$$

using the mixed $P(n\text{-}Bu)_3$ and $P(OMe)_3$ systems. Loss of L from $V(CO)_5L$ (eq 9) precedes CO loss (eq 10) when $V(CO)_5L$ is treated with an excess of L′. In the case of L = $P(OMe)_3$ and L′ = $P(n\text{-}Bu)_3$, eq 9 is rapid and $V(CO)_5[P(n\text{-}Bu)_3]$ is observed in the IR spectrum. The measured rate of eq 10 (Table III) agrees well with the value determined for the reaction between $V(CO)_5[P(n\text{-}Bu)_3]$ and $P(n\text{-}Bu)_3$ in the absence of $P(OMe)_3$. Conversely, when L = $P(n\text{-}Bu)_3$ and L′ = $P(OMe)_3$, eq 9 limits the rate. Phosphine replacement by phosphite also follows a second-order rate law, as depicted in Figure 2. Replacement of $P(n\text{-}Bu)_3$ by $P(OMe)_3$ may indicate that π-bonding ligands stabilize the electron-rich transition state. In addition, *phosphite exchange occurs on a time scale similar to that of CO substitution when $V(CO)_5[P(OMe)_3]$ is reacted with an excess of $P(OEt)_3$. Thus, both phosphorus ligands and carbon monoxide are subject to associative replacement from the labile 17-electron vanadium center.* This resembles the kinetic behavior of $Mn(CO)_3L_2$ (L = bulky alkyl phosphine) complexes,[13] in which associative replacement of both CO and phosphine occurs upon reaction with isotopically labeled CO.

Conclusion

Vanadium hexacarbonyl and its phosphine- and phosphite-substituted derivatives are quite labile relative to 18-electron analogues. Substitution takes place exclusively by an assocaitive mechanism, and the rate of reaction depends markedly on the electronic properties of the nucleophile and the metal center. Two factors seem important in this reactivity. Vanadium can readily expand its coordination sphere to allow for a seven-coordinate transition state. Most importantly, the hole in the bonding d^5 t_{2g} orbital set permits facile nucleophilic attack compared with electronically saturated organometallic systems. Apparently the transition state is reached at a relatively long V–nucleophile distance. Two-center three-electron bonding is probably crucial for stabilizing the 19-electron transition state or intermediate. Dissociative processes, which would involve a 15-electron intermediate, are not observed. Other metal radicals which possess these properties would be expected to react in a similar manner. The rate of nucleophilic attack at 17-electron metal complexes decreases in the series $Mn(CO)_5$(?),[12a] $Re(CO)_5$[12e] > $Mn(CO)_4L$[12a] > $Re(CO)_3L_2$[28] > $Mn(CO)_3L_2$[13] > $V(CO)_6$ > $V(CO)_5L$ > $V(CO)_4L_2$ ≫ Mn(1,4-butadiene)$_2$CO.[15] An increase in the basicity of the metal center or a decrease in the steric accessibility of the metal to an approaching nucleophile results in a reduced rate of associative substitution. The first and last members of this series exhibit anamolous behavior. In the case of $Mn(CO)_5$, compelling evidence for an associative ligand substitution mechanism is lacking, despite extensive investigation of its chemistry.[29] The observation that the 17-electron Mn(η^4-butadiene)$_2$CO complex is substitution inert can be rationalized. Molecular orbital calculations suggest that the HOMO is protected by the butadiene ligands from nucleophilic attack, and there is a large energy barrier to ligand rearrangement in this complex.[15]

Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen, and solids were transferred in a nitrogen-filled Vacuum Atmospheres glove box. Vanadium hexacarbonyl was prepared from $[Et_4N][V(CO)_6]$ and 100% H_3PO_4 by the method of Ellis and co-workers.[8a] Liquid phosphines and phosphites were obtained from commercial sources, distilled from sodium metal and stored under nitrogen. Triphenylphosphine and bis(1,2-diphenylphosphino)ethane were recrystallized twice from absolute ethanol and dried under vacuum. Hexane was stored over H_2SO_4 and then distilled from Na/benzophenone. Methylene chloride was dried with P_2O_5 and toluene with sodium metal. All solvents were rigorously degassed prior to use. Mass spectra were obtained by Dr. D. Hung of the Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 15-eV ionization. Microanalysis were performed by Galbraith Laboratories, Knoxville, TN.

Spectral Studies. Infrared spectra were recorded in 0.1-mm CaF_2 cells on a Perkin-Elmer 283 or a Nicolet 7199 FT-IR spectrometer. Substitution products were characterized by IR (supplementary table) as well as by chemical methods (see below). Visible spectra were recorded on a Perkin-Elmer 320 spectrometer in 1.00-cm quartz cells modified for work with air-sensitive compounds. Low-temperature kinetic runs were performed in a 4-cm Pyrex cell (with an integral dewar for temperature regulations) on a Cary 14 spectrometer. Appropriate liquid nitrogen slush baths[29] provided low temperatures. Phosphorus NMR spectra were recorded on a JEOL FX-90Q spectrometer.

Kinetic Methods. All reactions were carried out under pseudo-first-order conditions with the concentration of the nucleophile at least an order of magnitude greater than that of $V(CO)_6$. Substitution of $V(CO)_6$ by incoming nucleophiles to afford $V(CO)_5L$ was monitored by visible spectroscopy. Reactions were initiated by injecting a hexane solution of $V(CO)_6$ into the thermally equilibrated cell containing a solution of phosphine in hexane. The cell was briefly removed from the cell compartment and thoroughly mixed by shaking, and then the change in absorbance at an appropriate wavelength (usually between 400 and 450 nm) was recorded as a function of time. Isosbestic points were observed for the following nucleophiles: PPh_3 (404, 307 nm), $AsPh_3$ (415, 350 nm), $P(O\text{-}i\text{-}Pr)_3$ (427 nm), and $P(i\text{-}Pr)_3$ (415 nm). Plots of ln $(A_\infty - A)$ vs. time were linear for more than 3 half-lives and k_{obsd} was determined from the slope of this line by least-squares analysis. Rate constants were reproducible to ±5%.

The second substitution step was monitored by IR, FT-IR, and visible spectroscopy. Excellent agreement was obtained between the three methods. The bulk of the data was obtained at room temperature on the Perkin-Elmer 283 instrument; care was taken to avoid heating of the IR cell by the beam of the spectrometer. Substitution could only be followed for approximately 1 half-life because of overlapping IR bands. The change in absorbance of the strongest band of $V(CO)_5L$ was usually monitored, but good (±5%) agreement was also obtained when other peaks were chosen for analysis. Activation parameters for eq 4, L = $P(OMe)_3$, were determined by visible spectroscopy (isosbestic points at 465 and 440 nm).

Isolation of $[Et_4N][V(CO)_5L]$ from $V(CO)_5L$. This procedure was used to characterize $V(CO)_5L$ for L = $P(OMe)_3$, $P(n\text{-}Bu)_3$, and $AsPh_3$, and the following describes the procedure for L = $P(OMe)_3$. To a −78 °C toluene (50 mL) slurry of $V(CO)_6$ (0.68 g, 2.95 mmol), $P(OMe)_3$ (0.35 mL, 2.95 mmol) was added dropwise by syringe. Over the course of 30 min the solution was allowed to warm to 0 °C with stirring. An IR spectrum taken at this point revealed only $V(CO)_5[P(OMe)_3]$. An excess of sodium amalgam (0.7% Na by weight, 15 mL) was added, and a yellow solid began to precipitate. After 14 h, the toluene was removed in vacuo, and the resulting solid was dissolved in 25 mL of degassed acetone. The acetone solution was syringed into a degassed solution of Et_4NBr (1.5 g, 7.1 mmol) in 50 mL of water. Immediate precipitation of yellow product occurred, and this solid was filtered, washed with water, and dried in vacuo. The crude product was recrystallized from acetone/ether resulting in yellow microcrystalline $[Et_4N][V(CO)_5P(OMe)_3]$ (0.9 g, 72% yield): IR (THF) 1974 (m), 1856 (s), 1829 (vs). Anal. Calcd for $C_{16}H_{29}NO_8PV$: C, 43.15; H, 6.56; N, 3.15. Found: C, 43.19; H, 6.48; N, 3.02.

***cis*-$V(CO)_4[P(OMe)_3]_2$.** A heterogeneous mixture of 0.525 g (2.40 mmol) of $V(CO)_6$ and 0.67 mL (5.68 mmol) of $P(OMe)_3$ in 8 mL of hexane was stirred under nitrogen for 2.5 h at room temperature. Gas evolution was essentially complete after this time and a bright yellow precipitate had formed. The solid was isolated by filtration, washed twice with hexane, and dried under vacuum. The yellow powder (0.74 g, 74%

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(30) **Note Added in Proof:** Recent laser flash photolysis studies and low-temperature matrix-isolation experiments show that CO substitution in $Mn(CO)_5$ proceeds by an associative mechanism (Yesaka, H.; Kobayoshi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249–6252; Hepp, A. F.; Wrighton. M. S. *Ibid.* **1983**, *105*, 5934–5935).

yield) was identified as $V(CO)_4[P(OMe)_3]_2$ by its IR [toluene, 2007 (m), 1905 (sh), 1885 (s), 1865 (sh) cm^{-1}] and mass spectrum (*m/e* 411). On standing overnight under nitrogen or under vacuum, the compound acquires a drab green color and some $V(CO)_3[P(OMe)_3]_3$ (*m/e* 508) was detected in the mass spectrum. An elemental analysis of the drab green powder was obtained. Anal. Calcd for $V(CO)_4[P(OMe)_3]_2$: C, 29.2; H, 4.42; P, 15.07. Found: C, 25.7; H, 4.44; P, 15.85.

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Registry No. $V(CO)_6$, 14024-00-1; PMe_3, 594-09-2; $P(n\text{-}Bu)_3$, 998-40-3; $PMePh_2$, 1486-28-8; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; $P(i\text{-}Pr)_3$, 6476-36-4; $AsPh_3$, 603-32-7; $V(CO)_5P(n\text{-}Bu)_3$, 87739-19-3; $V(CO)_5PMePh_2$, 87739-24-0; $V(CO)_5P(O\text{-}i\text{-}Pr)_3$, 87739-25-1; $V(CO)_5P(OMe)_3$, 87739-26-2; $V(CO)_5PPh_3$, 72622-82-3; $[Et_4N][V(CO)_5P(OMe)_3]$, 75009-05-1; *cis*-$V(CO)_4[Ph(OMe)_3]_2$, 87739-27-3.

Supplementary Material Available: Tables of infrared spectral data for the substitution products and observed rate constants as a function of ligand concentration and temperature for all reactions studied (4 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of Lewis Base Induced Disproportionation of Vanadium Hexacarbonyl and Its Phosphine-Substituted Derivatives

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Abstract: Vanadium hexacarbonyl readily disproportionates upon treatment with oxygen and nitrogen Lewis bases. The reaction is first order with respect to Lewis base and $V(CO)_6$. Nucleophilic attack on the metal center appears to be the rate-determining step. Second-order rate constants in dichloromethane decrease in the series py > Et_3N > MeCN > MeOH > acetone > THF > 2,5-Me_2THF > DME > $MeNO_2$ > Et_2O, with a factor of 10^4 separating the first and last members of this group. Activation parameters for disproportionation by THF are in accord with an associative mechanism: $\Delta H^{*} = 14.2 \pm 1.2$ kcal/mol and $\Delta S^{*} = -21.5 \pm 4.2$ cal/mol·deg. The structure of the disproportionation product is also dependent on the nature of the Lewis base. For Et_2O, the bridging isocarbonyl complex $[V(Et_2O)_4][O\text{-}C\text{-}V(CO)_5]_2$ can be isolated from CH_2Cl_2–Et_2O solution. For stronger oxygen and nitrogen bases (B), $[V(B)_6][V(CO)_6]_2$ is the final product. In the case of B = pyridine, a bridging isocarbonyl intermediate can be detected as a kinetic product of the disproportionation process. This intermediate reacts with additional pyridine to afford $[V(B)_6][V(CO)_6]_2$. The observation of an isocarbonyl-bridged intermediate suggests that electron transfer may take place through an isocarbonyl ligand. Phosphine-substituted derivatives of $V(CO)_6$ undergo disproportionation much more slowly than $V(CO)_6$, although the rate-limiting step also appears to be CO substitution by the Lewis base. For example, disproportionation of $V(CO)_5P(n\text{-}Bu)_3$ induced by CH_3CN is five orders of magnitude slower than that of $V(CO)_6$.

Vanadium hexacarbonyl undergoes a disproportionation reaction[1,2] when treated with hard Lewis bases, eq 1. Similar

$$3V(CO)_6 + 6B \rightarrow [V(B)_6]^{2+} + 2[V(CO)_6]^- + 6CO \quad (1)$$

base-induced disproportionation reactions have been observed for the homoleptic carbonyls of manganese, iron, cobalt, and nickel.[3] In addition, photochemical disproportionation of a number of metal carbonyl complexes has been reported.[4] Presumably, these disproportionation reactions involve both ligand substitution and electron-transfer processes. As a complement to our study[5] of the mechanism of ligand substitution of $V(CO)_6$, we have investigated the kinetics and mechanism of the Lewis base induced disproportionation of this molecule. Despite the importance of disproportionation processes in metal carbonyl chemistry, we are aware of only three previous kinetic studies of this transformation.[6] These all involved $Co_2(CO)_8$, and the complex behavior observed[6] tended to hamper the study of the reaction mechanism. In a broader context, the redox behavior of the 17e $V(CO)_6$ species may provide a general model for the base-induced disproportionation of organometallic radicals. A portion of this work has

Table I. Second-Order Rate Constants for the Disproportionation of $V(CO)_6$ by Nitrogen and Oxygen Lewis Bases in CH_2Cl_2–Hexane Solution at 25 °C

base	k, M^{-1} s^{-1}	isosbestic points, nm
py	1.22	397, 368
Et_3N	0.765	422
MeCN	0.284	457
MeOH	2.29×10^{-2}	430
acetone	1.93×10^{-2}	414
THF[a]	4.35×10^{-3}	423
2,5-Me_2THF	1.06×10^{-3}	421
DME[b]	2.80×10^{-4}	*c*
$MeNO_2$[d]	1.05×10^{-4}	*c*
Et_2O	9.63×10^{-5}	428

[a] $\Delta H^{\ddagger} = 14.2 \pm 1.2$ kcal/mol; $\Delta S^{\ddagger} = -21.5 \pm 4.2$ cal/mol·deg; uncertainties represent three standard deviations. [b] Temperature = 21 °C. [c] Reaction monitored by FT-IR. [d] Reaction carried out in neat $MeNO_2$; temperature = 21 °C.

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